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PREPARATION AND CHARACTERIZATION OF POLYMERS FORMED BY IRRADIATION OF β-PINENE AND OTHER MONOMERS

A Dissertation

Presented for the

Doctor of Philosophy

Degree

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Ashok Mohan Adur

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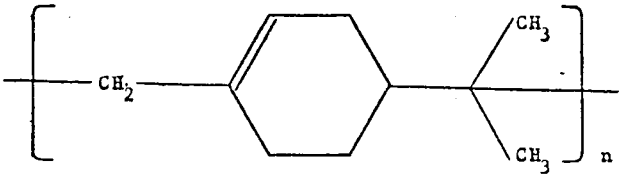
ABSTRACT

The gamma radiation-induced cationic polymerization of β-pinene was carried out under super-dry conditions. Chemical characterization by means of nmr, ultraviolet, and infra-red spectroscopic techniques and elemental analysis showed the repeat unit to be



X-ray diffraction methods were used to obtain crystallinity data and other morphological information. Thermal and solubility characterizations were also carried out. Auto-oxidation of the polymer resulted in the formation of peroxy and ketonic groups. Elemental analysis was used to determine the amount of oxygen incorporated in the auto-oxidized polymer. These results are discussed in comparison to those obtained for the commercial Polyterpene Resin, prepared by Lewis acid catalysis.

Poly(β-pinene) was also prepared by thermal polymerization at 160°C. The effect of additives indicated that the mechanism involved free radical propagation. The results of the X-ray diffraction and proton nmr spectroscopy of this polymer were similar to those of the polymer prepared by gamma irradiation indicating that the same repeat unit as well as the same crystalline unit cell were present in both of these polymers.

The radiation-induced copolymerization of β-pinene with styrene and with α-methyl styrene results in the formation of copolymers which

are probably random. Their molecular weights were very close to those for poly(β-pinene). The mechanism for these copolymerizations has been discussed in terms of the importance of chain transfer reactions during cationic propagation.

The radiation-induced polymerization of 2,5-norbornadiene occurs four to five times faster in the solid state at -78°C than in the liquid state at ca. 250°C. In both cases the repeat unit was found to be a nortricyclene structural unit with one norbornene unit as one of the end groups of the polymer chain. At conversions greater than 19 %, the solid-state irradiations resulted in gelation. These results have been interpreted on the basis of cationic propagation and with the possibility of topochemical, crosslinking, and other reactions taking place in the case of the solid-state polymerizations.

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INTRODUCTION

A. POLYMERS AND POLYMERIZATION

Polymers are those high molecular weight compounds whose entire structure consists of repetition of one or more chemical units. The chemical unit that repeats itself is called a monomer unit and the reaction by which a monomer is converted to a polymer is known as polymerization, the monomer units being connected to one another by covalent bonds. In cases where two monomers are used to form a homopolymer, such as in the formation of a polyester from a diacid and a diol, the term structural unit is used. The repeating unit of the chain consists of two structural units, one each of the diol and the diacid. In addition polymerization, the monomer unit and the structural unit may be the same as the repeating unit. The number-average degree of polymerization is the average number of structural units per polymer chain.

Polymerization reactions may be classified to be either of the step-growth or of the chain-growth type, based on differences in their mechanisms. Step-growth reactions proceed, as the name suggests, by stepwise reaction between functional groups of reactants.[1] Since this dissertation deals only with chain-growth reactions, step-growth polymerization will not be discussed here.

Chain growth polymerization, on the other hand, takes place when monomer molecules add on to form polymer molecules by a chain reaction, usually by addition to a double bond or by opening of a ring. It occurs by the propagation of a reactive species (either a free radical or an

ion) through the successive addition of a large number of monomer molecules. One of the characterizations of such a reaction is that polymers of high molecular weight are produced at all stages of the reaction, even during the early stages of the reaction. Chain growth polymerizations are considered to take place in three steps: initiation, propagation, and termination. Initiation consists of the production of a reactive species as well as the addition of this species to one monomer molecule. Propagation consists of the attack of this reactive species at one of the olefinic carbon atoms of the monomer, regenerating the active center without modification. This resulting species can then attack another monomer molecule thus propagating the chain. Thus the macroion or macroradical can keep reacting with monomer molecules to form a high molecular weight species by successive addition. The growth of the macroion or macroradical can be stopped by termination or transfer reactions. The nature of these reactions depends on the chemical nature of the monomer, on the presence of impurities, solvents, or any other molecules added to the system, and on the type of the polymerization mechanism, i.e. whether it occurs by a cationic, anionic, or free radical mechanism. Termination takes place when the propagating radical or ionic species is destroyed.

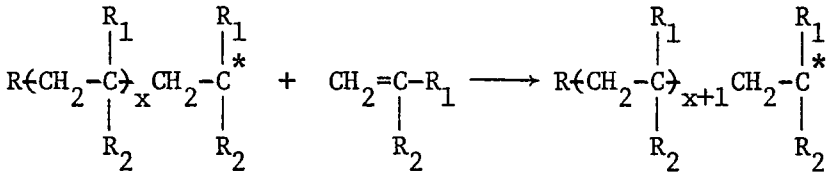
All these component reactions can be represented as follows:

Initiation:

$$\text{Initiator} \longrightarrow R^{*} \qquad (1)$$

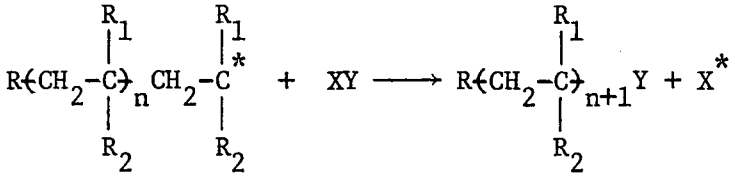
$$CH_2{=}\underset{\displaystyle R_2}{\underset{|}{C}}{-}R_1 \;+\; R^{*} \longrightarrow R{-}CH_2{-}\underset{\displaystyle R_2}{\overset{*}{\underset{|}{C}}}{-}R_1 \qquad (2)$$

Propagation:



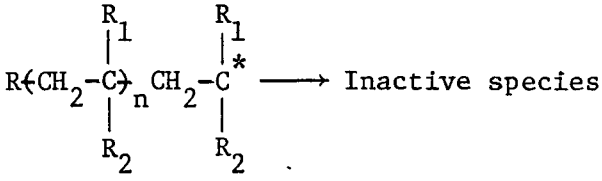
(3)

Transfer:



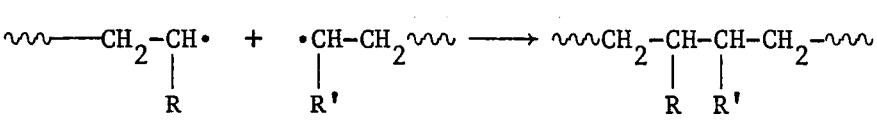
(4)

Termination:



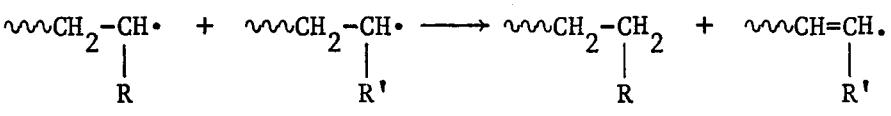
(5)

where R_1 and R_2 are any alkyl, aryl, vinyl, or halogen groups and XY can be either a solvent molecule, a monomer molecule, or a chain transfer agent. In the case of free radical polymerization, termination can take place by combination of two propagating ends,



(6)

or by disproportionation,



(7)

In the case of cationic polymerization, termination can result from recombination,

$$\sim\sim CH_2\text{-}\underset{\displaystyle R}{\underset{|}{CH}}^{+} \;+\; X^{-} \longrightarrow \sim\sim CH_2\text{-}\underset{\displaystyle R}{\underset{|}{CH}}\text{-}X \qquad (8)$$

or by elimination of a proton to a negative ion,

$$\sim\sim CH_2\text{-}\underset{\displaystyle R}{\underset{|}{CH}}^{+} \;+\; X^{-} \longrightarrow \sim\sim \underset{\displaystyle R}{\underset{|}{CH}}\text{=}CH \;+\; HX \qquad (9)$$

In intermolecular transfer reactions, the active center from one growing chain is transferred to a monomer molecule and rarely to a polymer molecule. The growth of the first chain is stopped while that of another is started. Such reactions are of significance in determining the molecular chain length and consequently the molecular weight of the polymer. However the rate of propagation is maintained only if the active center produced by transfer has the same (or greater) reactivity as the propagating species. Alternatively, in cases where transfer to a monomer molecule or to some other reagent molecule results in the formation of active centers of low reactivity, degradative chain transfer is said to take place. In these cases, both the kinetic and the molecular chain lengths are affected resulting in lower polymerization rates (for the same initiation rate) as well as lower molecular weights.

Polymerizations occur only when the appropriate chemical, thermodynamic, and kinetic requirements are fulfilled. Thus, addition polymerization is possible only when the chemical requirement is met, namely, the monomer must possess either unsaturation or a ring structure.

From a thermodynamic point of view, the Gibbs free energy change of the polymerization, $\Delta G_{m\rightarrow p}$, must be negative. In principle, all propagation and polymerization reactions are reversible and for the reaction,

$$M + M_n^* \rightleftharpoons M_{n+1}^*, \tag{10}$$

one can think of a situation where this reaction is in equilibrium, and show that

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = - RT \ln \frac{[M_{n+1}^*]}{[M_n^*][M]} = -RT \ln \frac{1}{[M]} , \tag{11}$$

where [M] is the monomer concentration and the standard states for the monomer and the polymer are taken as unit concentration.[2] ΔG°, ΔH° and ΔS° refer to the changes in free energy, enthalpy, and entropy respectively in the standard state.

This equation can be rewritten as

$$T_c = \frac{\Delta H^\circ}{\Delta S^\circ + R \ln[M]_e} , \tag{12}$$

where $[M]_e$ is the equilibrium monomer concentration and T_c is the ceiling temperature which is defined as the temperature at which the propagation and depropagation rates are equal. At the ceiling temperature the net rate of polymer production is zero. In the case of bulk polymerization, a singular value of the ceiling temperature,

$$T_c = \left(\frac{\Delta H^\circ}{\Delta S^\circ}\right)_{bulk} \tag{13}$$

is obtained by the choice of pure monomer and solid polymer as the standard states.

At the usual temperatures used for carrying out the reaction, most vinyl monomers polymerize with a rate of propagation much higher than that of depropagation such that the equilibrium position for the propagation-depropagation equilibrium lies far to the right. For most common vinyl monomers the ceiling temperature is ca. 300-350°C.

However, poly(α-methyl styrene) has a low ceiling temperature (ca. 70°C) and when heated above this temperature depropagates back to the monomer.

Since propagation, and hence polymerization, involves a decrease in entropy (ΔS is negative), the reaction has to be sufficiently exothermic ($-\Delta H > -T\Delta S$) for the formation of a polymer. In the case of polymerization of a compound with a carbon-carbon double bond to a polymer with single bonds, the typical enthalpy of polymerization is about -95 kJ/mole of monomer. However, conformational and steric effects together with ring strain can greatly alter the value of the reaction enthalpy. Thus this value changes to -155 kJ/mole for tetrafluoroethylene, to -70 kJ/mole for styrene, and to -35 kJ/mole for α-methyl styrene.[3]

The kinetic and mechanistic requirement for a chain reaction is that a mechanism must be available which permits the reaction to proceed at a sufficient rate so that the kinetic chain length, ν, defined as the ratio of the rate of propagation to that of initiation, is appreciable (>100). For polymerization to take place, an additional requirement is that the degree of polymerization given by the ratio of the rate of propagation to the sum of the rates of termination and transfer must be sufficiently high.

B. SCOPE OF RADIATION SCIENCE AND TECHNOLOGY

Radiation may be either particulate or non-particulate in nature. Particulate radiation includes high energy beams of electrons, protons, neutrons, deuterons, alpha particles, and fission fragments, while non-particulate radiation consists of electromagnetic waves of various

wavelengths from radiowaves at one end of the electromagnetic spectrum to cosmic rays at the other. Both gamma rays and X-rays lie in the same energy region of a few KeV to 100 MeV, the only difference being the origin of the radiation. Gamma radiation originates from the nuclear disintegration of the atom, whereas X-rays are given off when electrons undergo transitions from electronic levels of higher energy to the lower energy levels corresponding to the inner K and L shells. X-rays can also be generated by machine sources of high energy particles. Gamma rays and X-rays are forms of ionizing radiation and then chemical effects are different from those produced by lower energy photons such as infra-red, visible, or ultraviolet rays. This is primarily because, when a high energy photon interacts with matter, it loses some of its energy to the electron, which is ejected out of the atom, producing ionization. The scattered photon causes further ionizations. The ejected electron retains sufficient energy to produce another sequence of ionizations and excitations leading to a characteristic track structure, which is never produced by photons of less than 20 eV. Even in the case of ultraviolet photon-induced ionic reactions, where photons have sufficient energy ($\sim$20 eV) to produce ionizations, the recoil electrons do not produce either a track structure or spurs of localized excitations and ionizations. The ability of the recoil electrons to produce a well-defined track of excitations and ionizations in the sample, whereby many secondary electrons of lower energy are produced, is the characteristic feature of radiation chemistry and separates this branch of science from photochemistry.

All the irradiation studies during the course of this work were

carried out using gamma rays from a cobalt-60 source. This radio isotope is produced in a nuclear reactor by irradiating cobalt-59, a stable isotope, with thermal (slow) neutrons. Cobalt-60 has a half-life of 5.27 years and it decays with gamma photon energies of 1.17 and 1.33 MeV, thus giving off a total of 2.5 MeV per disintegration. Gamma radiation is more penetrating than particle beams of the same energy with the result that gamma irradiation is carried out more homogeneously than with particle beams, where the irradiation zone is restricted to within a few millimeters of the surface. However, gamma ray sources require large amounts of shielding.

Irradiation, as a means of effecting transformations has been practiced for many years with several different radiation sources and types of radiation energy used. Radiation has been useful for a broad spectrum of applications - from helping to understand fundamental aspects in scientific research to being used for large scale commercial applications.

Radiation has proved to be a useful tool in research. Radiation chemical techniques have been applied in the study of intermediate species. Radiation has been used to generate short-lived species as well as stabilized ions and free radicals in frozen crystalline and glassy media. Irradiation has proved to be an easy convenient method to prepare these species and to study them using techniques such as pulse radiolysis and electron paramagnetic resonance spectroscopy. Electrons are produced when ionizing radiation interacts with matter. In the condensed phase, these electrons often become solvated or trapped by the surrounding solvent or matrix molecules. The properties of

trapped electrons have been studied in several different matrices.[4] The ability of radiation to generate such species without the formation of ion pairs in gases, liquids, and solids provides the investigator with the means to study these species without interference from counterions. This is generally not possible with other methods of generating ions. Hydrated electrons were first produced by irradiation. Radiation chemical techniques have also been used to study electron transfer reactions between simple biological molecules such as amino acids as well as in micellar, protein, enzyme, and other more complex systems.[6]

Several radiation-induced chemical reactions of industrial significance such as sulfoxidation and sulfochlorination of hydrocarbons as well as oxidation of benzene to phenol and chlorination of benzene to hexachlorobenzene have been studied.[7] No successful commercialization of these reactions has taken place mainly because conventional catalytic systems are more efficient and the radiation process has no special advantages to compete against existing technology. It now appears that radiation is best exploited where existing techniques cannot be used and where several processes such as polymerization in the solid state, grafting, and crosslinking offer advantages not available by conventional methods. The development of the radiation chemical industry is not only a matter of economics, for it also depends to a considerable extent on the acceptability of radiation methods by industry. The change in radiation costs since the early fifties has been very dramatic and the megarad-pound cost is now on the order of one cent or less.[8] In the radiation-induced crosslinking of polyethylene, for example, the low energy requirement and the rapid throughput combine to

provide a lower unit cost than the use of conventional peroxide catalysts in the chemical crosslinkable materials.[9] However the resultant savings have to be such as to offset the cost of dismantling an existing processing plant and setting up a new one.

Radiation chemical processes offer several attractive features as compared to conventional processes.[10] Some of the more interesting practical applications of radiation chemistry which have reached some degree of commercial status include:

(a) vulcanization of rubber,[11]

(b) crosslinking of polyethylene for wire and cable,[12]

(c) curing of glass-reinforced polyester sheets,[13]

(d) curing of adhesives,[13]

(e) curing of organic coatings on various substrates,[14]

(f) ion-implantation for semi-conductor manufacture,[15]

(g) manufacture of wood-polymer composites,[16] and

(h) modification of textile fibers and fabrics for incorporating crease-resistance and stain and soil-release properties.[17]

Much of the general interest in radiation effects arose originally from the biological effects of radiation exposure, which are extremely damaging to most organisms. This aspect has been taken advantage of in applications of radiation in which malignant cells or harmful organisms are destroyed by irradiation. Cobalt-60 gamma radiation has been routinely used for several years to kill cancerous cells in the treatment of Hodgkin's disease and other forms of cancer.[18] Sterilization of disposable medical products, which involves destroying bacteria and other micro-organisms, has reached commercialization.[19] Considerable

research has also been carried out in the area of preservation of food materials such as potatoes, onions, grain, and meat.[20]

C. INTERACTION OF RADIATION WITH MATTER

The absorption of infra-red, visible, and ultraviolet light depends on the molecular structure of the absorber and only indirectly on its atomic composition. High energy radiation, on the other hand, is almost entirely absorbed by exciting and ejecting electrons from the atoms of the materials through which they pass, and this process is almost independent of the manner in which these atoms are combined into molecules. Consequently, for materials of low atomic number, the attenuation of high energy photons (X- and gamma rays) and of particle beams (alpha and beta radiation) is almost independent of the chemical composition as that for a given radiation, the mass absorption coefficient defined as μ/ρ is largely independent of the nature of the absorber where μ is the linear absorption coefficient and ρ is the density of the irradiated medium. Hence, the absorption of these ionizing radiations is much less selective than that of visible or ultraviolet light.

When high energy radiation interacts with matter, a variety of processes occurs by which the energy of the radiation is transferred to the medium through which it passes.[21] Interactions of electromagnetic high energy radiation with matter can take place by pair production, by the Compton effect, and by the photoelectric effect while interactions for charged particles occur by bremsstrahlung and inelastic of elastic scattering. The relative importance of these interactions is

determined by the energy of the incident radiation, by the mass of the charged particle, and by the electron density of the absorbing material as well as an electronic attenuation coefficient Q. The electron density or the number of electrons per gram of the material is proportional to the ratio of Z, the sum of the atomic numbers of the atoms constituting the molecules of the irradiated material to A, the sum of the atomic weights of those atoms. The electronic attenuation coefficient, Q is different for each of the three interaction modes as will be discussed below. The mass absorption coefficient for attenuation, μ/ρ, is given by the equation,

$$\frac{\mu}{\rho} = N_A \times \frac{Z}{A} Q \qquad (14)$$

where N_A is the Avogadro number.

Compton effect is the dominant mode of energy absorption for radiation of photon energy, roughly 0.5 to 5 MeV. Such an interaction of a photon with a bound electron results in a sharing of the energy and of the momentum of the incident photon between the scattered photon of lower energy and a recoil electron which has been ejected from the molecule. Usually a large fraction of the energy of the incident photon is transferred to the recoil electron. The electronic attenuation coefficient for the Compton effect is a constant, independent of Z, the effective atomic number of the stopping material.

The photoelectric effect is another mode by which the photon energy can be observed. In this case the photon is completely absorbed, giving all its energy to an atomically bound electron which is ejected from the molecule with a kinetic energy equal to the photon energy less the binding energy of the electron. The photoelectric component of the

electronic attenuation coefficient is proportional to the cube of the effective atomic number of the irradiated material. Photoelectric absorption falls off rapidly as the radiation becomes more energetic and for radiation of energy greater than 1 MeV, the contribution of the photoelectrons to the total energy absorption can be neglected.

The third mode by which high energy photons transfer their energy is by pair production. Electromagnetic radiation of energy greater than 2 MeV can create the direct transformation of energy into matter requiring 1.02 MeV, according to Einstein's equation $\Delta E = mc^2$, the excess energy being taken up as kinetic energy of the particles. This process in which an electron and a positron are produced is called pair production. The positron continues its motion until it encounters an electron, when both disappear, with the formation of two quanta each of energy 0.51 MeV. The energy of the electron formed by pair production is degraded by the processes described below for charged particles. The electronic attenuation coefficient Q for pair production is directly proportional to the effective atomic number of the absorbing material. Pair production is of importance only for radiation of energy greater than 5 to 10 MeV.

For the work carried out for this dissertation, cobalt-60 gamma radiation was used to irradiate hydrocarbon monomers. Consequently, the most important interaction in the range of interest is the Compton effect. The Compton electrons lose their energy by the mechanisms discussed below.

In contrast to high energy photons, beams of charged particles interact with matter by two mechanisms, <u>bremsstrahlung</u> and elastic or

inelastic scattering. In the former process, electromagnetic radiation in the characteristic X-ray region is emitted as a result of deceleration of a fast particle as it passes close to the nucleus of the atom. Scattering of a particle as a result of collision with a neutral molecule can be either inelastic or elastic, depending on whether the molecule acquires or does not acquire internal energy respectively. The excess internal energy is manifested as excitation or ionization of the molecule which can then undergo chemical reactions. Electrons liberated by this process are capable of inducing further ionizations and excitations, losing energy with each event until they are thermalized.

For incident beams of fast electrons and a target with high atomic number, bremsstrahlung becomes the dominant process of energy loss only at electron energies greater than 10 MeV, while inelastic scattering predominates at lower energy for materials of low atomic number. Elastic collisions are rare except when heavy charged particles react with matter.

Thus, the modes of interaction with matter of both high energy electromagnetic radiation and charged particle beams all result in the production of primary or recoil electrons with high energy, which give rise to a track structure. Since gamma rays and X-rays can penetrate through large thicknesses of material, the recoil electrons are generated more or less randomly throughout the medium. The track structure produced by recoil electrons is identical to that from electrons of similar energy produced by an accelerator. The presence of such a track structure provides a practical basis for distinguishing between

radiation chemistry and photochemistry as pointed out in section B of this chapter.

Since gamma rays usually possess an energy range from several KeV to a few MeV, and since the binding energy of the electron is much less, a considerable amount of energy is available to the ejected electron in the form of kinetic energy. This energy is sufficient to produce further ionizations and excitations as a secondary effect along the track as the energetic electron passes. The electrons produced by these secondary ionizations also produce tertiary events of ionization which can generate electrons with sufficient energy to produce further ionizations and hence electrons. Along with all these ionizations, excitations of the molecules will also occur. Thus an average secondary event involving 100 to 120 eV of energy will cause a little cluster of ionizations and excitations. Since collisions frequently deviate the path of the low energy scattered electrons, the ions will not lie in a straight line but will be clustered within an almost spherical volume, which is referred to as a "spur" on the main track of a primary Compton recoil electron. These spurs have a diameter of about 20 $\mathring{A}$ and are usually 10^4 $\mathring{A}$ apart for 1 MeV electrons in water and in organic liquids.[22] In time, the species in the spur diffuse, leading to an increase in the spur size until ultimately a homogeneous distribution is set up in the steady state.

Geminate charged pairs, resultant from irradiation, are subject to Coulombic attraction towards one another. In a condensed medium, a significant fraction of the initial yield of electrons disappears by recombination with positive ions. There is a characteristic distance

r_c between the two ions at which the electrostatic and thermal energies are equal, as defined by

$$r_c = \frac{e^2}{\varepsilon kT} , \tag{15}$$

where e is the charge of the electron, ε is the dielectric constant of the medium, k is the Boltzmann constant, and T is the absolute temperature.

Onsager[23] has shown that the escape probability for a single pair of ions undergoing Brownian motion and separated by a distance r is given by $\exp(-r_c/r)$. In liquids of low dielectric constant, r_c is large and only a small fraction of the ions drift apart by diffusion against the inter-ionic force field and become separated. These separated ions are called "free ions" while those that do not escape are called "geminate ions." This distinction is reflected experimentally in the lifetimes of the ions. Ions which undergo geminate recombination have extremely short lifetimes, during which they may or may not be solvated by the medium. Free ions, which undergo random recombination in the bulk of the solution have much longer lifetimes (microseconds or longer); they definitely become solvated. Evidence for the difference comes from chemical experiments with ionic scavengers, from pulse radiolysis studies of transient species, and from electrical conductivity measurements during irradiation.[24] These studies have shown that in liquids of low dielectric constant such as hydrocarbons, most (but not all) of the ions produced by radiation recombine rather quickly (between 10^{-9} to 10^{-7} sec) and that the yield of these free ions is about 0.1 ions/100 eV.[25] This is much less than the total yield

(ca. 2.6) of ion pairs as determined by chemical scavenging techniques.[26] The results of radiation-induced ionic polymerization provides indirect evidence for the existence of free ions. Electrical conductivity measurements have been used to study transient free ions during irradiation[27] and such experiments provide physical evidence for their existence. These studies have shown that the rate of production of free ions is only of the order of one-tenth to one-hundredth the rate of production of free radicals. It has been shown that the steady state concentration of free ions is a factor of 100 lower than that of free radicals.[28] The effect of this on the mechanism of polymerization will be dealt with later in this dissertation.

Ions and excited molecules are the primary radiolytic products formed on irradiation. At a later stage, these primary species may break down and/or react with the substrate to form free radicals and eventually bring about chemical reactions. Free radicals can be formed by unimolecular dissociation of excited molecules,

$$AB^{*} \longrightarrow A\cdot + B\cdot \qquad (16)$$

by abstraction reactions,

$$A^{*} + RH \longrightarrow AH\cdot + R\cdot \qquad (17)$$

by ion-molecule reactions,

$$A^{+} + RH \longrightarrow AH^{+} + R\cdot \qquad (18)$$

The formation of free radicals and ions is directly related to the absorption of energy by the irradiated material and their rate of formation is directly proportional to the dose rate. Free radicals and ions formed are largely responsible for the chemical reactions that take place and generally dominate mechanisms postulated for radiation-induced polymerization.

A term introduced by Burton[29] and which has found wide acceptance in radiation chemistry is that of the G-value, or the radiation-chemical yield. This is analogous to the quantum yield used in photochemistry. It is defined as the number of species (atoms, molecules, ions, radicals, etc.) which are formed (or which disappear) when the system has absorbed 100 eV of ionizing radiation energy and is designated by the symbol G. G(X) refers to the number of molecules of X formed and G(-Y) refers to the number of molecules of Y that is destroyed for an energy deposition of 100 eV. For example $G(-Fe^{++})$ indicates the number of Fe^{++} ions which have reacted per 100 eV. Generally the G-value of a radiation chemical reaction does not exceed 10 molecules per 100 eV for a non-chain reaction and it can be as high as 10^7 in some chain reactions.[30]

D. RADIATION-INDUCED POLYMERIZATION

Radiation-induced polymerization is a direct application of radiation chemistry to the synthesis of polymers. It is now well established that the initiation step in addition polymerizations requires the creation of suitable reactive intermediates. In radiation-induced polymerization, the energy for this step is supplied by the ionizing radiation. However, once the reaction chains are started, they proceed to grow according to conventional kinetic rules. Thus the main features of radiation-induced polymerization are comparable to those of conventional free radical, cationic, or anionic polymerization, the radiation chemical act being limited to the primary events, which lead to the production of free radicals and ions, and to some other molecular processes.

The use of ionizing radiation for initiating the chain polymerization of vinyl monomers is not a new application. The first use of radiation for effecting polymerization was by Lind and Bardwell in 1925.[31] They found that gaseous acetylene, irradiated with alpha particles from radon, polymerized to produce a black polymer which they called cuprene. To account for this polymerization, they suggested the "ion cluster" theory, according to which, the positive ion formed by the radiation attracted other neutral molecules to it by "polar forces," (now interpreted as ion-induced dipole interactions) so that a large ion was produced. On neutralization this macroion was thought to give rise to the final polymer molecule. This theory was critized by Eyring et al.[32], who pointed out that an ion large enough to give a polymer molecule on neutralization would probably not be stable. They emphasized also the importance of excitation and its role in the production of free radicals. Hopwood and Phillips[33] were the first to follow the kinetics of radiation-induced polymerization of methyl methacrylate, styrene, and vinyl acetate systematically.

Following World War II, radioisotopic sources became increasingly available and a large number of studies were carried out especially when it became apparent that large radiation sources could be designed and manufactured.[34] Dainton and Collinson[35] studied the kinetics and mechanism of radiation-induced polymerization of aqueous solutions of acrylanitrile. Magat, Chapiro et al.[36], in their study of gamma radiation-induced polymerization of vinyl monomers in bulk and in solutions, showed that these reactions were inhibited by diphenyl picryl hydrazyl (DPPH), a well known free radical scavenger. These two studies showed

that radiation-induced polymerization took place via a free radical mechanism. This was supported by the work of Seitzer and Tobolsky,[37] who studied the radiation-induced copolymerization of styrene and methyl methacrylate. It had been shown by Walling et al.[38] that an equimolar mixture of styrene and methyl methacrylate, when polymerized by free radical initiators, led to a copolymer containing 50% styrene and 50% methyl methacrylate; with anionic initiators, methyl methacrylate polymerizes much faster than styrene and the resulting polymer is essentially pure poly(methyl methacrylate); while with cationic initiators, polystyrene is almost exclusively formed. Tobolsky et al.[37] with fast electrons, and Ballantine et al.[39] with gamma rays showed that the copolymer, obtained by irradiating an equimolar mixture of the two monomers at room temperature, contained approximately 50% of each of the two components. The same result was obtained by irradiating this monomer mixture at -78°C in the solid state.[40] These results demonstrate that free radical processes are responsible for the polymerizations occurring under these conditions. This was generally accepted to be the case because other monomer pairs polymerized by radiation also led to copolymers with the composition expected on the basis of a free radical polymerization.[41]

In 1957, Davison, Pinner and Worrall[42] studying the polymerization of isobutylene at -78°C found that this monomer, hitherto polymerizable only with ionic catalysts, would polymerize under the action of high energy radiation. Furthermore, it was found that di-isobutylene, which is an inhibitor for the conventional ionic polymerization, also inhibited the radiation-induced polymerization. Besides, in

a normal free-radical polymerization, the rate is proportional to the square root of the radiation intensity, whereas in this case the rate was directly proportional to the intensity. The inability of DPPH to inhibit the polymerization of isobutylene was further proof of an ionic mechanism.[43]

For some years after that, it was generally believed that at low temperatures radiation can initiate ionic polymerization, but at room temperature and above, many monomers appear to polymerize by a free radical mechanism. The argument was that ionic polymerization should proceed with a very low activation energy in the propagation step, while free radical polymerization has a larger activation energy. Hence at high temperature, the rate of propagation of free radical polymerization will be much greater than the rate of ionic propagation, while at low temperature the opposite is the case. Experimental evidence for this was shown by Anderson,[44] who found that both polymerization rates and molecular weights of the polymers increased as the reaction temperature decreased from 0° to -195°C in the case of radiation-induced polymerization of butadiene. Similar results were obtained for isoprene by Burlant and Green,[41] although the kinetic chain lengths obtained by these researchers and by Anderson[44] were quite low.

Several investigators[45-47] showed that the polymerization rates of monomers such as styrene and isobutylene increased in the presence of zinc oxide, calcium oxide and silica. No satisfactory explanation was available for this observed increase at that time. The low temperature polymerization of styrene in various chlorinated solvents was shown to be cationic by several researchers.[40,48,49] The rate of this

reaction at -78°C was unaffected by the presence of oxygen or benzoquinone and was found to be directly proportional to the radiation intensity. Chapiro and Stannett[40] also found a significant contribution of an ionic polymerization when styrene was irradiated at room temperature in the presence of chlorinated alkanes, or even in bulk with radiation of very high dose rate.[50] The copolymerization of an equimolar mixture of styrene and methyl methacrylate led to a 1:1 copolymer at -78°C in the solid state while irradiation of the same mixture in the presence of a chlorinated solvent, such as methylene chloride, yielded copolymers with styrene content of 60-90% depending on the dose rate.[40,48,49] The contribution of the ionic mechanism was found to increase with the irradiation dose rate as expected, since free radical polymerization is one half order with respect to dose rate, while ionic polymerization should show first order dependence.

These ideas had to be modified considerably in the early sixties due to the work of Williams et al., who first recognized the importance of drying the monomer. They polymerized β-pinene[51,52] under ultra-dry conditions. Subsequent work along similar lines on α-methyl styrene,[52-54] styrene,[55-57] isobutylene[58] and some other monomers[59-62] also pointed to the importance of extreme dryness in successfully polymerizing these monomers with radiation. The work on β-pinene[51] and isobutylene[58] is especially important because of the inability of these monomers to respond to free radical initiation. Success in effecting their polymerization was sufficiently strong presumptive evidence that radiation-induced cationic polymerization was possible at room temperature, even in liquids of low dielectric constant such as

bulk hydrocarbon monomers, provided that extreme care was employed in removing water from both the bulk monomer and all glassware that it might come into contact with. This work casts doubts on the interpretation of previous results obtained without any special drying techniques. A possible explanation of the greater contribution of ionic propagation at lower temperatures could be that the small amount of water, which suppressed ionic propagation at elevated temperatures, remained frozen at the lower temperatures and was thus not available for destroying the kinetic chain length of the ionic propagation. Also the acceleration observed due to solids such as zinc oxide and silica gel could be explained due to the drying effect of these solids on the monomer.

It is now generally accepted that radiation induced polymerization takes place by anionic, cationic, or free radical mechanism or by a combination of these competitive mechanisms. Styrene, for example, which has been polymerized by all three types of mechanisms using conventional catalyst systems, has been shown to polymerize almost exclusively by cationic propagation under extremely dry conditions. In such a case, the cationic process overshadows the free radical process, which would normally have occurred under "moderately dry" conditions. K. Hayashi *et al.*[63] have shown that 10^{-7} molar concentration of water in styrene is enough to inhibit the cationic contribution to the overall polymerization.

From a variety of investigations in the early sixties, independent evidence became available for ions in liquids and solids and for lifetimes of electrons and ions beyond the previously postulated

recombination time of about 10^{-13} seconds in liquid systems.[22] In a rigid hydrocarbon glass such as 3-methyl hexane after gamma irradiation at 77°K in the dark, one can observe optical and ESR spectra which can be assigned to a trapped electron, showing physical evidence for charge separation.[64] Later, transient absorption spectra from trapped or solvated electrons have been observed in viscous hydrocarbon liquids with low dielectric constants upon irradiation.[65]

Chemical experiments with ionic scavengers have also been used to provide chemical evidence for the presence of positive ions using isotopic labelling experiments, e.g. ND_3 and C_2H_5OD in cyclohexane.[26] By the choice of suitable scavengers such as biphenyl, anthracene and similar aromatic molecules, one can identify the ionic species directly by means of its optical spectrum and, through time-resolved spectra, obtain an idea of the lifetime distribution or the time profile of the ions that are produced.

It has been shown using chemical and pulse radiolysis studies of ion scavenging that, in liquids of low dielectric constants such as hydrocarbons, most (but not all) of the ions produced by radiation combine rather quickly by a process called "geminate recombination." Within about 10^{-9} second and certainly less than 10^{-7} second, this fast process of geminate or cage recombination is complete due to the mutual attraction between the pair of ions.[24] However, a small fraction of the ions drift apart by diffusion against the inter-ionic force field and become separated. These ions have much longer life-times (about 10^{-2} second at a dose rate of 1 Mrad/hr.) than those undergoing geminate recombination. It is now generally accepted that it is these free ions

which are responsible for most of the ionic polymerization observed. From electrical conductivity studies it has been shown that the rate of production of these free ions is only of the order of one-tenth to one-hundred the rate of production of free radicals.[27] However, due to the higher rate of recombination of the free ions, the typical steady state concentration can be calculated for hydrocarbons ($\varepsilon = 2$) at a dose rate of 1 Mrad/hr. to be 2×10^{-10} molar whereas the free radical concentration is around 1.6×10^{-8} molar.[28] This clearly indicates that radical polymerization will predominate in any system unless the propagation rate constant for ions exceeds that for radicals so as to overcome this difference of 10^2 in the relative concentrations.[65]

Quantitatively, it can be shown by using basic kinetic equations that the high propagation rates for free ion polymerization cannot be achieved unless the monomer system is extremely pure and free from water and other molecular species which can take up protons. Several studies have shown the need to eliminate water and also that the addition of ammonia in concentrations much less than 10^{-3} molar was sufficient to completely suppress the radiation-induced ionic polymerization in the dry system. These experiments confirmed that polymerization in such systems results from a small concentration of free ions which are easily terminated by an effective scavenger, according to the equation

$$R_p = \frac{k_p [M] R_i}{k_{tx} [X] + (R_i k_t)^{1/2}} \qquad (19)$$

where k_{tx} is the rate of termination by an impurity or added scavenger X, while $(R_i k_t)$ represents the mutual bimolecular termination between ions. For a very dry monomer, this equation reduces to

$$R_p = k_p[M] \ (R_i/k_t)^{1/2} \qquad (20)$$

and the result is a half power dependence of the rate of ionic polymerization on dose rate.

It has been shown that the radiation-induced polymerizations of styrene,[56] α-methyl styrene,[67] isobutylene[58] and several other monomers[59,62] are severely inhibited by low concentrations of ammonia and tertiary amines. Since these bases are known to react only with cationic species and not with anionic species, these results show that these monomers polymerize by cationic propagation rather than via an anionic mechanism. The relatively high incidence of chain transfer reactions reported in the literature on the radiation-induced polymerization of these monomers also argues against cationic propagation.

The values of k_p for several monomers are in the range 10^5-10^9 M^{-1} sec^{-1}, which is much higher than the values commonly reported in the past for cationic polymerization of these monomers by catalyst systems. This difference has been attributed to differing cationic mechanisms.[24] The radiation-induced polymerization takes place via a free ion type of mechanism while conventional catalyst systems probably involve some form of ion pair. This is supported by the work of Bawn, Ledwith, and their coworkers,[68] who have achieved high k_p values by free cations in the solution polymerization of isobutyl vinyl ether initiated by carbenium ion salts. With the super drying technique similar to that used for the radiation polymerization, these values have been increased[69] so that they are comparable to those obtained by irradiation.[60,66]

Thus, radiation-induced polymerization is initiated by generation

of free radicals and ions. In the case of free radical propagation, the kinetic features are essentially the same for polymerization by both radiation-initiation and conventional catalyst systems. Perhaps the only significant difference is that the radiation-prepared polymer is a cleaner polymer because of the absence of catalyst in the polymer.[70] However, in the case of cationic propagation, the nature of the propagating ions is different. Radiation-induced ionic polymerization takes place by free ion propagation while most catalytic ionic polymerizations are thought to occur by the propagation of an ion in close proximity to a counter-ion leading to considerable differences, discussed in this section, in kinetics and mechanistic details.

E. EVOLUTION OF THE PROBLEM

On reviewing the large amount of literature available in the area of radiation-induced polymerization, one finds that most of the commonly available monomers have been investigated for their polymerization kinetics and for determination of their mechanism of polymerization under various conditions. Thus, the effect of various parameters (such as dose rate and temperature) and of the addition of various substances (inhibitors, accelerators, solvents, etc.) to the monomer have been studied. From these studies, a basic understanding of radiation-induced polymerization has been achieved. In recent years interest has shifted from kinetics and mechanisms to the polymers and their characterization. This is due, in part, to the more sophisticated instrumentation that has become available. Huang, for example, has carried out an extensive study on the molecular weight distribution of the polymer formed by

radiation-induced polymerization of styrene and other monomers.[71] Molecular weight determinations have also been used to characterize polymers formed by radiation-induced polymerization of isobutylene[72] and copolymerization of isobutylene-isoprene.[73] Such studies show that the polymers formed by radiation have a much higher molecular weight than similar polymers formed by catalytic methods. Other techniques of characterization have also been used to study polymers prepared by radiation. Henderson, Stannett *et al.*[74] investigated the thermal stability of poly(vinyl chloride) prepared by radiation polymerization. Morphological studies on polyethylene prepared by gamma radiation-induced polymerization have been reported.[75] Polymers prepared by gamma irradiation have been tested for shear and compression strength.[75]

The salient features of radiation-induced polymerization have been discussed in part D of this chapter. As pointed out there, Bates, Williams *et al.*[51-53] carried out a rather extensive study of the kinetics of polymerization of β-pinene and of α-methyl styrene. They also studied the effect of water on inhibiting these reactions and concluded that the polymerizations were cationic in nature. In one of the papers,[5] it has been reported that the radiation-prepared poly(β-pinene) which was insoluble in the monomer at room temperature was found to be birefringent. Similarly, it has been reported by Pinner[77] that the higher molecular weight ($\bar{M}_n \sim 2720$) polymer isolated from the irradiation of β-pinene, was birefringent and soluble in hot chlorobenzene. No further work on radiation-induced polymerization of β-pinene has been reported since then.

More recently, J. P. Kennedy and T. Chou[78] have reported the

formation of a crystalline polymer by thermal polymerization, the method consisting of heating the neat monomer at 160°C in an atmosphere of nitrogen for a week. Kennedy[79] has suggested that a further investigation of the physical properties of those polymers would be of theoretical and practical significance.

A study of radiation-induced polymerization of β-pinene was carried out, emphasizing characterization of the polymer formed so that further information would be known about this interesting polymer. Since β-pinene has been shown to copolymerize with other monomers catalytically, and such radiation-induced copolymerizations had not been studied, this was investigated as well. The comonomers used were styrene and α-methyl styrene since both these monomers were known to polymerize cationically. The copolymers formed were analyzed to determine the monomer contents and further characterized by infra-red spectroscopy, molecular weight measurements and other techniques.

β-Pinene is a monomer that polymerizes by a ring-opening mechanism in the propagation stage of the reaction, yielding a monocyclic repeat unit from a bicyclic repeat unit. Such an isomerization step, sometimes referred to as "phantom" propagation,[80] takes place only in the case of a few monomers. 2,5-Norbornadiene is another monomer which can form a polymer via an isomerization step. This transannular polymerization yields a nortricyclene repeat unit. Since 2,5-norbornadiene also gives an isomerized repeat unit, homopolymerization of this monomer was also studied, both at room temperature and at -78°C. The polymers formed were also characterized.

CHAPTER II

EXPERIMENTAL - PREPARATION OF POLYMER

A. MATERIALS

All chemicals used in the research described in this dissertation were obtained from commercial suppliers, as indicated in Table I. Special purifications were carried out on all the monomers used. Bromobenzene needed to be vacuum distilled. All other chemicals including polymers and drying agents were used as such without further purification.

B. IMPORTANCE OF DRY MONOMER

As discussed in Chapter I of this dissertation, it is now widely accepted that radiation-induced polymerization of vinyl monomers takes place by propagation of an ion or a free radical or by a combination of these mechanisms. It has been pointed out there that generally a free radical mechanism will predominate unless the monomer is sufficiently dry. Styrene, for example, undergoes a free radical polymerization when not sufficiently dry. On ultra-drying, however, it polymerizes by a cationic propagation. The work of Williams, Bates, et al.[52,53] on β-pinene and α-methyl styrene has shown the need for rigorously drying the monomers in obtaining radiation-induced ionic polymerization. They have demonstrated further that the rates of polymerization increased with improvement in monomer drying techniques.[51,53] Deliberate addition of water[52] or similar scavengers like ammonia[56] caused a strong inhibition of polymerization. The rates for thoroughly dried samples

TABLE I

LIST OF MONOMERS, POLYMERS AND OTHER CHEMICAL SUPPLIES

List of manufacturer/supplier	Chemical*
(a) Monomers	
Aldrich Chemical Company, Inc.	bicyclo[2,2,1]hepta-2,5-diene α-methyl styrene myrcene (-)-β-pinene styrene
(b) Polymers	
Arizona Chemical Company	Polyterpene Resin, Zonarex type B-115,
(c) Drying Agents	
Barium and Chemicals, Inc.	barium oxide, 1/4 x 1/8" mesh
Davison Chemical	silica gel, dessicant grade 950, 60-200 mesh
Fisher Scientific	silica gel, indication tell-tale type, 6-16 mesh
Union Carbide Corp., Linde Division	molecular sieves, 5A pellets, size 1/16
(d) Solvents and other Chemicals	
Aldrich Chemical Company, Inc.	benzil bromobenzene-d_5 (99% + D) 1-bromonaphthalene 1,4-dioxane
Allied Chemical Corp	sulfuric acid
Eastman Organic Chemicals	methyl cyclohexane 1,1,2,2-tetrabromoethane 4-tert-butyl catechol tetrachloroethylene tripropylamine

TABLE I (CONTINUED)

List of manufacturer/supplier	Chemical*
Fisher Chemical Co.	acetonitrile
	benzene
	bicyclohexyl
	bromine
	bromobenzene
	carbon disulfide
	carbon tetrachloride
	chlorobenzene
	chloroform
	cyclohexane
	cyclopentane
	cumene
	cymene
	n-decane
	1,2-dibromoethene
	1,2-dibromoethylene
	o-dichlorobenzene
	1,2-dichloroethane
	dichloromethene
	dicyclohexyl amine
	ethanol
	ethyl acetate
	ethylbenzene
	ethylene bromide
	ferrous ammonium sulfate
	n-hexane
	iodine monochloride
	methanol
	nitrobenzene
	nitroethane
	nitromethane
	n-octane
	pentachloroethane
	n-pentane
	potassium bromide
	potassium iodide
	sodium chloride
	sodium dichromate
	sodium hydroxide
	tetrahydrofuran
	tetrahydronaphthalene
	1,1,2-trichloroethane
	trichloroethylene
	o-xylene

TABLE I (CONTINUED)

List of manufacturer/supplier	Chemical*
Ladd Research Industries	colloidoin solution
Mallinkroft Chemical Works	toluene
Matheson, Coleman & Bell	1,2-dichloroethane
Norell Chemical Co.	benzene-d_6 (min 99.5% D) tetramethyl silane

*All chemicals are A.C.S. reagent grade or better unless otherwise stated.

of β-pinene and α-methyl styrene were larger by three orders of magnitude than those for water-saturated samples.[52,53] That ionic propagation rates might be greatly accelerated for other monomers by careful drying has been confirmed by several different researchers for styrene,[56] alkyl vinyl ethers,[81] and cyclohexene oxide.[82]

The mechanism by which very small concentrations of water can inhibit a radiation-induced ionic polymerization can be explained by reactions of the type,

$$\sim\sim CH_2\text{-}CH_2^+ + H_2O \longrightarrow \sim\sim CH{=}CH_2 + H_3^+O \quad (21)$$

$$H_3^+O + Y^- \longrightarrow H_2O + HY \quad (22)$$

where Y^- is the negative ion in the system. By these reactions, the original scavenger, water is regenerated. Thus, a proton scavenger like water could transfer protons from a growing propagating cation to the negative ions in the system without being used up.

In order to effect high rates of polymerization, therefore, it is very important to use very effective drying techniques. Silica gel was used to predry the monomer before irradiation by Bates et al.[52,53] in the case of β-pinene and α-methyl styrene, although several other drying agents such as magnesium perchlorate, phosphorus pentoxide and calcium hydride, and alumina were also tried in earlier work on β-pinene.[51] Hirota and Katayama[83] used sodium drying to get G(-M) values as high as 3.7×10^4 for α-methyl styrene while Stannett et al.[84] dried isobutylene with calcium hydride and then flamed out the sample ampoules under vacuum to obtain G(-M) values up to 1.6×10^4.

Soon after, Kristal'nyi and Medvedev[85] obtained values up to 9 x 10^6 molecules per 100 eV by drying out isobutylene with pretreated zinc oxide. Taylor[58] obtained the highest values reported for isobutylene - G(-M) ca. 1.75 x 10^8 - by using a combination of vacuum distillation of isobutylene into flasks, freshly mirrored with sodium-potassium alloy as a pretreatment, followed by passing the gaseous monomer via refluxing metal alloy at 300°C into sample ampoules prebaked at 500°C in an oven. Metz et al. used silica drying along with a bakeout vacuum apparatus to get high G-values for styrene[86,87] and for α-methyl styrene.[88] Thus several improvements in drying techniques were made.

Taylor's method[58] gave the ultimate limiting values of k_p for isobutylene, which fitted the half power dependence on the dose rate, attainable for negligible termination by water or other impurities. This method is not so suitable for monomers of low volatility such as β-pinene and 2,5-norbornadiene. Besides, Taylor's method is very elaborate although it has the advantage of being able to obtain high G-values.

For the research conducted by the author, it was therefore decided to compromise between the high G-values obtainable by Taylor's technique and the need for greater convenience. Hence, Metz's method[87] of baking the glassware with silica gel in it was used with a few minor modifications. The main thrust of the research was not to obtain kinetic data but to characterize the polymers formed by radiation-induced polymerization. As discussed in Chapter I, the molecular weight is mainly a function of chain transfer, so that termination by water or other impurity only affects the molecular weight when the

kinetic chain lengths (or G-values) becomes very low. Hence, it was only necessary to obtain modestly high G-values, by adequate drying, so as not to affect the molecular weights significantly.

One modification from Metz's apparatus was the use of two vessels with silica gel in them instead of one. In the case of the homopolymerizations, the additional drying stage provided greater drying efficiency as well as reproducibility, although the extent of the drying efficiency is hard to compare since Metz's work was with styrene and α-methyl styrene while the author's research deals with the homopolymerization of β-pinene and 2,5-norbornadiene. The two vessels were also useful in the case of the copolymerizations because this enabled each vessel to be used for one of the comonomers. This necessitated further alterations in the glassware so that the comonomer ratios could be varied. This was done by introducing two greased stopcocks in the system, which probably had the effect of reducing the drying efficiency. Hence the G-values obtained for poly(β-pinene) and its copolymers in these latter experiments are much lower than those obtained for the poly(β-pinene) using the setup without these stopcocks.

Another modification was that the baked out glassware was sealed off from the vacuum line in the oven and then attached to another vacuum line for the sake of convenience. Bubbling dry argon gas through the liquid monomer just before sealing off the monomer vessel was another change from Metz's method. This enabled much faster degassing.

C. PRETREATMENT AND PURIFICATION OF MONOMER AND SAMPLE PREPARATION

All the monomers, *viz.* β-pinene, styrene, α-methyl styrene, myrcene, and bicyclo[2.2.1]hepta-2,5-diene were purified first by distilling on a Nester-Faust spinning band column under reduced pressure. Gas chromatography was employed to check for impurities, using a 10 % FFAP (free fatty acid phase, Carbowax 20M reacted with nitroterephthalic acid) with 60-80 % Chromosorb W solid support column, supplied by Varian Associates, Inc., in a Varian 2700 Moduline Gas Chromatograph.

The glassware for handling the monomer and for carrying out the drying procedure is shown in figure 1. The part of the vacuum manifold shown in figure 2, was baked in an oven at 400°C for 2 days at a vacuum of 2×10^{-8} mm Hg with silica gel or with one of the other drying agents in vessels A and B. It was then sealed off in the oven from the pump and connected to vessel C, which was attached to another vacuum line. The glassware at this stage looked exactly as in figure 1. Vessel C was flamed out to get rid of moisture sticking to the glassware. The monomer was introduced into the set up through two vertical columns, the upper one, 50 mm in length, filled with predried sodium hydroxide pellets and the lower one, 300 mm in length, filled with predried silica gel. The sodium hydroxide absorbed any possible inhibitor such as *t*-butyl catechol that might still have been present in the monomer, while the silica gel would rid the monomer of any moisture. Oxygen-free argon gas was bubbled into the monomer in vessel C for 10 minutes to drive off any dissolved oxygen. The argon was flushed through a tube

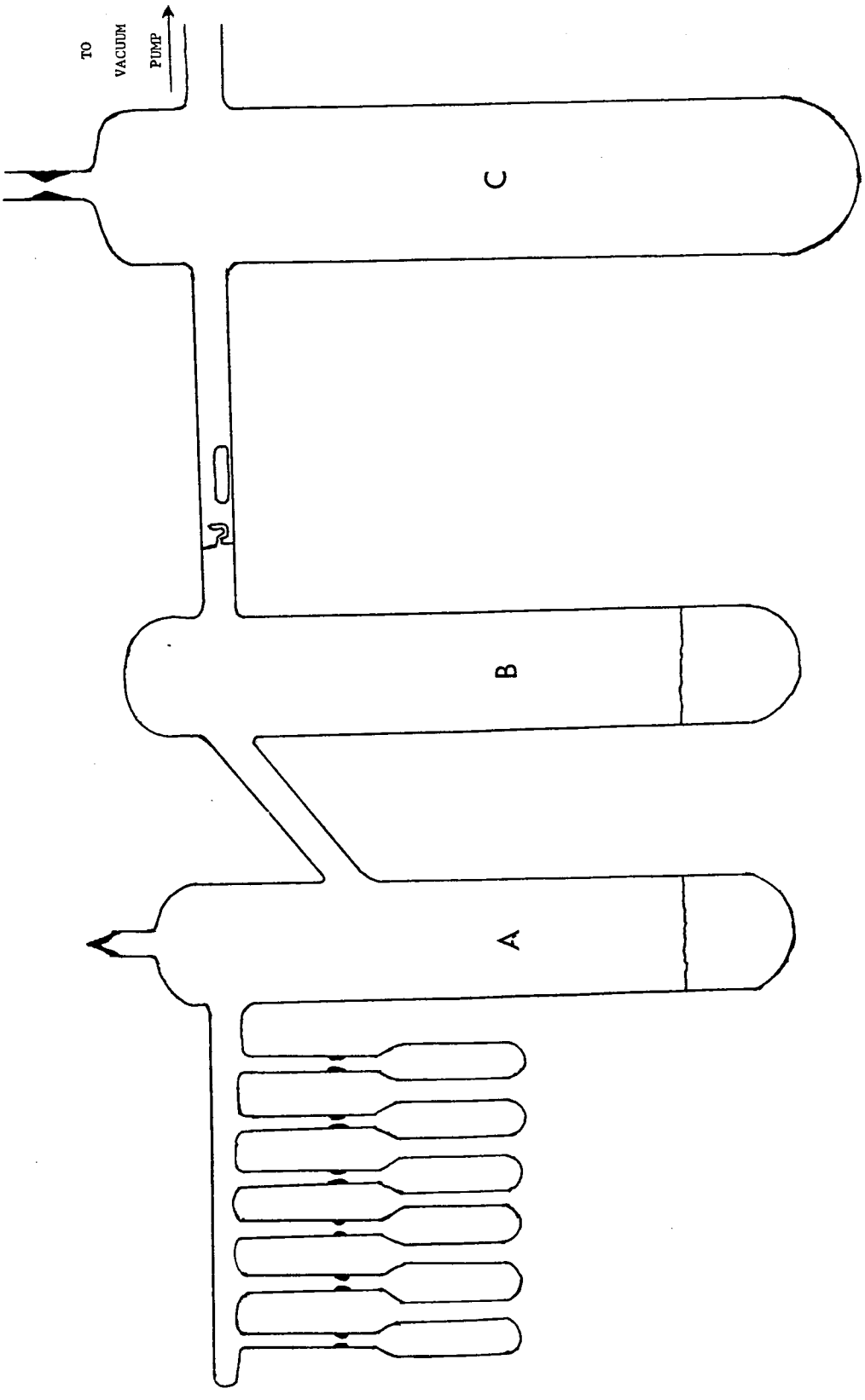


Figure 1. Glassware for the preparation of monomer samples.

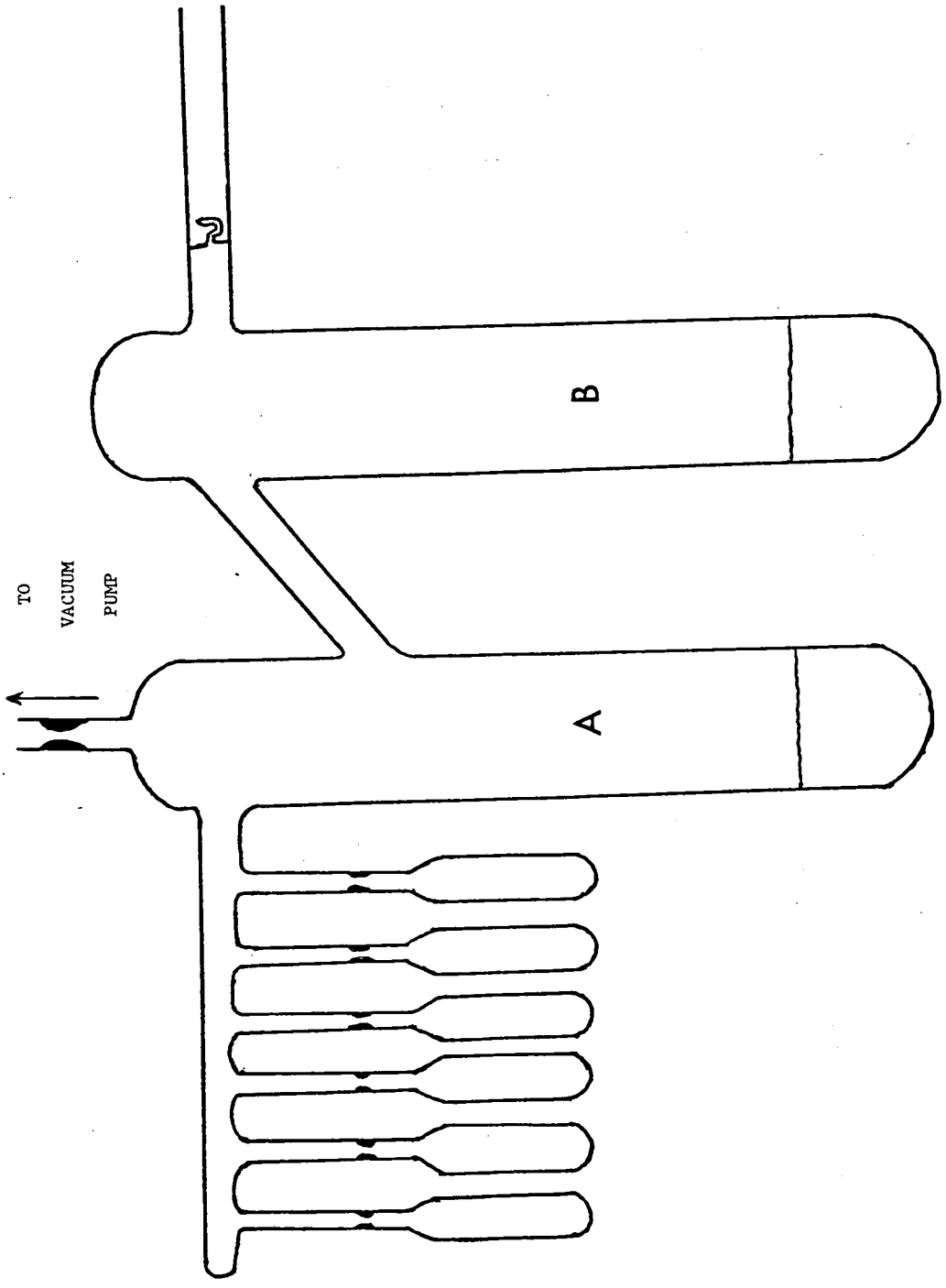


Figure 2. Part of the glassware baked in the oven at 400°C.

containing anhydrous calcium chloride to ensure that it did not introduce any moisture in the monomer. The system was then sealed off at the constriction on the top of vessel C. The monomer was then degassed using freeze-pump-thaw cycles. The argon gas helped to decrease the number of freeze-pump-thaw cycles and the time needed to degas the monomer. Yet, typically 15 to 18 cycles were still needed taking up a total degassing time of about 8 to 10 hours.

After degassing was completed - no more bubbles were seen on two consecutive thawings - the break-seal in the tube connecting vessels B and C was broken off with an external magnet. The monomer was transferred from vessel C to vessel B containing silica gel with liquid nitrogen and then from vessel B to vessel A and subsequently on to the sample tubes, in the shape of ampoules, which were then sealed off.

When it was necessary to use two different monomers and follow the above procedure, a slight modification of the glassware became necessary. Another vessel D was used and connected to vessel B in a similar fashion to vessel C. Vessel D was used to degas the second monomer. In order to conveniently handle dispensing of the two monomers stopcocks were introduced between vessel C and its break-seal and between vessel D and its break-seal. It was thus possible to transfer a portion of monomer from vessel C onto vessel B and then to vessel A and to one of the ampoules and to keep the stopcock at C closed overnight so that all the monomer remaining in vessels A and B would get transferred to the ampoule. Then the stopcock at D would be opened to let the required amount of the second monomer into the system. By this change in the glassware it was possible to dispense varying amount of monomers of roughly predetermined monomer compositions.

The exact monomer compositions were determined using a polarimeter. The glass ampoules were placed vertically (with the sealed end on top) so that the polarized light passed through these ampoules in the region where the monomer mixture was present. It was necessary to calibrate this technique because of the fact that the path length of the polarized light through the monomer was not the standard 1 dm or 0.5 dm but rather the diameter of the ampoule (∿22.5 mm). The calibration was carried out using an ampoule, of the same dimensions but with an opening at the top, and mixtures of β-pinene with styrene and α-methyl styrene. β-Pinene has a specific rotation of -21° and since β-pinene was present in almost all the copolymerization samples, optical activity was the preferred method of non-destructive analysis. Infrared and visible/ultraviolet spectroscopy were not useful since the ampoules were made of glass. The dimensions of the sample tubes were inconvenient for in situ analysis by nuclear magnetic resonance spectroscopy. This technique of measuring monomer composition by optical activity gave reproducible results within an experimental error of ± 1.5 %.

D. RADIATION DOSIMETRY AND IRRADIATION

1. Radiation Dosimetry

The field concerning the measurement of radiation dose is known as radiation dosimetry. Absorbed dose is defined as the energy of ionizing radiation absorbed by unit mass of the irradiated system.[21,30] The unit of absorbed dose is a rad, which is equivalent to the absorption of 100 ergs of energy per gram of the irradiated system.

$$1 \text{ rad} = 100 \text{ ergs } g^{-1} = 6.24 \times 10^{13} \text{ eV } g^{-1} \quad (23)$$

and

$$1 \text{ Mrad} = 10^{8} \text{ ergs } g^{-1} = 6.24 \times 10^{19} \text{ eV } g^{-1} \quad (24)$$

Although both rads and eV g^{-1} are commonly used,[21] the dose rate, in this dissertation, will be expressed in the units of Mrad $hour^{-1}$.

Absorbed dose, in radiation chemical studies, is generally measured with a chemical dosimeter called the Fricke dosimeter, which is based on the amount of oxidation, of ferrous ions in aqueous sulfuric acid to ferric ions, that takes place on irradiation. This method, first suggested by Fricke[89] and modified to increase the accuracy and convenience[90] of using it, gives excellent results in the dose range of 2×10^{3} rads to 4×10^{4} rads and a dose rate range up to 10^{8} rad sec^{-1}.[21,30]

Fricke's solution was prepared so that the concentration of the reagents were as follows:

Fe^{++}: 0.001 Molar (0.39162 g of $FeSO_4.(NH_4)_2SO_4.6H_2O$)

$Na^{+}Cl^{-}$: 0.001 Molar (0.0595 g of NaCl)

H_2SO_4: 0.80 Normal (22.5 ml of 90% H_2SO_4)

The reagents were dissolved in double distilled water, whose volume was made up to 1 liter by adding more double distilled water. All reagents used were of at least analytical reagent grade. Five ml, 10 ml, and 15 ml portions of the Fricke solution were then pipetted out into ampoules, similar to those used for irradiating monomer samples. This was done to ensure that the absorbed dose would be correctly measured and the only corrections then needed would be due to differences in the electron densities of the samples. Irradiations

of the Fricke solution were carried out for 5 to 10 minutes, the exact time being measured on a stopwatch with care being taken to ensure that the same Dewar, as that used for irradiating monomer samples, was employed for keeping the ampoule in the gamma cell.

The reactions taking place during the oxidation of Fe^{++} ions have been identified to be the following:[90,91]

$$H_2O \rightsquigarrow H\cdot + \cdot OH \quad (25)$$

$$Fe^{++} + \cdot OH \longrightarrow Fe^{+++} + OH^- \quad (26)$$

$$H\cdot + H\cdot \longrightarrow H_2 \quad (27)$$

$$\cdot OH + \cdot OH \longrightarrow H_2O_2 \quad (28)$$

$$\cdot OH + H_2 \longrightarrow H_2O + H\cdot \quad (29)$$

$$\cdot H + H_2O_2 \longrightarrow H_2O + \cdot OH \quad (30)$$

During irradiation it is essential that oxygen be present in the solution since it also takes part in the reaction.

$$H\cdot + O_2 \longrightarrow HO_2\cdot \quad (31)$$

$$Fe^{++} + HO_2 + H^+ \longrightarrow Fe^{+++} + H_2O_2 \quad (32)$$

$$Fe^{++} + H_2O_2 \longrightarrow Fe^{+++} + OH^- + \cdot OH \quad (33)$$

$$Fe^{++} + H_2O_2 + H^+ \longrightarrow 2Fe^{+++} + 2H_2O \quad (34)$$

$$\text{Thus } G(Fe^{+++}) = 2\,G_{H_2O_2} + G_{\cdot OH} + G_H = 15.5 \quad (35)$$

The sodium chloride is added to prevent the reaction,

$$\cdot OH + H_2 \longrightarrow H_2O + H\cdot \quad (36)$$

which would occur in the absence of the chloride ion. The chloride ion prevents the above reaction from taking place by reacting preferentially with the hydroxyl radical as follows:

$$\cdot OH + Cl^- \longrightarrow Cl\cdot + {}^-OH \quad (37)$$

and

$$Cl\cdot + Fe^{++} \longrightarrow Fe^{+++} + Cl^- \quad (38)$$

After the irradiations were carried out, the optical densities of the irradiated samples were measured using unirradiated samples as blank. The ferric ion gives an ultraviolet absorption peak at 304 mμ and hence the optical density was measured from 300 to 310 mμ on a Cary 17 spectrophotometer. The extinction coefficient has been determined,[92] by using standard mixtures of ferric ammonium sulfate solutions along with Fricke's solution, to be 2174 ± 6 liter $mole^{-1}$ cm^{-1} at 23.7° with a temperature coefficient of +0.7% per degree.

From Beer-Lambert Law, the optical density is given by the product of the molar extinction coefficient ε in liter $mole^{-1}$ cm^{-1}, the path length ℓ in cm, and the concentration of the solution, C in moles per liter.

$$\Delta(O.D.) = \varepsilon\ C\ \ell \tag{39}$$

Hence, the concentration of ferric ions produced in moles $liter^{-1}$ is given by

$$c = \frac{\Delta(O.D.)}{\varepsilon\ell} \tag{40}$$

and when this is converted to molecules per gram becomes,

$$c = \frac{\Delta(O.D.)}{\varepsilon\ell} \times \frac{6.023\times10^{23}}{1000\ \rho} \text{ molecules gram}^{-1} \tag{41}$$

where ρ is the density of the Fricke solution, 1.025 g cm^{-3}.

From the definition of the G-value,

$$G(Fe^{+++}) = \frac{c \text{ molecules } g^{-1}}{\text{Absorbed dose eV } g^{-1}} \times 100 \text{ eV} \tag{42}$$

$$\text{But } 100 \text{ eV } g^{-1} = 1.602 \times 10^{-18} \text{ Mrad} \tag{43}$$

Combining equations 41 with 42 and 43, we get

$$\text{Absorbed dose rate} = \frac{\Delta O.D.}{\varepsilon \ell} \times \frac{6.023 \times 10^{23}}{G(Fe^{+++})} \times \frac{1.602 \times 10^{-18}}{1000\ \rho \times t} \text{ Mrad hr}^{-1} \qquad (44)$$

where t is the time of irradiation in hours,

$G(Fe^{+++})$ is 15.5^{90} and $\ell = 1\ cm^{-1}$.

Using the method detailed above the absorbed radiation dose rate was determined three times during the course of this research. The data obtained is shown in table II.

TABLE II

FRICKE DOSIMETRY OF GAMMA IRRADIATOR

Date	Irradiation Time (minutes)	Optical Density	Dose Rate (Mrad hour^{-1})
Aug 2, 1976	5.00	0.72	0.242
May 12, 1978	6.00	0.59	0.166[a]
Jan 12, 1979	6.00	0.54	0.151[a]

[a]Irradiations in a dewar flask with a larger shielding factor.

The absorbed dose rate thus measured needs to be corrected[21] since this varies with the electron density of each monomer system irradiated and hence depends on its Z and A values, where Z is the sum of its atomic number and A is the sum of its atomic weight according to the formula,

$$\text{Dose Rate} = K\left(\frac{Z}{A}\right) \qquad (45)$$

Hence

$$\text{Dose Rate}_{(\text{Monomer})} = \frac{(Z/A)_{\text{Monomer}}}{(Z/A)_{\text{Fricke solution}}} \times \text{Dose Rate}_{(\text{Fricke})} \qquad (46)$$

when the dose rates are expressed in Mrad hour^{-1}.

Thus the dose rate for each polymer system was calculated separately using the dose rate correction factors shown in Table III.

TABLE III

DOSE RATE CORRECTION FACTORS (K)

Monomer	Mol. Formula	ΣZ	ΣA	K
β-pinene	$C_{10}H_{16}$	76	136	1.0105
styrene	C_8H_8	56	104	0.9738
α-methyl styrene	C_9H_{10}	64	118	0.9808
2,5-norbornadiene	C_7H_8	50	92	0.9828

Z/A value for the Fricke solution has been shown to be 0.553.[21]

2. Radiation Source

All irradiation was carried out in a "Gammacell 200" unit manufactured by the Atomic Energy of Canada, Limited. When it was loaded on September 14, 1971 with 3000 curies of cobalt-60 as slugs in 14 pencils, the central field dose rate was 0.463 Mrad hr^{-1}. The irradiator is shown in figure 3 (p 47). The gammacell has a cylindrical irradiation space of 1180 cc (18.5 cm in height and 9 cm in diameter).

3. Irradiation

In all cases the samples for irradiation at room temperature (25° ± 1°C) were kept in a Dewar, specially designed to fit snugly into the irradiation chamber. In case it was necessary to change the temperature of irradiation to say -78°C, finely powdered dry ice was placed

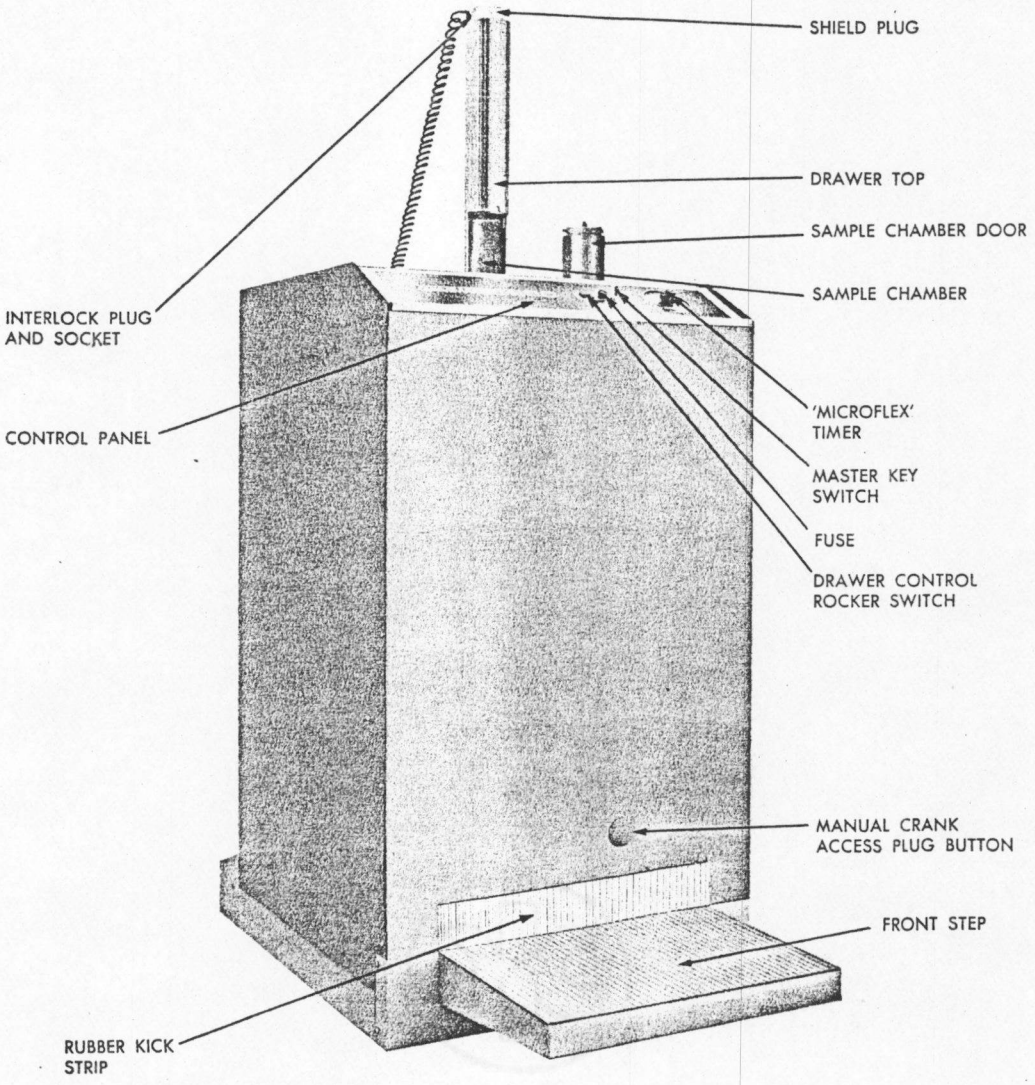


Figure 3. Overall view of Gammacell 200 cobalt-60 irradiator.

in with the sample tube in the Dewar, which was placed in the irradiation chamber and the shaft lowered into the cavity.

E. RECOVERY, PURIFICATION AND ESTIMATION OF POLYMER

The irradiated samples contained polymer as well as unreacted monomer. It was necessary to develop methods to recover, purify, and estimate the polymer formed, by separating it from the monomer without allowing any side reactions: post-polymerization, autooxidation, or depolymerization. Post-irradiation polymerization was not a serious problem except possibly in samples irradiated at dry ice temperature (-78°C). Autooxidation was a problem in all polymers containing β-pinene repeat units. This was avoided either by handling all processing in an oxygen-free inert atmosphere using glove-bag techniques or by conducting all the processing in the dark (it was found that very little autooxidation took place in the absence of light). Depolymerization was a problem if the sample of polymers containing a high percentage of α-methyl styrene were evacuated in order to remove monomer/methanol. Hence evacuation of any kind was not resorted to in the case of these polymer samples.

Two alternate methods were generally used. Methanol (200 ml) was placed in a large beaker (1000 ml capacity) with a magnetic stirrer. The irradiated sample was weighed, broken open just below the neck and the monomer-polymer mixture added as slowly as possible into the swirling methanol. Last traces of the mixture were removed from the irradiated sample tube with a couple of washings of tetrahydrofuran, chloroform, or carbon tetrachloride. After the polymer was completely

precipitated in a powdery form (the copolymers with high β-pinene content remained as viscous gels) the polymer was recovered from the methanol by filtration through a medium porosity fritted disc filter. This was repeatedly washed with methanol until 1% solutions in CCl_4 gave no discernable peaks for monomers in ^1H n.m.r. spectra. In several cases it was necessary to purify the polymer from any contaminants, usually monomers, by redissolving the polymer in a suitable solvent like chloroform, tetrahydrofuran, or carbon tetrachloride and reprecipitating it in methanol. Even the copolymers with high β-pinene content, which had remained as viscous gels after the first precipitation, became powdery after redissolution and reprecipitation.

The other method, mainly used for homopolymers of β-pinene and 2,5-norbornadiene, was to break open the glass ampoule, transfer the contents to a preweighed beaker, wash off the remaining contents with chloroform or carbontetrachloride to get all the polymer into the beaker, and then evacuate the beaker to constant weight in a vacuum dessicator to get rid of the monomer. A comparative study of the two methods showed identical results. The latter method was not used for polymers with high α-methyl styrene content because of the possibility of depolymerization reactions. This method was easier to use with the inert-atmosphere glove-bag technique.

From the weights of the monomer used and the polymer recovered, the percentage conversion and the G-value were calculated using the formulae:

$$\text{Percentage Conversion} = \frac{\text{Weight of polymer formed (g)}}{\text{Weight of monomer irradiated (g)}} \times 100 \qquad (47)$$

$$G(-M) = \frac{\text{Number of molecules of monomer converted to polymer}}{\text{eV of energy absorbed}} \times 100$$

$$= \frac{\text{Wt of polymer (g)}}{\text{Wt of monomer (g)}} \times \frac{N_A(\text{molecules/mole})}{\text{M.W.}_{\text{monomer}}\ (\text{g/mole})} \times$$

$$\frac{1}{\text{Absorbed dose (Mrad)}} \times 1.602 \times 10^{-20} \frac{(\text{Mrad})}{(\text{eV g}^{-1})} \times 100 \qquad (48)$$

where N_A is the Avogadro Number, 6.023×10^{23}.

This works out to

$$G(-M) = \frac{96.4885}{\text{M.W.}_{\text{monomer}}} \times \frac{\text{Wt of polymer (g)}}{\text{Wt of monomer (g)}} \times \frac{1}{\text{Dose (Mrads)}} \times \frac{1}{K} \qquad (49)$$

where K is the correction factor for the absorbed dose, the correction being due to the differences in the energy absorbed during irradiated by materials of different electron density, as explained in Chapter I, section D of this dissertation.

F. THERMAL POLYMERIZATION

As mentioned in Chapter I of this dissertation, Kennedy and Chou[78] obtained a crystalline polymer by the thermal polymerization of β-pinene. Some experiments were carried out to polymerize β-pinene by this method and to characterize the polymers formed especially because, from their data, it appeared that the thermally prepared poly(β-pinene) showed a different X-ray diffraction pattern as compared to that exhibited by the radiation-prepared polymer.

Kennedy *et al.*[78] had heated the neat monomer in capped glass vials to 160° for a week under a blanket of dry nitrogen. A similar set up was used to duplicate his work. β-Pinene was heated in a three-necked flask at 160°. Dry nitrogen was bubbled through the monomer.

A thermometer was placed inside the flask to monitor the temperature of the hot monomer. A reflux condenser was used so that the monomer would not evaporate.

The effect of inhibitors was studied using dicyclohexylamine and tripropyl amine as cationic scavengers and 4-tert-butyl catechol as a free radical inhibitor.

The flask was heated for a week and then cooled to room temperature. The polymer which precipitated was filtered out while the soluble fraction was isolated by dilution with methanol.

CHAPTER III

EXPERIMENTAL - CHARACTERIZATION OF POLYMERS

Characterization of polymers is very important in modern science and technology because a complete characterization of a polymer enables one to define the structure as well as the reactivity and other properties of the polymer. Determination of the structure involves defining the size of the macromolecular chain, the chemical nature and the tacticity of the repeat unit, and the morphology of the polymer. Studying the reactivity of the polymer with respect to heat, light, various chemicals, high energy radiation, and chemical reactions such as oxidation enables one to determine whether the polymer degrades or if the polymer can be modified for a suitable application. Determination of the properties of the polymer in solution and in the molten state finds use in the processing of the polymer. Determination of physical and mechanical bulk properties are also sometimes considered to be part of the characterization of the polymer.

Characterization of new polymers plays a vital step in its development for industrial use. Correlation of the knowledge of polymer chemistry and characterization data with the physical properties of the polymer is useful in determining the relationship between the chemistry of the polymers and their performance.

Chemical tests and classical qualitative organic analysis have been used for characterizing polymers since they were first made over fifty years ago. Besides these classical methods, most modern characterization on a systematic basis also involves the use of sophisticated instrumentation based on various physico-chemical techniques.

For the sake of convenience and systematization, all the characterization techniques used during the course of this research have been discussed under the following headings:

A. Chemical Characterization.

B. Molecular Weight Studies

C. Morphological Studies.

D. Solubility Characteristics.

E. Thermal Properties.

F. Auto-oxidation.

A. CHEMICAL CHARACTERIZATION

Chemical characterization was carried out to determine the nature of the chemical repeat unit and to check the absence of monomer and other impurities in the polymer. The following techniques were used:

1. infra-red spectroscopy,
2. nuclear magnetic resonance (nmr) spectroscopy, both ^{1}H and ^{13}C,
3. ultra-violet spectroscopy,
4. elemental analysis, and
5. chemical tests.

In one instance, electron paramagnetic resonance (epr) spectroscopy was also used to study the formation and decay of free radicals formed during the solid-state polymerization of 2,5-norbornadiene. The epr spectra were obtained with a Varian V-4502 spectrometer system equipped with a variable-temperature controller. The magnetic field strengths required for spectral calibration were obtained through use of a Walker/Magnemetrics Precision nmr Gaussmeter Model G-502 in combination

with a System-Donner 1037 frequency counter. The spectra were recorded on a Hewlett-Packard 7001 AM x-y recorder.

1. Infra-red Spectroscopy

This method is very valuable in obtaining information about the functional groups in a polymer.[93-94] Two different techniques of sample preparation were used. In the first, the polymer was dissolved in a suitable solvent and a film cast on a clean and dry NaCl plate. The solvent was then evaporated and the film along with the NaCl plate was clamped into a sample holder, which was placed in the sample beam of the spectrometer. The other technique consisted of pelletizing the polymer with anhydrous NaCl or KI. The polymer was crushed in a mortar to a fine powder, which was then placed in a pellet mold and pressed till a transparent pellet was obtained. The latter technique was used only for polymers which were difficult to dissolve. Samples of all the other polymers were prepared by the film technique. A Perkin Elmer 257 double beam grating infra-red spectrophotometer was used to obtain the infra-red spectra. Calibration was generally carried out with the standard absorptions of a polystyrene (atactic) film at 2851, 1601 and 918 cm^{-1}. It was thus possible to obtain infra-red spectra of polymers from 4000 to 625 cm^{-1}.

2. Nuclear Magnetic Resonance Spectroscopy

This technique has been used to identify repeat unit structures, to identify polymer mixtures and copolymers and estimate the percent composition of their individual components and to determine the micro-tacticity of some portions of the polymer chain.[93,95,96] The polymer

was dissolved in a suitable solvent and the solution introduced into a nmr sample tube. The solvents used were carbon tetrachloride, perchloroethylene, chloroform-d_3, benzene-d_6, bromobenzene, bromobenzene-d_5, and methylene chloride. Two different nmr spectrometers were used to obtain proton magnetic resonance spectra. The T-60A Varian nmr spectrometer was used to get the spectra at room temperature while the Varian Associates' HA-100 nmr spectrometer was used for high temperature studies. To obtain Carbon-13 nmr spectra, the Nicolet model TT-14 instrument with pulsed Fourier Transform capability using a multiphase generator and a mini computer NIC-80 was employed. The conditions and settings for recording the spectra are given in Chapter IV.

3. Visible and Ultraviolet Spectroscopy

Absorptions in the visible and ultraviolet region are useful in identifying molecules with certain functional groups such as olefinic double bonds and ketone groups.[93,97] The polymers were either cast into translucent pellets with anhydrous KI in the case of polymers which were not easily soluble, or dissolved in suitable solvents which would not absorb in the region of interest. The Cary 17 ultraviolet-visible-infra-red spectrophotometer was used to obtain absorption spectra.

4. Elemental Analysis

Carbon and hydrogen analyses were carried out by the combustion method.[98] Samples were sealed in vacuum to ensure no autooxidation took place before the samples were analyzed. These analyses were carried out by Galbraith Laboratories, Knoxville, Tennessee. Elemental analysis data was used to monitor the extent of auto-oxidation.

5. Chemical Tests

Two types of chemical methods were employed to determine the extent of unsaturation. Addition of iodine monochloride to the polymer was carried out as per standard procedure.[99] Bromination was also used for this purpose employing the usual procedure.[100]

B. MOLECULAR WEIGHTS

The molecular weights of the polymers were determined either by viscometry or by vapor pressure osmometry. The only polymers for which viscometry was suitable were the homopolymers of styrene and α-methyl styrene because the Mark-Houwink parameters are known for these polymers.[101] These parameters are not known for either poly(β-pinene) or for poly(2,5-norbornadiene). They are also not available for the copolymers of β-pinene with styrene and α-methyl styrene.

Toluene was used as a solvent and the viscosities determined for polystyrene and for poly(α-methyl styrene) at various concentrations with the Ubbelohde viscometer. The limiting viscosity at zero concentration was determined for each polymer. The molecular weights were determined using the Mark-Houwink parameters, $K = 9.2 \times 10^{-3}$ ml g^{-1} and $a = 0.72$ at 30°C for polystyrene[102] and $K = 2.2 \times 10^{-3}$ ml g^{-1} and $a = 0.80$ at 30°C for poly(α-methyl styrene),[103] on the assumption that the polydispersity ratio, $\bar{M}_w/\bar{M}_n$ was between 1.30 and 1.75.[101]

All the polymers prepared, except polystyrene, were characterized for molecular weight by vapor pressure osmometry (V.P.O.). Since this method is not very reliable for molecular weights beyond 10,000,[104] it could not be used for polystyrene, which had a molecular weight very much beyond this range. Carbon tetrachloride was used as a solvent for

all the polymers. Poly(β-pinene), which would not completely dissolve in this solvent, was the only polymer for which molecular weights of only the soluble fraction were determined after the insoluble fraction was filtered out. The osmometer was calibrated by taking readings of solutions of known concentrations of benzil in carbon tetrachloride. From the readings, the calibration factor K_{cal} in units of divisions liter $mole^{-1}$ was determined as the intercept on the y-axis of the plot of the ratio of the readings (converted to full scale of 128) to the molar concentration of benzil against the concentration of the solutions in moles $liter^{-1}$. Table IV gives the results of the osmometry with benzil solutions, while figure 4 is the plot from which K_{cal} is determined.

TABLE IV

CALIBRATION OF V.P.O. WITH BENZIL

No.	Concentration* (mg ml^{-1})	Concentration*† moles l^{-1}	Average** Reading	Reading and (moles l^{-1})	K_{cal}
1	2.4303	0.01156	64	5536	
2	4.2551	0.02024	106	5236	5576
3	10.5157	0.05002	251	5021	
4	17.8275	0.08480	396	4670	

*solution in carbon tetrachloride

†molecular weight of benzil = 210.23 g $mole^{-1}$

**converted to readings on scale of 128

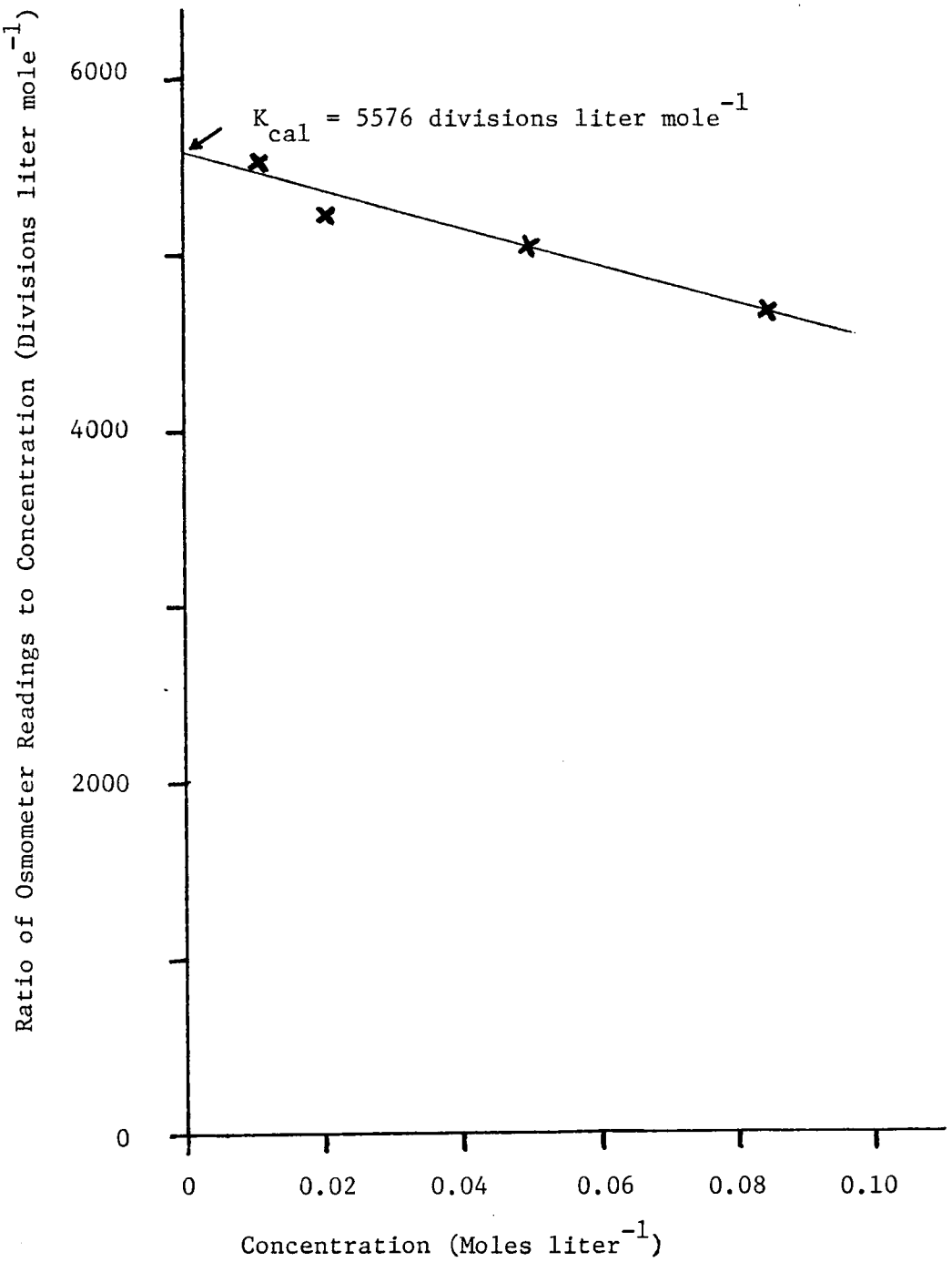


Figure 4. Calibration curve for vapor pressure osmometry with benzil in carbon tetrachloride.

Solutions of the various polymers were prepared in at least five different concentrations. Readings were taken on a Knauer Vapor Pressure Osmometer, semimicro type M. The readings were plotted with the ratio of the readings (converted to the maximum scale of 128) to the concentration in mg ml^{-1} on the y-axis and the concentration in mg ml^{-1} on the x-axis. The intercept K in units of divisions ml mg^{-1} from these plots were determined and the number-average molecular weights calculated as the ratio of K_{cal} to K. Because the molecular weights of most of the polymers prepared were lower than 5000, they were below the range suitable for determining weight-average molecular weights by light scattering.

C. MORPHOLOGICAL STUDIES

Morphology is the study of the physical form and structure of a material. It includes a wide range of characteristics, extending from the external size and shape of large articles to dimensions of a crystal lattice.[105] The morphological studies carried out during the course of this research were concerned with obtaining qualitative and quantitative information involving features larger than the unit cell. For this purpose, the polymers obtained were studied using polarizing optical microscopy, X-ray methods, and density measurements.

1. Optical Studies

Optical studies were carried out with a Leitz-Wetzlar Ortholux Optical Microscope. A Polaroid camera was attached to the top for photographic recording purposes. The slides for looking at birefringance were prepared by placing a drop of the polymer solution

in a suitable solvent on a microscope glass slide, carefully placing another glass slide on top of the solution so that the polymer solution spread evenly, and then taping the slides together. The slides were then evacuated in a vacuum dessicator to remove the volatile solvent and then viewed under cross-polarizers. For taking pictures, the image is focused on the camera observation plate, the film is inserted and the picture taken using automatic exposure.

2. X-Ray Methods

Wide angle X-ray scattering (WAXS) patterns were obtained with a Phillips Norelco X-ray generator and a flat plate camera. The sample to film distance was 5.0 cm. The radiation used was nickel-filtered copper Kα of wavelength 1.542 Å, with the X-ray unit operating at 35 kV and 15 mA. Exposure times varied from 2 hours to 6 hours depending on sample thickness.

X-Ray diffractometry was carried out with a Norelco X-Ray generator and a Phillips diffractometer provided with a monochromator and a scintillation counter with ORTEC counter circuitry. Nickel-filtered radiation from a copper target operated at 35 kV and 15 mA was used and a 2θ scan obtained using suitable sample holders for the powdered polymers. The percentage crystallinity was calculated using the standard procedure, first proposed by Matthews and his coworkers,[106] and discussed later in Chapter IV of this dissertation.

3. Density Measurements

The densities of the poly(β-pinene) were measured using two

different methods. The density gradient column, prepared from chloroform and ethanol was used in the first method. Four calibration beads of known density and a piece of the solid polymer were carefully placed into the column. After equilibrium was attained, the positions of the bead and the polymer sample were measured. From a calibration curve the density of the polymer sample was determined.

Densities were also determined by the floatation method. The polymer sample was placed in a calcium chloride solution of known concentration in a beaker, the concentration being such that the sample sank in the solution. Water was allowed to fall dropwise from a burette till the polymer sample started to float. From the amount of water added to the calcium chloride solution, it was possible to calculate the density of the solution which was then the same density as that of the polymer.

D. SOLUBILITY CHARACTERIZATION

The radiation-prepared polymers were characterized by their solubility properties. The poly(β-pinene) was insoluble in most solvents at room temperature, probably due to its high crystallinity and it was necessary to carry out a complete solubility characterization[107] to determine the solvents that would readily dissolve it. All the other polymers dissolved in a wide range of solvents and were not studied for their solubility behavior. Standard procedure[107] was used to determine whether the polymer was soluble in a particular solvent. This consisted of placing a gram of the solid polymer in a test-tube and adding 5 ml of the solvent slowly (1 ml every ten minutes). It is important to

note that polymers which are soluble in concentrated solutions sometimes form two phases in dilute solution. The mixture was stirred to speed up dissolution. Heating the solution helped dissolution in some cases. For the purpose of classifying the solvent behavior, it was decided to rate them as belonging to one or more of the following classes:

O - dissolves at room temperature in one week or less;

X - dissolves at 80°C (or at its boiling point, if lower) in 24 hours;

Y - dissolves at 160°C (or at its boiling point, if lower) in 24 hours;

Z - swells at room temperature in 24 hours;

N - does not even swell.

E. THERMAL PROPERTIES

Thermal properties were determined by two techniques:

(1) differential scanning calorimetry, and

(2) hot stage microscopy.

1. Differential Scanning Calorimetry

Polymer samples, 25 mg each, were carefully weighed out in pans, which were then sealed air-tight with a crimper. These pans were then placed in the sample chamber of the instrument, a Perkin Elmer DSC 1B model and heated at the rate of 10°C per minute. Indium was used as a calibration standard. The peaks obtained corresponded to phase transitions. The instrument was not sensitive enough to determine some glass transition temperatures. However, melting points of the polymers could be obtained easily.

2. Hot Stage Microscopy

The behavior of the polymers was examined with increasing temperature by a hot stage microscope, Thomas model 40, metal stage, Kofler type with an attached polarizer.

F. AUTO-OXIDATION

Some of the polymers contained a double bond in their repeat units and hence were susceptible to oxidation. In the presence of light, auto-oxidation took place quite rapidly even at room temperature. This was monitored by ultraviolet and infrared spectroscopy as well as by elemental analysis. The samples for ultraviolet and infrared spectroscopy were prepared by preparing KI pellets as described in section A, subheading 1 of this chapter. The pellets were left exposed to air in the presence of light for various durations and spectra obtained. From the spectra it was possible to analyse the extent of auto-oxidation from a molecular standpoint. By carrying out elemental analysis of solid polymers similarily exposed the amount of oxygen absorbed could be estimated. The elemental analyses were carried out by Galbraith Laboratories.

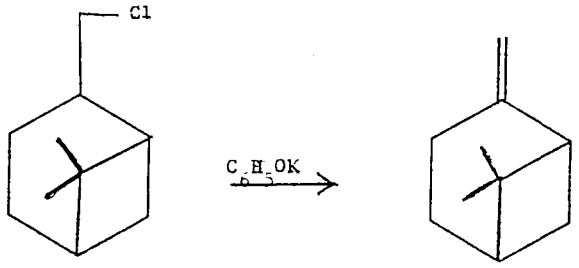
CHAPTER IV

POLY(β-PINENE)

A. INTRODUCTION

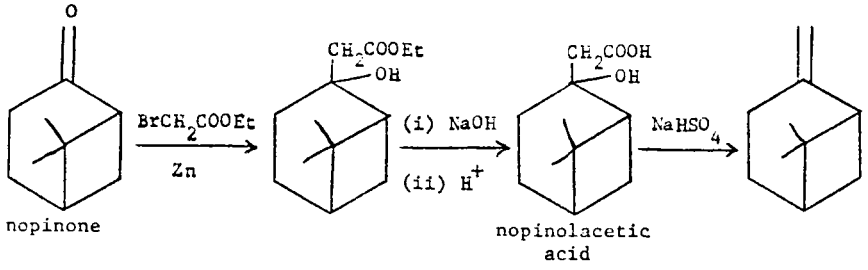
β-Pinene occurs in nature as a constituent of pine oil, mostly as the laevorotatory isomer.[108] The source of β-pinene and most of its derivatives is turpentine.[109] Along with α-pinene, β-pinene has considerable industrial importance since a large part of the synthetic perfume industry[110] as well as some commercial adhesives[111] are based on reactions involving them as starting materials.

β-Pinene has been synthesized by the dehydrohalogenation of 7-chloropinene.[112]



(50)

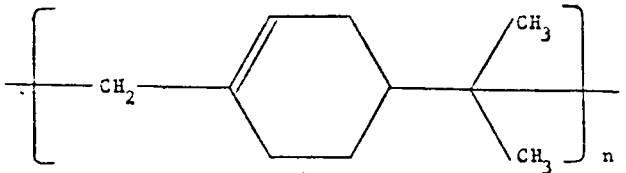
It has also been prepared by decarboxylation and dehydration of nopinolacetic acid, which is the product of the condensation of ethylbromoacetate and nopinone.[113]



(51)

β-Pinene has also been synthesized by Guha et al. and by Komppa by other methods.[114]

β-Pinene has been shown to polymerize by Lewis acid catalysts such as $AlCl_3$.[115-120] For example, Roberts and Day[117] obtained polymers with a molecular weight range of 650-1500 using several Friedel-Crafts initiators. Certkova and Mitarbeiter[117] are reported to have used H_2F_2, BF_3, and other catalysts to obtain polymers with molecular weights about 540, indicating that tetramers were mostly formed. Roberts and Day[116] postulated that the propagation mechanism involved the opening of the bicyclic bridge structure to give a repeating unit as in structure (I)



(I)

Huet and Marechal[118] studied the polymerization kinetics of β-pinene with BF_3, BF_3-$O(C_2H_5)_2$, $AlBr_3$, and $TiCl_4$ in solvents such as ethyl chloride, methylene chloride, and tetrachloroethane. Poly(β-pinene) has also been prepared by Pietila and his coworkers[119] with $AlCl_3$, although their emphasis was to study the copolymerization of β-pinene with styrene and α-methyl styrene. Rengachary[120] studied the effect of solvents and their polarity on the Lewis acid polymerization of β-pinene.

This monomer has also been polymerized with Ziegler-Natta initiators.[121-122] Achon and his coworkers[121] obtained polymers with molecular weights from 390 to 2300 and softening points of 108-121°C by polymerizing β-pinene with $Al(C_2H_5)_2Br$-$TiCl_4$ in a benzene-toluene

mixture. Marvel et al.[123] used triisobutyl aluminum with titanium tetrachloride in n-heptane and obtained polymers with softening points in the range 94-118°C. No molecular weight data were reported by them.

β-Pinene has not been polymerized by free radical initiation. For example, the addition of carbon tetrachloride to β-pinene initiated by benzoyl peroxide[123] and by ionizing radiation[124] leads to an almost quantitative yield of 1:1 addition product without the formation of even a telomer, in constrast to the telomerization of other vinyl monomers observed in similar circumstances.[125] Also, Kennedy et al.[78] report no increase in the formation of polymer in the thermal polymerization of β-pinene by the addition of cumene peroxide.

As pointed out in Chapter I of this dissertation, Bates, Best, and Williams showed that β-pinene could be polymerized by gamma radiation.[51,52,126] They obtained G(-M) values of 500-2000 depending on the extent of drying. The polymer was partially insoluble in the monomer and precipitated out as a white solid. The soluble fraction had an average molecular weight of 550 while the value of 1450 was obtained for the portion of the sample dissolving in chloroform at its boiling point.[51,126] The insoluble fraction was shown to be birefringent but had essentially the same chemical repeat structure as the polymer prepared by either Friedel-Crafts or Ziegler-Natta catalyst systems prepared by other researchers.[116,121] Pinner[77] has also reported that the radiation-induced polymerization of β-pinene gives a high molecular weight polymer, which is birefringent and soluble in hot chlorobenzene. No further work on the radiation-induced polymerization of β-pinene has been reported since then.

Kennedy and Chou[78] have recently reported the formation of a crystalline polymer by thermal initiation, the method consisting of heating the bulk monomer at 160°C in an inert atmosphere of nitrogen for a week.

It was therefore decided to carry out a study of the radiation-induced polymerization, emphasizing the characterization of the polymer formed, and comparing it to a commercial polymer, Polyterpene Zonarex Resin B-115 prepared by Lewis acid initiation by Arizona Chemical Company, Stamford, Connecticut. An effort was also made to prepare the polymer by thermal initiation as a part of this research so that its characteristics could also be compared.

B. POLY(β-PINENE) PREPARED BY RADIATION-INDUCED POLYMERIZATION

1. Results of Preliminary Work on Polymer Preparation

After distillation under reduced pressure (ca. 1 mm of mercury) on a Nester-Faust spinning band column, the monomer was checked for purity on a gas chromatograph, as mentioned in Chapter II, section C of this dissertation. The chromatograph obtained with a column temperature of 140° consisted of only a single peak, showing the absence of impurities such as α-pinene above the detection limit of ca. 0.1 %.

Previous to the work which is reported in detail, later in this chapter, several preliminary experiments were performed using a comparatively crude set-up. The manifold for the preliminary monomer handling consisted of several sample tubes connected to the manifold, which was connected to one vessel into which the monomer, β-pinene, was introduced, degassed, and then transferred to the sample tubes which

were then sealed off. The main difference between this preliminary set-up and the one used for later work and described in the experimental section of this dissertation (Chapter II) is that the glassware was not baked. However, this crude set-up gave sufficient drying, especially when the monomer was first passed through a column filled with predried silica gel and anhydrous $CaCl_2$, to give a polymer on irradiation. The results are shown in Table V. Some of the experiments utilized predried BaO in the vessel.

TABLE V

RESULTS OF PRELIMINARY EXPERIMENTS WITH β-PINENE

No.	Predrying	BaO used	Dose[@] (Mrad)	Monomer (g)	Polymer (g)	Percent Conversion	G(-M)
1.	No	No	1.45	2.056	0	0	0
2.	No	No	3.01	1.985	0	0	0
3.	Yes	No	3.01	2.073	0.0171	0.82	19.2
4.	Yes	No	3.86	1.023	0.0083	0.81	14.7
5.	Yes	Yes	0.48	2.168	0.0015	0.07	10.1
6.	Yes	Yes	0.96	2.092	0	0	0
7.	Yes	Yes	1.45	2.314	0.0138	0.60	28.9
8.	Yes	Yes	3.01	1.941	0.0215	1.11	25.8
9.	Yes	Yes	3.86	1.856	0.0163	0.88	16.0

[@]Calculated on the basis of a dose rate ∿0.241 Mrad $hour^{-1}$. Irradiation was carried out at ∿25°C.

These results indicated that β-pinene is sensitive to the extent of drying, which was a confirmation of the work of Bates et al.[51-52] Although these percentage conversions and G-values were low, they pointed to the need for achieving two objectives: firstly, the need for more sophistication of technique in order to achieve better drying efficiency and thereby higher conversions and G-values, and secondly, the need to achieve better reproducibility of results.

Hence the set-up described in Chapter II section C was used.

2. Results of Experiments to Prepare Poly(β-pinene) with Bakeout Vacuum Apparatus

Initially, barium oxide was used as the drying agent. However, the barium oxide used was probably impure. It had been exposed to the atmosphere and consequently had been partially converted to the carbonate and possibly to the hydroxide. Heating this impure barium oxide to a high temperature (over 400°C) was expected to purify it. However, the oxide formed a hard cake, which on cooling back to room temperature seemed to stick to the glass and the glass apparatus cracked. Due to this problem occurring frequently, it was decided to switch to silica gel.

Two grades of silica gel were used. It was found that the silica gel (dessicant grade 950,60-200 mesh) which was white in color gave results which were not very reproducible even in the same batch. Some of the results are presented in Table VI. The other grade of silica gel used was the indicator, tell-tale type, 6-16 mesh, which was blue in color when heated for predrying. It gave much better reproducibility and at the same time gave high G-values (ca. 1000). The results of

TABLE VI

RESULTS OF IRRADIATION OF β-PINENE PREDRIED WITH DESSICANT GRADE SILICA GEL*

No.	Monomer (g)	Irradiation Dose@ (Mrad)	Polymer (g)	Percent Conversion	G-value
I-1	19.874	0.440	0.519	2.613	416.5
I-2	20.786	0.440	0.963	4.634	738.6
I-3	17.325	0.560	0.005	0.030	3.8
I-4	21.950	0.560	0.229	1.042	130.5
II-1	16.593	0.440	0.866	5.222	832.4
II-2	21.699	0.560	0.016	0.072	9.0
II-3	19.412	0.440	0.006	0.033	5.2
II-4	18.593	0.560	1.325	7.127	892.7
II-5	19.762	0.560	1.866	9.440	1182.3

*Silica gel was dessicant grade 950, 60-200 mesh, supplied by Davison Chemical Company.

@Dose rate ca. 0.220 Mrad $hour^{-1}$; Irradiation was carried out at ca. 25°C.

some of these irradiations are presented in Table VII. In these tables, the sample were numbered as follows: the Roman numerals indicated the batch numbers while the Arabic numerals indicated the sample numbers in each batch.

Satisfactory reproducibility was only obtained with the indicator grade silica gel. Extremely good reproducibility was neither found nor expected in this work. This is because the samples of monomer are so very sensitive to the presence of water or any other scavenging agent

TABLE VII

RESULTS OF IRRADIATION OR β-PINENE PREDRIED WITH INDICATOR GRADE SILICA GEL*

No.	Monomer (g)	Dose Rate@ (Mrad hour^{-1})	Dose (Mrad)	Polymer (g)	Percent Conversion	G(-M)
III-1	19.763	0.210	0.420	1.421	7.19	1201
III-2	19.876	0.210	0.420	0.984	4.95	827
III-3	17.325	0.210	0.420	1.137	6.57	1096
III-4	18.592	0.210	0.420	1.042	5.61	936
IV-1	23.459	0.200	5.500	15.621	66.59	849
IV-2	21.772	0.200	5.500	16.844	77.36	987
IV-3	19.245	0.200	3.500	9.475	49.23	987
IV-4	16.501	0.200	3.500	7.171	43.46	871
V-1	14.470	0.200	5.750	12.289	84.93	1036
V-2	15.213	0.200	5.750	12.058	79.26	967
V-3	12.563	0.200	5.750	10.019	79.75	973
V-4	10.489	0.200	4.900	9.055	86.33	1236
V-5	11.568	0.200	4.900	8.595	74.30	1064
V-6	13.231	0.200	4.900	10.545	79.70	1141
VI-1	15.596	0.165	1.485	3.849	24.68	1166
VI-2	16.716	0.165	1.485	3.651	21.84	1032
VI-3	18.330	0.165	2.310	5.432	29.64	900
VI-4	17.590	0.165	2.310	6.003	34.13	1036
VI-5	19.278	0.165	2.310	4.891	25.37	770

*Silica gel was indicator grade, tell-tale type, 6-16 mesh supplied by Fisher Scientific.

@Irradiation was carried out at ∿25°C.

that both the percentage conversion and consequently the G(-M) value are adversely affected by even trace quantities of such impurities. However, since standard monomer and system preparation techniques were used, a fair degree of reproducibility was found. The samples, irradiated after treatment with the indicator type of silica gel, gave an average G(-M) value of 1004.

The results given in tables V, VI and VII refer to the total polymer formed on irradiation. However, a part of the polymer formed is insoluble in the monomer at room temperature and was therefore separated out in some cases as explained in Chapter II, section E, by filtration. The soluble fraction was isolated by precipitation with methanol. Table VIII gives the results of this fractionation of the poly(β-pinene). Only two batches of the polymers prepared using the indicator type of silica gel were fractionated in this manner. The amounts of the monomer irradiated, the dose rates, and the doses of irradiation are the same as those in Table VII (p 71). Roughly half of the polymer is insoluble in the monomer. All the other batches of poly(β-pinene) were not fractionated by filtration. Rather, they were separated by evaporation of the monomer from the irradiated sample and both fractions of the polymer were collected together. By varying the technique of polymer isolation and recovery, it was possible to prepare samples of polymers with varying amounts of crystallinity. This will be discussed in greater detail later in this section. The two methods of recovery of the polymer, namely, evaporation of the monomer and precipitation from methanol, gave similar yields, thus confirming that no polymerization took place during evacuation. Addition of methanol

TABLE VIII

RESULTS OF FRACTIONATION OF POLYMER AFTER IRRADIATION OF β-PINENE

No.	Insoluble Polymer (g)	Soluble Polymer (g)	Percent Conversion (Insoluble)	Percent Conversion (Soluble)	G(-M) (Insoluble)	G(-M) (Soluble)	%Insoluble of Total Polymer
IV-1	7.866	7.755	33.49	33.06	427	422	50.4
IV-2	8.738	8.106	40.13	37.23	512	475	51.9
IV-3	4.843	4.631	25.17	24.07	504	482	51.1
IV-4	3.746	3.426	22.70	20.76	455	416	52.2
V-1	6.145	6.145	42.47	42.47	518	518	50.0
V-2	6.041	6.017	39.71	39.55	484	482	50.1
V-3	4.989	5.030	39.71	40.04	484	488	49.8
V-4	4.745	4.310	45.24	41.09	648	588	52.4
V-5	4.458	4.138	38.54	35.78	581	512	53.1
V-6	5.483	5.062	41.44	38.26	593	548	52.0

to the irradiated monomer-polymer mixtures before evacuation helped increase the rate of monomer evaporation.

At a later stage of this research, it was decided to compare the effect of tertiary amines on the radiation-induced and thermal polymerization since these amines are known to act as cationic scavengers.[127] One batch of experiments was carried out to study the effect of tripropyl amine on the radiation-induced polymerization of β-pinene and thus confirm the mechanism of propagation. The results are shown in Table IX.

TABLE IX

EFFECT OF TRIPROPYL AMINE ON RADIATION-INDUCED POLYMERIZATION OF β-PINENE

No.	Monomer (g)	TPA* (g)	Polymer# (g)	Dose@	Percent Conversion	G(-M)
VII-1	**	0	**	-	-	-
VII-2	11.276	0	0.631	3.775	5.60	104.0
VII-3	4.253	0	0.554	5.597	13.30	163.6
VII-4	2.190	0	0.428	8.003	19.53	171.2
VII-5	2.734†	∿0.05	0.000	5.587	0.00	0.0

*TPA ≡ tripropyl amine.

@Irradiation dose rate *ca.* 0.151 Mrad hour^{-1} at *ca.* 25°C.

**Sample broke before irradiation.

†includes tripropyl amine.

#polymer isolated by precipitation with methanol and evaporation of methanol.

The amounts of conversion of the pure β-pinene samples in this particular batch were comparatively low because the first sample broke during sample preparation, letting some moisture into the system. Although the G(-M) values for the three samples without tripropyl amine in this batch are much lower than those in table VII (p 71), these samples did yield polymer and, therefore, this set of experiments was valid enough to show that the sample containing ca. 2 mole percent tripropyl amine did not give any polymer.

3. Molecular Weight Studies

The poly(β-pinene) prepared by irradiation as well as that prepared by thermal initiation would not completely dissolve at room temperature in any of the over 35 solvents tried. The solubility characterization of this polymer is dealt with in greater detail later in this chapter. It was possible to dissolve the polymer completely in chlorobenzene, bromobenzene, β-pinene, and some other solvents at temperatures above 120°C in an inert atmosphere. However, when these solutions were cooled to room temperature, a part of the polymer precipitated out. Since the polymer auto-oxidized rapidly at higher temperatures, it was not possible to determine molecular weights of the polymer at elevated temperatures due to the complication of auto-oxidation.

Hence, solutions of poly(β-pinene) were prepared by heating the polymer in an inert atmosphere of nitrogen using carbon tetrachloride as a solvent. After the solution was cooled to room temperature, the precipitated polymer was filtered out. Thus, the molecular weights of only the soluble fraction of the polymer could be determined. Five

solutions of different known concentrations were prepared and their molecular weights obtained using a Knauer Vapor Pressure Osmometer, as described in Chapter III, section B of this dissertation. The results of the osmometry of a typical sample are shown in table X. The readings

TABLE X

VAPOR PRESSURE OSMOMETRIC DETERMINATION OF MOLECULAR WEIGHTS OF THE SOLUBLE FRACTION OF A TYPICAL SAMPLE OF POLY(β-PINENE)

No.	Concentration* (mg ml^{-1})	Average† Reading	$\frac{\text{Reading}}{\text{Concentration}}$†	K**	$\bar{M}_n = \frac{K_{cal}}{K}$
1	4.7	12.2	2.61		
2	13.7	36.0	2.64	2.59	2153
3	20.5	54.5	2.66		
4	30.8	82.6	2.68		
5	40.1	108.6	2.71		

*solution prepared from CCl_4 by filtering out insoluble polymer.

†converted to scale of 128.

**intercept value in divisions ml mg^{-1} from figure 5.

were converted from the scale of 64 to the scale of 128 by multiplying them by 2. The ratio of the readings to the concentration was plotted against the concentration and the straight line obtained extrapolated to zero concentration. The intercept value, obtained from this plot showing in figure 5 is 2.59 divisions ml mg^{-1}. Since the value of K_{cal} is 5576 divisions 1 $mole^{-1}$ from the calibration curve in figure 4

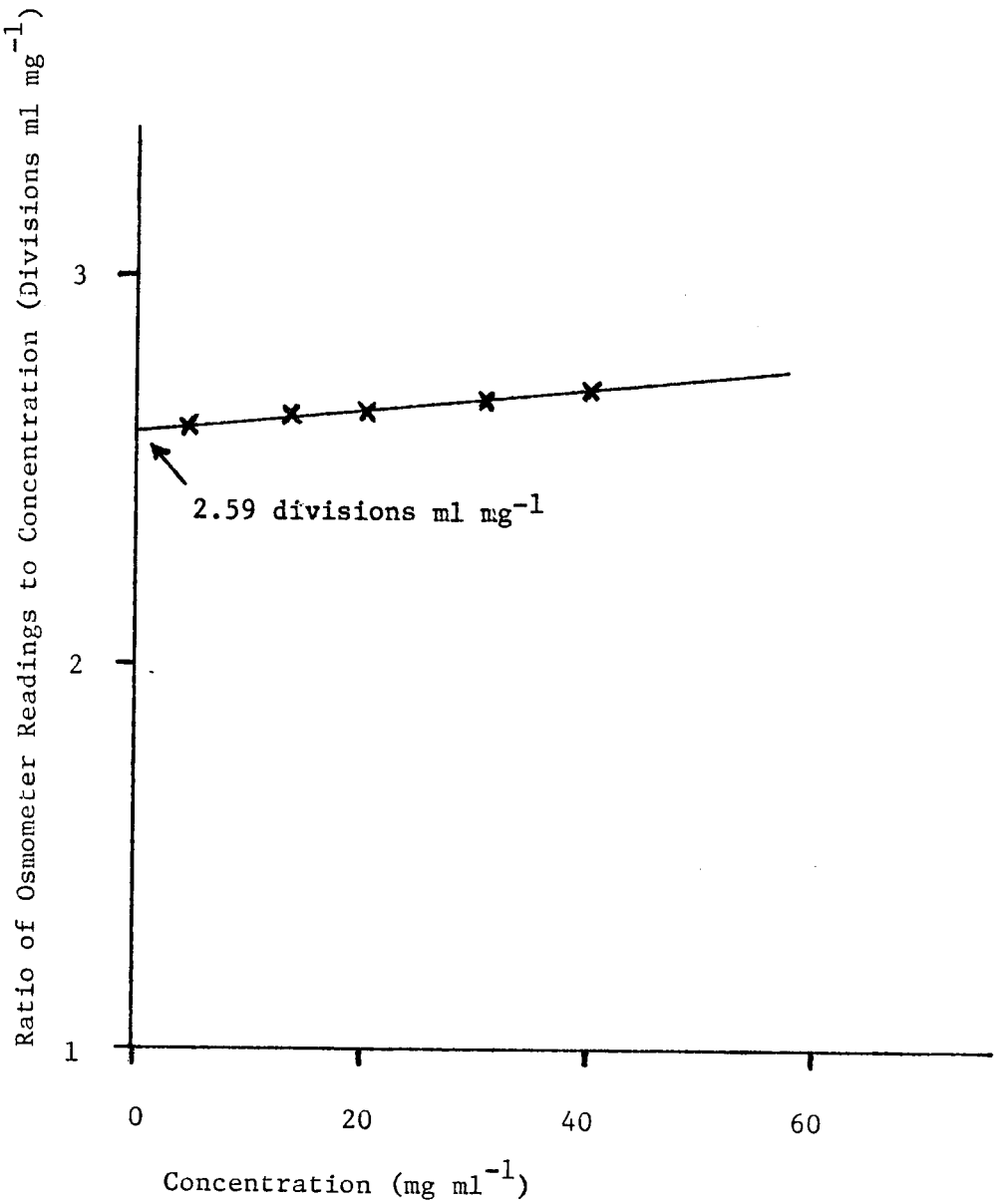


Figure 5. V. P. O. plot of soluble fraction of a typical poly(β-pinene) prepared by radiation-induced polymerization.

(p 58), the number-average molecular weight of the soluble fraction of poly(β-pinene) is 2153.

Using such determinations the number-average molecular weight were calculated. The results are shown in table XI.

TABLE XI

NUMBER-AVERAGE MOLECULAR WEIGHTS OF SOLUBLE FRACTION OF POLY(β-PINENE)

Sample No.	Percent Conversion	Dose (Mrad)	G(-M)	$\bar{M}_n$
III-2	4.95	0.42	826.5	1877
IV-4	43.46	3.50	870.9	2153
V-3	79.75	5.75	972.8	1890
V-6	79.70	4.90	1141	2363
VI-2	21.84	1.485	1032	2050
VI-5	25.37	2.31	770.4	1743

Since these molecular weights are very much below the range of the light scattering method, no use was made of this technique. It was also not possible to use viscometry to determine molecular weights because the Mark-Houwink parameters are not known for this polymer. These parameters are known for the commercial polymers of β-pinene with the same repeat unit, but these values cannot be used for the radiation-prepared polymer since the configuration of the polymer chains in the two cases are different. That the configurations are different is

apparent from the work on the crystallinity of the polymer dealt with later in this chapter.

4. Chemical Characterization

The proton nmr spectrum of the β-pinene monomer is shown in figure 6. This spectrum is identical to that reported in literature.[128] The mass spectrum of the monomer was also identical to that in literature,[129] thus showing that the monomer was sufficiently pure and more importantly that any possible impurities such as α-pinene, limonene, and myrcene were not present beyond the limits of their detection.

The polymer samples separated from the irradiated vial usually contained some monomer, as seen from figure 7, which shows the proton magnetic resonance (pmr) spectrum obtained from a typical unpurified sample. It was necessary to purify the polymer by suspending it in a solvent such as methylene chloride and reprecipitating it from methanol, followed by evacuating it to remove any traces of methylene chloride or methanol. After purification, the proton nmr spectrum of a typical sample of poly(β-pinene), shown in figure 8, did not contain any peaks due to protons from the monomer. Such peaks are easily spotted in the region around 4.57 ppm (δ) due to the protons in the vinylidene group, $>C=CH_2$; also the distinctive sharp methyl peaks at 0.72 and 1.25 ppm (δ) (cf. figure 5). Methylene chloride exhibits one peak at 5.3 ppm while methanol shows two at 1.4 and 3.5 ppm respectively and both these compounds are absent in the spectrum of the polymer as seen from figure 8.

The proton nmr spectrum of the Polyterpene Resin, Zonarex B-115, commercially manufactured by Lewis acid catalysis, is shown in figure 9.

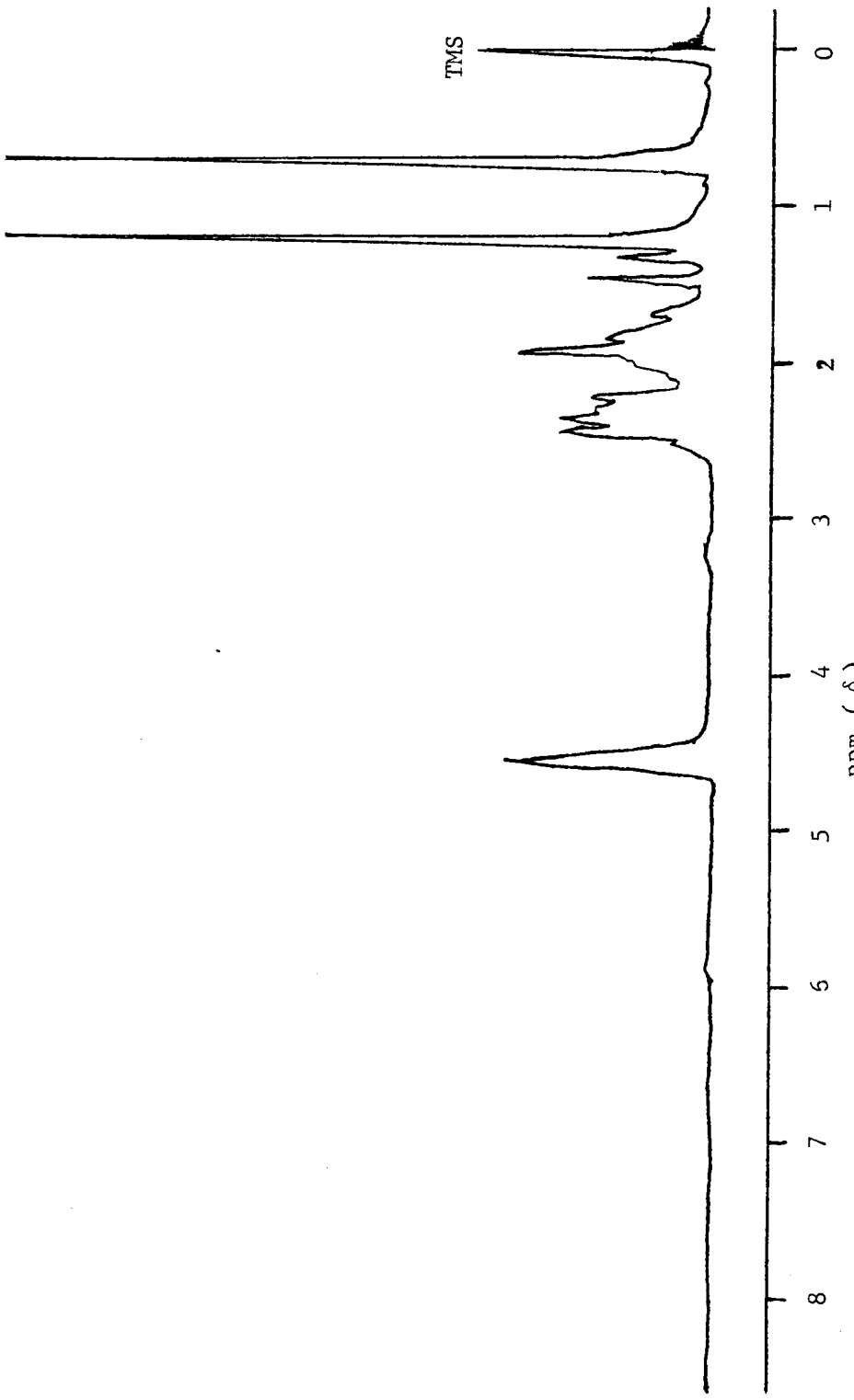


Figure 6. Proton nmr spectrum of β-pinene monomer

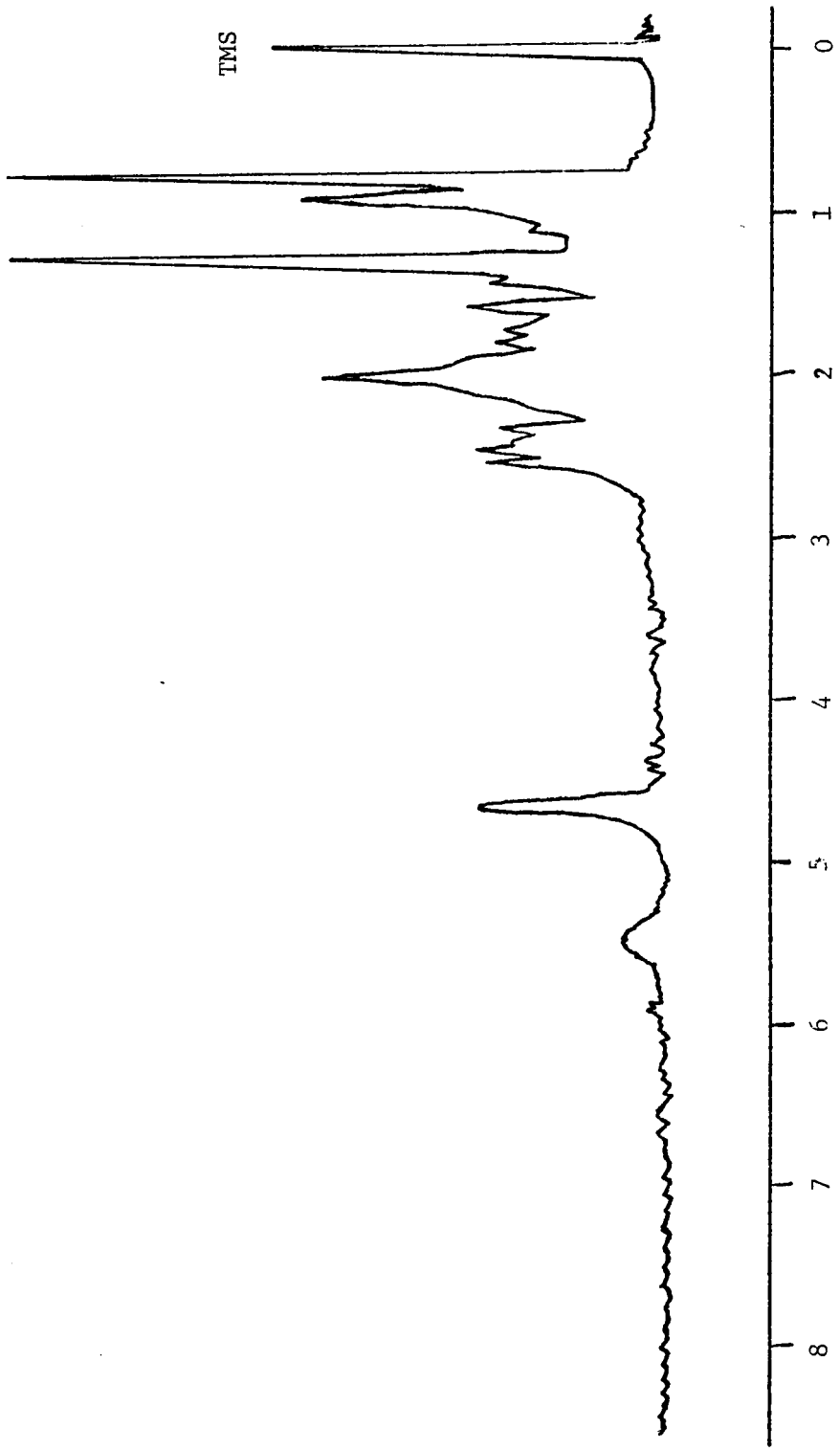


Figure 7. Proton nmr spectrum of radiation-prepared poly(β-pinene) still containing some monomer.

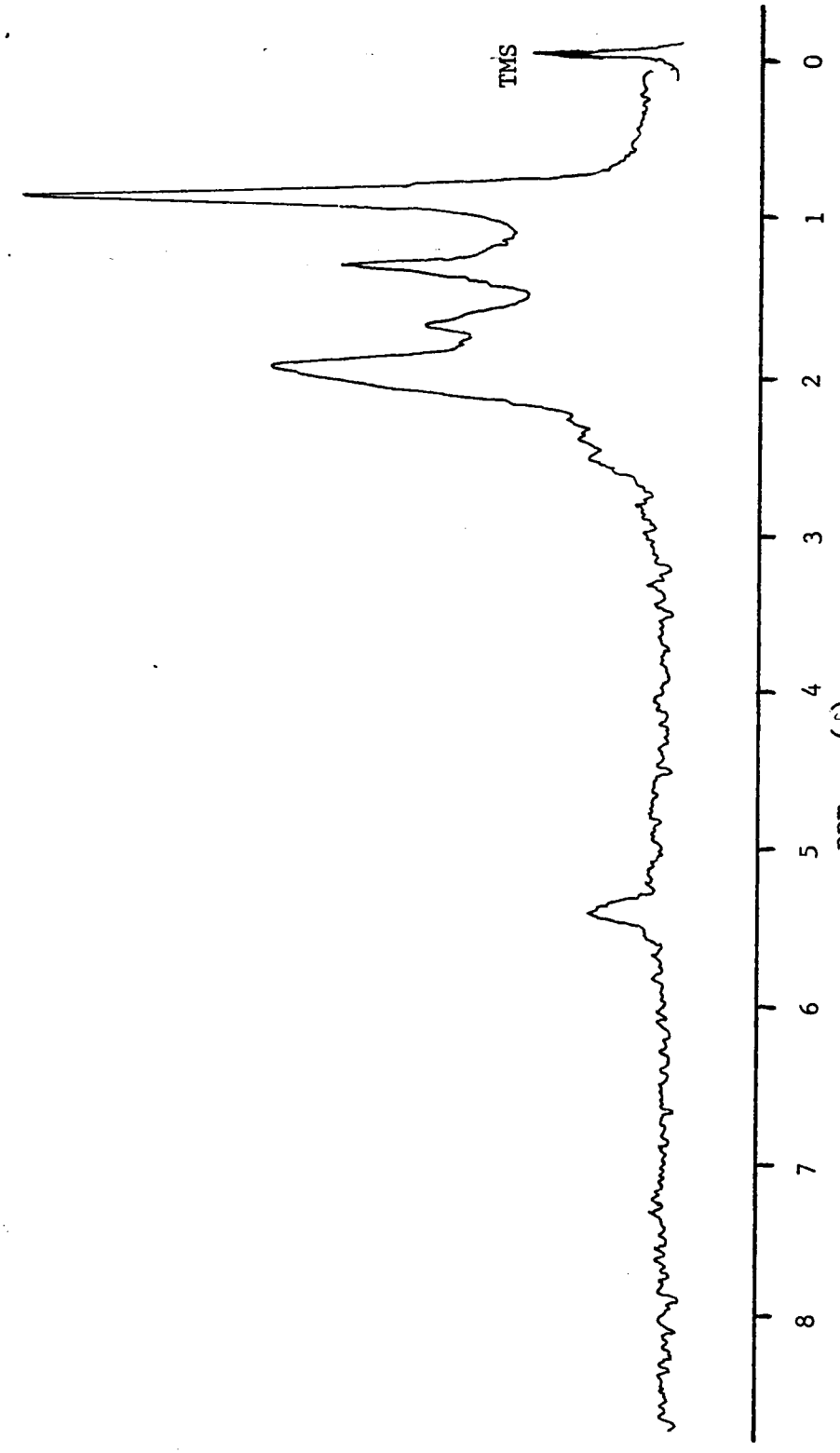


Figure 8. Proton nmr spectrum of purified poly(β-pinene) prepared by irradiation.

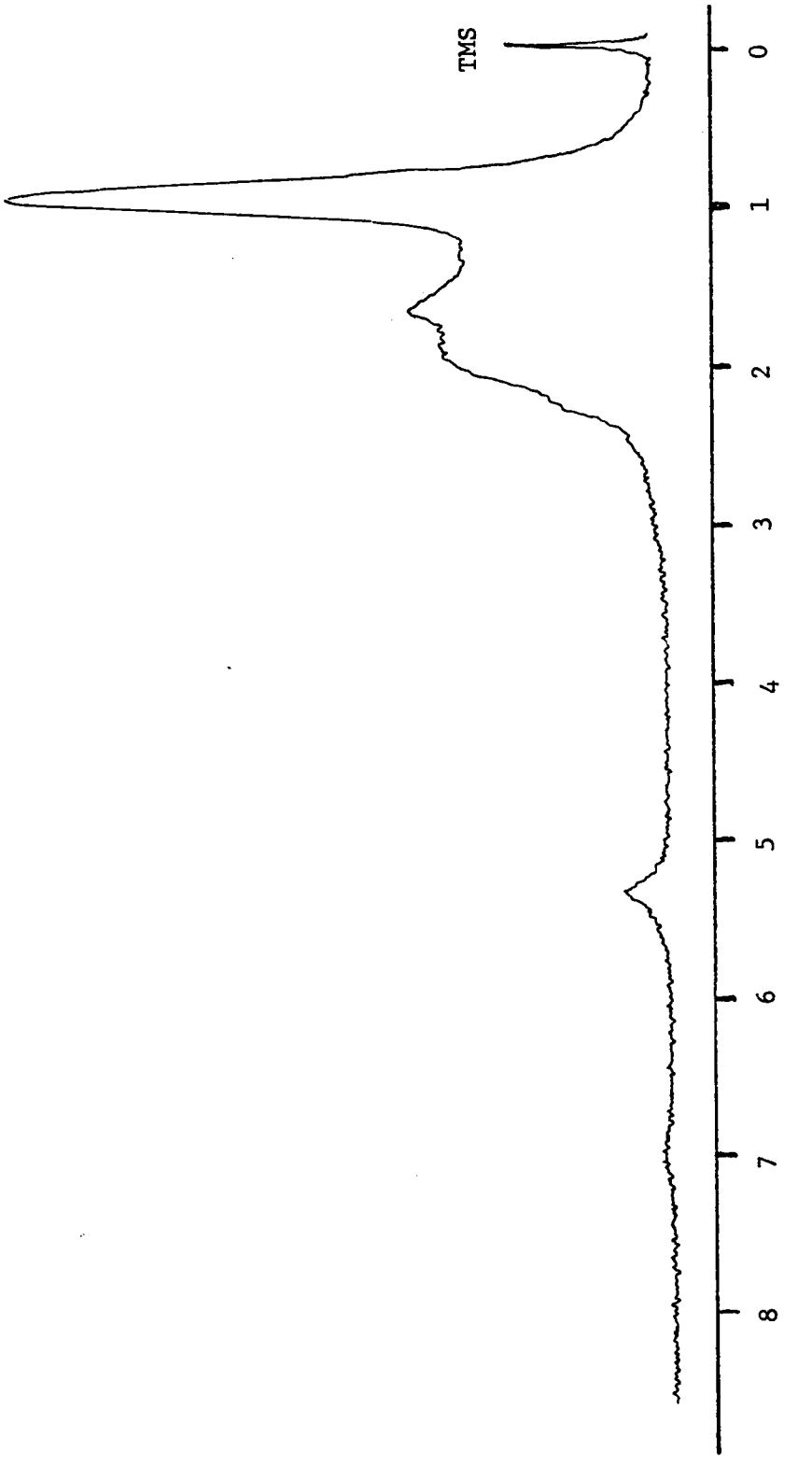
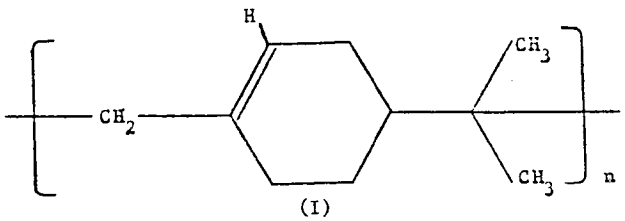


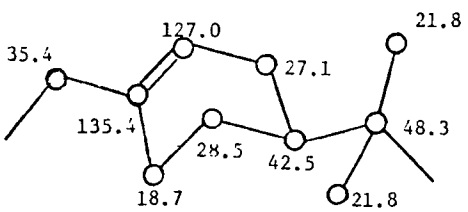
Figure 9. Proton nmr spectrum of commercial poly(β-pinene), prepared by Lewis acid catalysis and labelled as "Polyterpene Resin, Zonarex B-115" supplied by Arizona Chemical Company.

The strongest band in the spectra of these polymers is the one at ca. 0.90-0.95 ppm (δ) which represents the geminal dimethyl groups. The broad band around 5.4 ppm represents the resonance of the olefinic hydrogen in the cyclohexene ring systems. The remaining methylenes and methines of the general structure shown below resonate over the chemical shift range from 0.6 to 3.3 ppm.



(I)

The carbon-13 nmr spectrum is presented in figure 10. The assignments for the various peaks were assigned and shown below on the basis of the assignments for carbon atoms in standard spectra[130]



of compounds such as limonene and cyclohexene.

Figure 11 gives the infra-red absorption spectra of (a) the commercial Polyterpene Resin (PTR), obtained by casting a film from a carbon tetrachloride solution onto a NaCl plate, and of (b) the poly(β-pinene) polymerized by irradiation, obtained by pelletizing the polymer with anhydrous potassium iodide. The polymer produced by irradiation shows greater resolution of its absorption peaks, especially

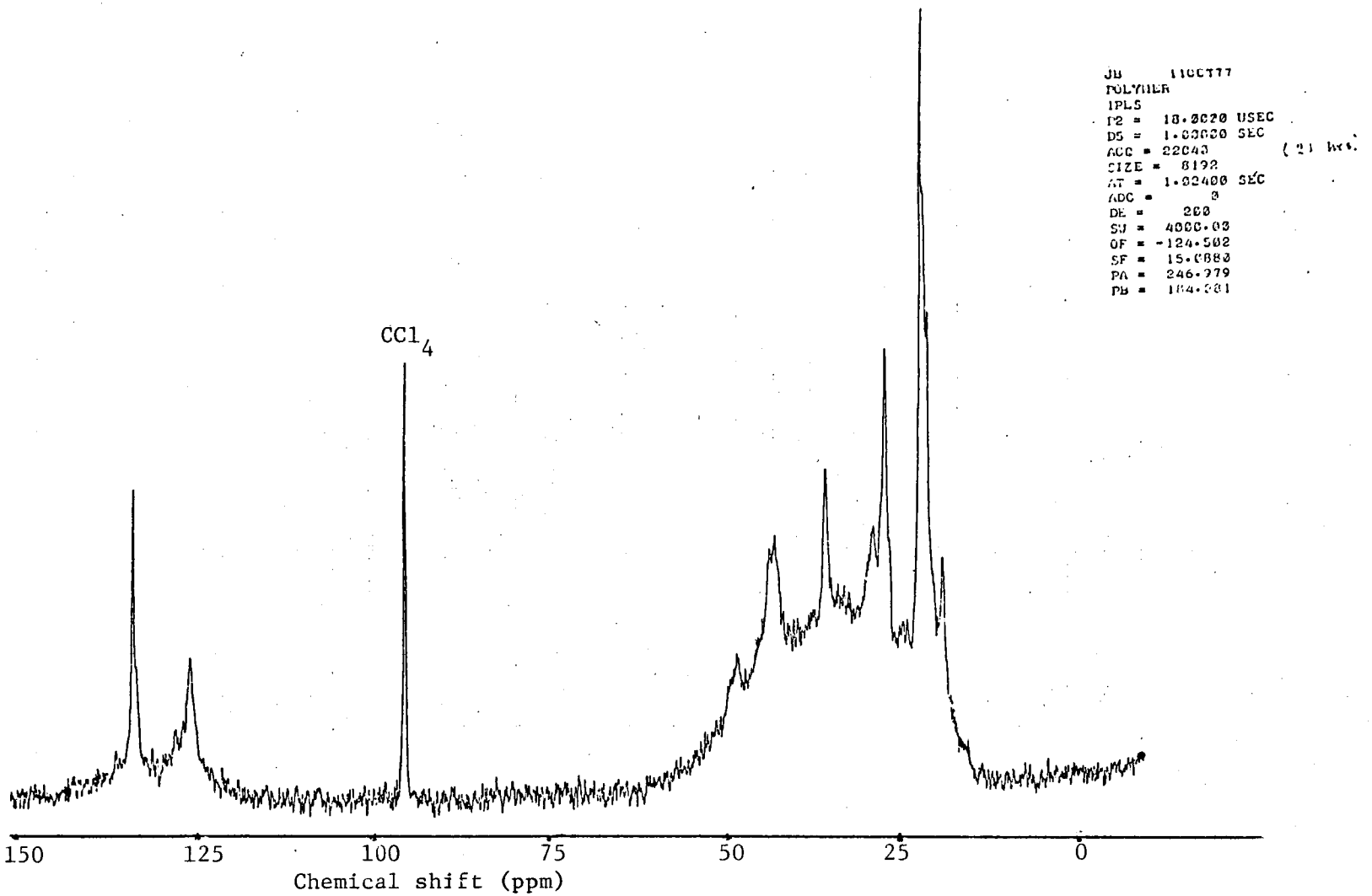


Figure 10. Carbon-13 nmr spectrum of radiation-prepared poly(β-pinene) in CCl_4.

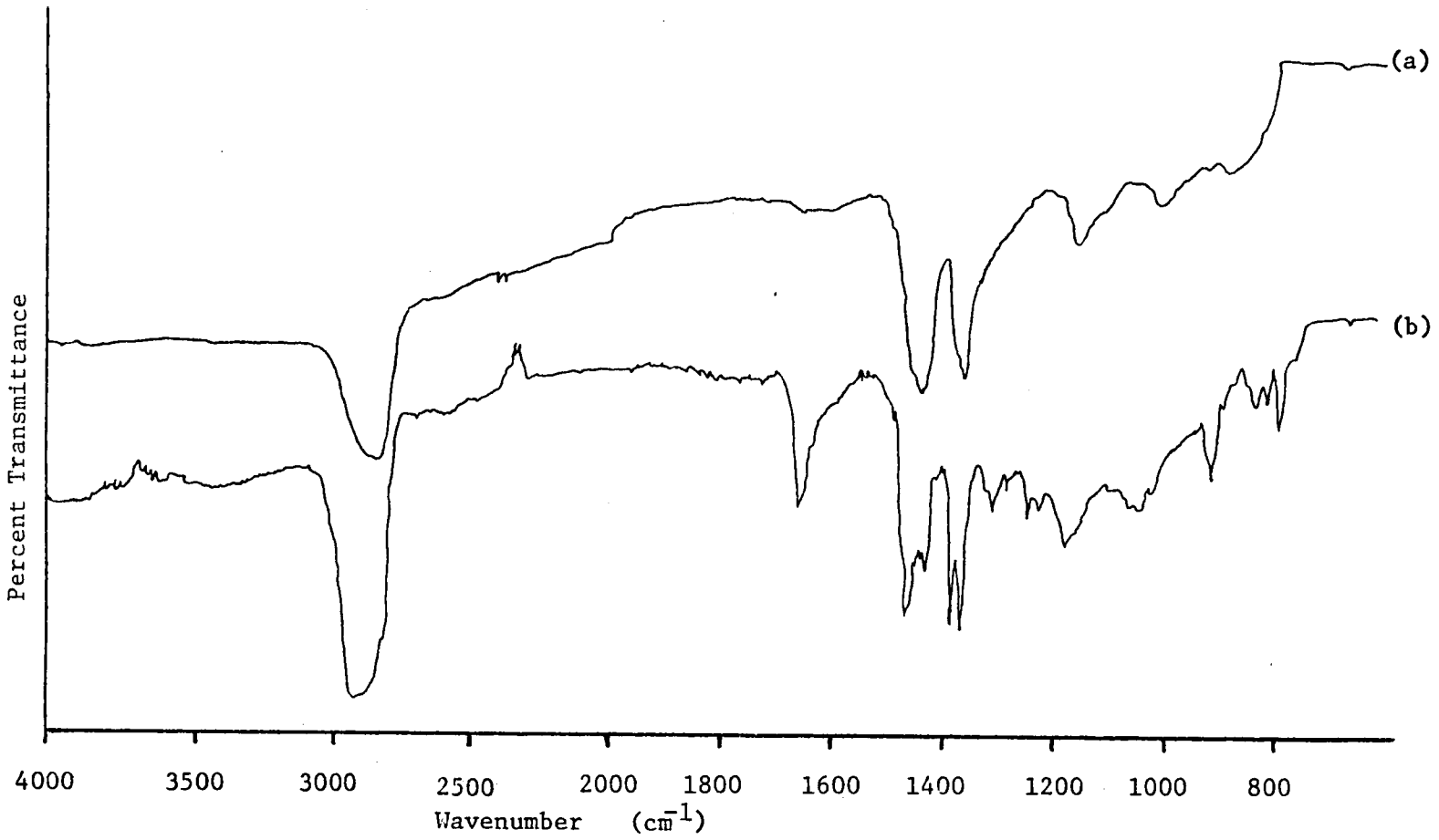


Figure 11. Infra-red absorption spectra of (a) Polyterpene Resin (PTR) obtained by casting a film from a CCl_4 solution onto a NaCl plate and of (b) radiation-prepared poly(β-pinene) obtained by pelletizing it with anhydrous KI.

evident with the gem dimethyl doublet at 1370 and 1390 cm^{-1}, than the commercial polymer. There is one other major difference. The polymer made by irradiation shows a peak at ca. 1660 cm^{-1} corresponding to the C=C stretching which is absent in the comercial resin.

The ultraviolet spectra of the polymers, poly(β-pinene) prepared by radiation and the commercial resin, are presented in figure 12. The maxima of the absorptions of the two polymers are very close to one another and appear to correspond to the maxima of compounds such as 1-ethylcyclohexene and limonene.

The elemental analysis for the freshly prepared polymer, when sent for analysis without any exposure to air, showed a carbon content of 88.15 % and a hydrogen content of 11.68 % corresponding to a total of 99.83 %. These percentages work out to a carbon-hydrogen atomic ratio of 10 to 16, which is the same as that of the monomer, β-pinene. The amount of oxygen content calculated by difference is 0.17 % by weight corresponding to 0.056 atom percent oxygen.

The experimental results for the determination of the extent of unsaturation in the polymer are shown in table XII.

TABLE XII

CHEMICAL TESTS FOR ESTIMATING EXTENT OF UNSATURATION

Reaction	Polymer (g)	Halogenated Polymer(g)	Halogen added(g)	Halogen per repeat unit
Bromination	0.3045	0.9973	0.6928	1.938
Iodochlorination	0.3559	0.9465	0.5906	1.391

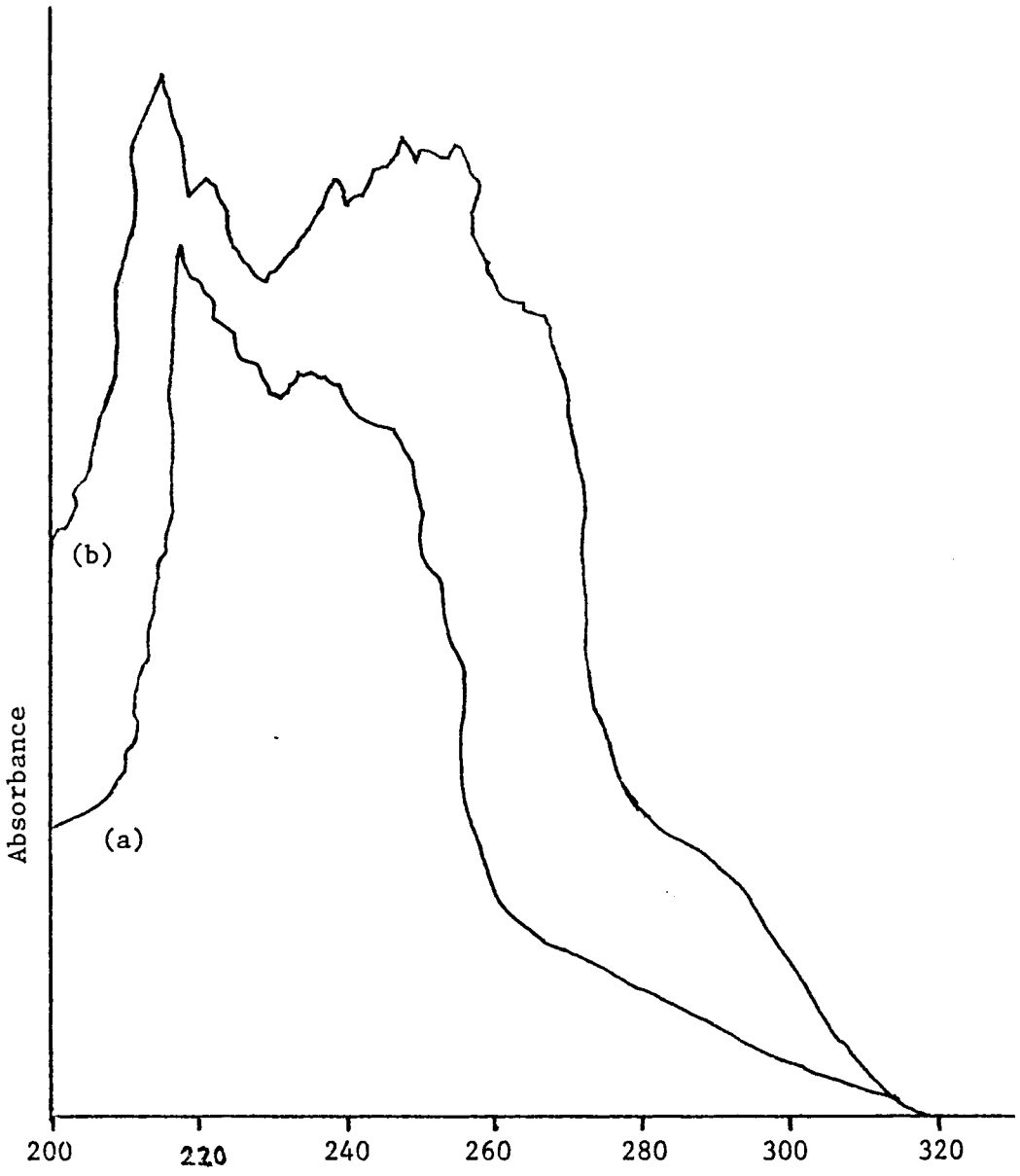


Figure 12. Ultraviolet spectra of (a) Polyterpene Resin solution in $CHCl_3$ and of (b) radiation-prepared poly(β-pinene) obtained by pelletizing the polymer with anhydrous KI.

These values are higher than expected on the basis of one double bond per repeat unit, indicating the possibility that some halogen substitution may have occurred.

5. Morphological Studies

The radiation-prepared polymer and the commercial resin were dissolved and sample slides prepared for optical microscopy as detailed earlier, in Chapter III, section C, subheading 1. The photomicrographs, obtained with the samples under crossed polarizers, are shown in figure 13. The polymer prepared by radiation-induced polymerization is indicated as "PβP" while the commercial Polyterpene Resin is marked "PTR." The photomicrographs illustrate that the radiation-prepared polymer is birefringent while the Lewis acid catalysed polymer is not.

Wide angle X-ray scattering (WAXS) patterns were obtained for the two polymers and these are presented in figure 14. These were obtained using a sample to film distance of 5.0 cm. The WAXS pattern shown in figure 14 a corresponds to the radiation-induced polymer while figure 14b shows the WAXS pattern for the Lewis acid catalyzed commercial resin. The pattern in figure 14a shows two sharp crystalline absorption rings with diameters of 2.70 and 3.15 cm corresponding to 2θ values of 15.1 and 17.5° respectively. Another ring of lower intensity with a diameter of 3.95 cm is also visible. This corresponds to a 2θ value of ca. 21.6. The WAXS pattern in figure 14b, on the other hand, shows only a diffuse ring indicating little or no crystallinity.

X-ray diffractometry was used as a technique to try to determine lattice spacings of these polymers. The commercial Polyterpene Resin

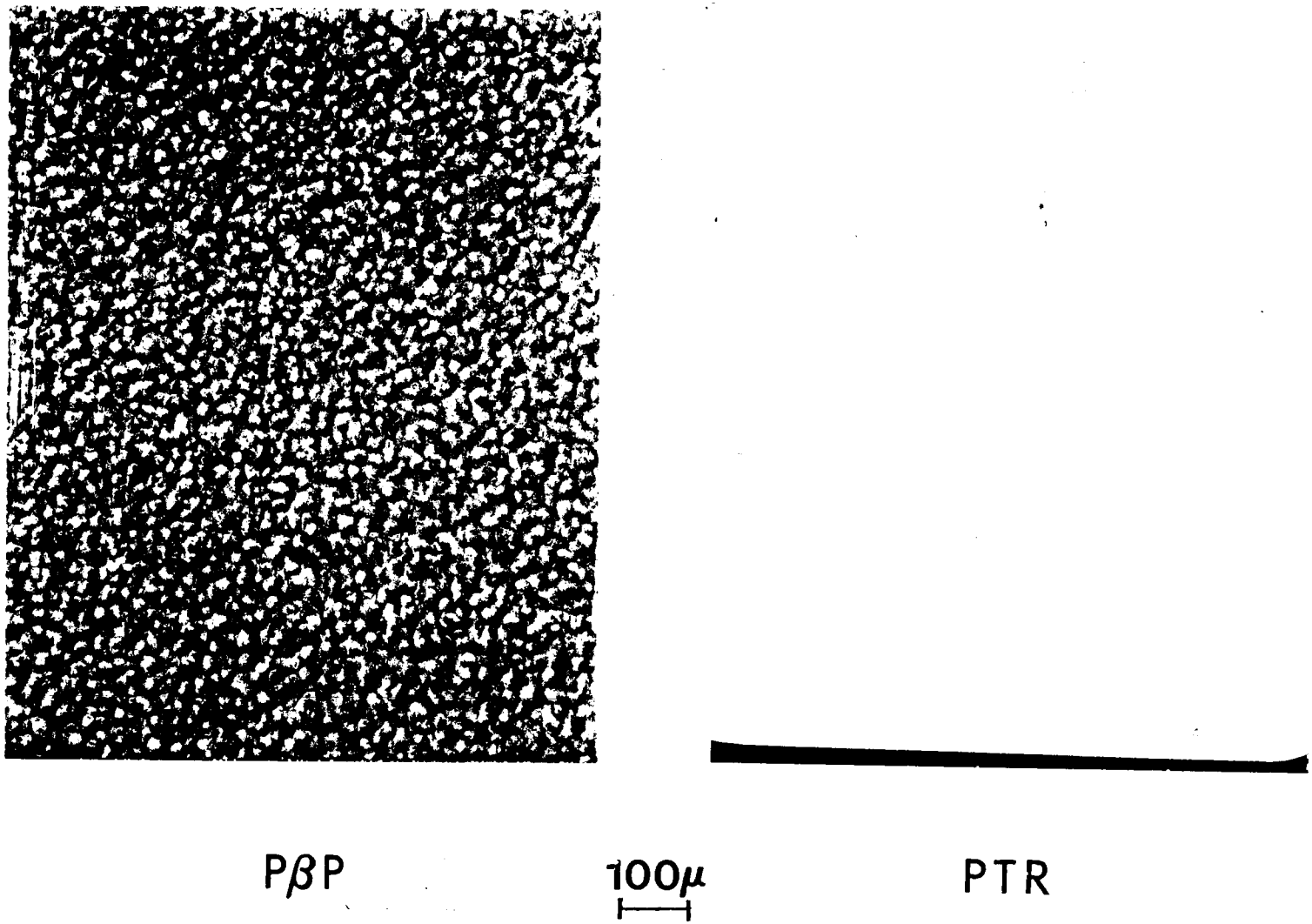
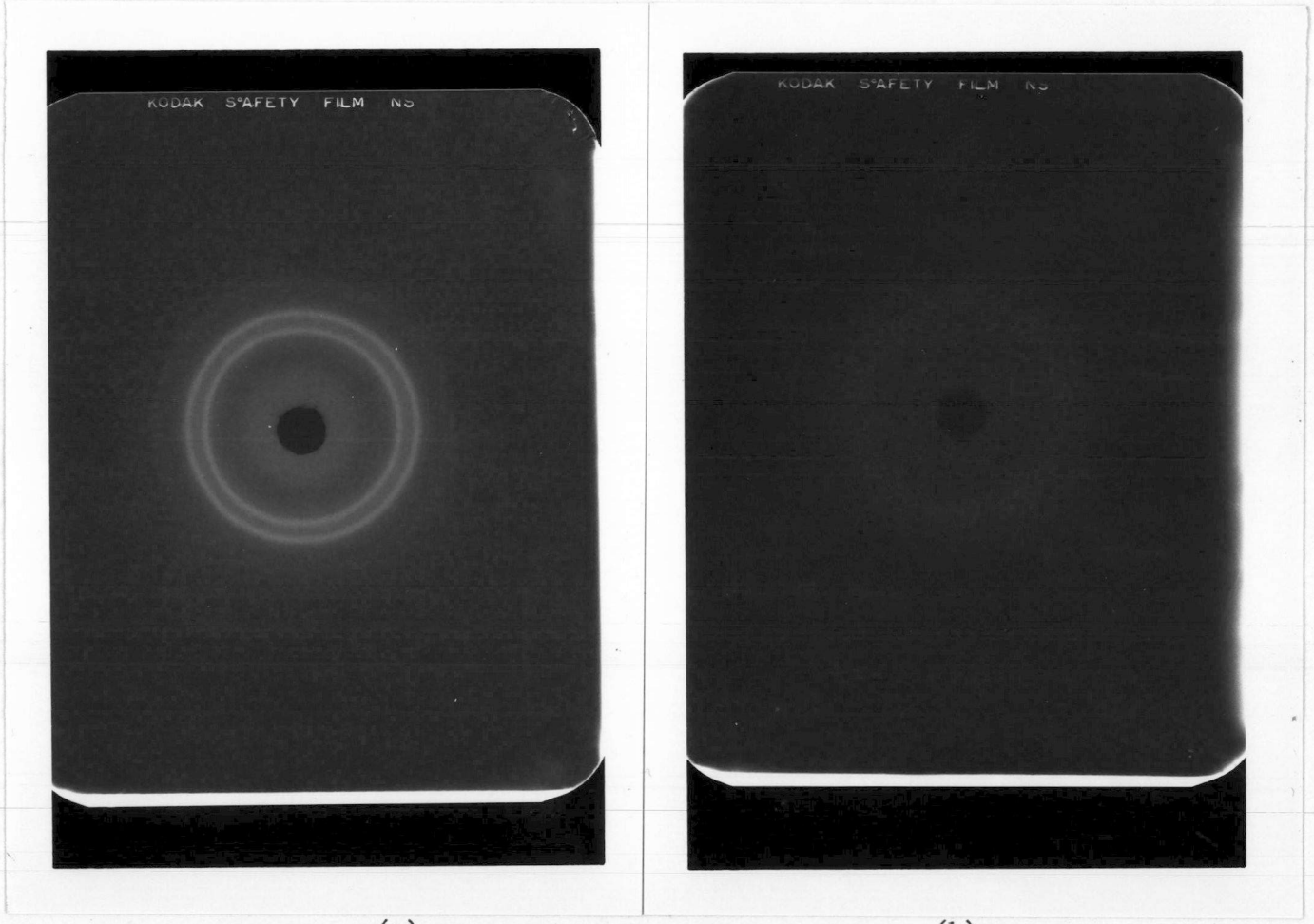


Figure 13. Photomicrographs with crossed polarizers of poly(β-pinene): (a) prepared by radiation-induced polymerization (PβP) and (b) of the commercial Polyterpene Resin (PTR).



(a) (b)

Figure 14. Wide angle X-ray scattering patterns of (a) radiation-prepared poly(β-pinene) and (b) commercial Polyterpene Resin.

gave virtually no crystalline peak as illustrated by the 2θ scan shown in figure 15. The poly(β-pinene) prepared by radiation, however, gave excellent sharp X-ray spectra. One typical scan is shown in figure 16. The crystalline peaks occur at 2θ values of 15.2 and 17.7°, which are very close to the values obtained earlier from WAXS measurements, within experimental error. These 2θ values were used to obtain the interplanar spacing d (in Å) from Bragg's law ($n\lambda = 2d \sin \theta$, where λ is the wavelength of the X-ray beam and n is the order of reflection). The 2θ values correspond to d spacings of 5.83 and 5.01 Å respectively.

From a scan such as in figure 16 (p 93) the intensities for the crystalline peaks and for the amorphous hump were determined using the method suggested by Matthews et al.[106] for polyethylene. First a straight line was drawn between the extreme wings of the measured diffraction trace and the figure above this line was redrawn. By this procedure the background-scattered intensity is removed. Next the redrawn curve was resolved into three symmetrical components: two sharp crystalline peaks and one amorphous hump. Finally, the areas under these were measured.

Various methods had been suggested[106,131,132] for determining the degree of crystallinity. Matthews et al.[106] had suggested that the degree of crystallinity is simply the fraction of the area under the crystalline peaks to the total area under the redrawn curve. However, the degree to which this holds true is limited by the extent to which one can associate the amorphous hump with the separate amorphous phase; some portion of the scattering by defective regions in the crystalline phase is included within the amorphous hump.[133] No account was taken

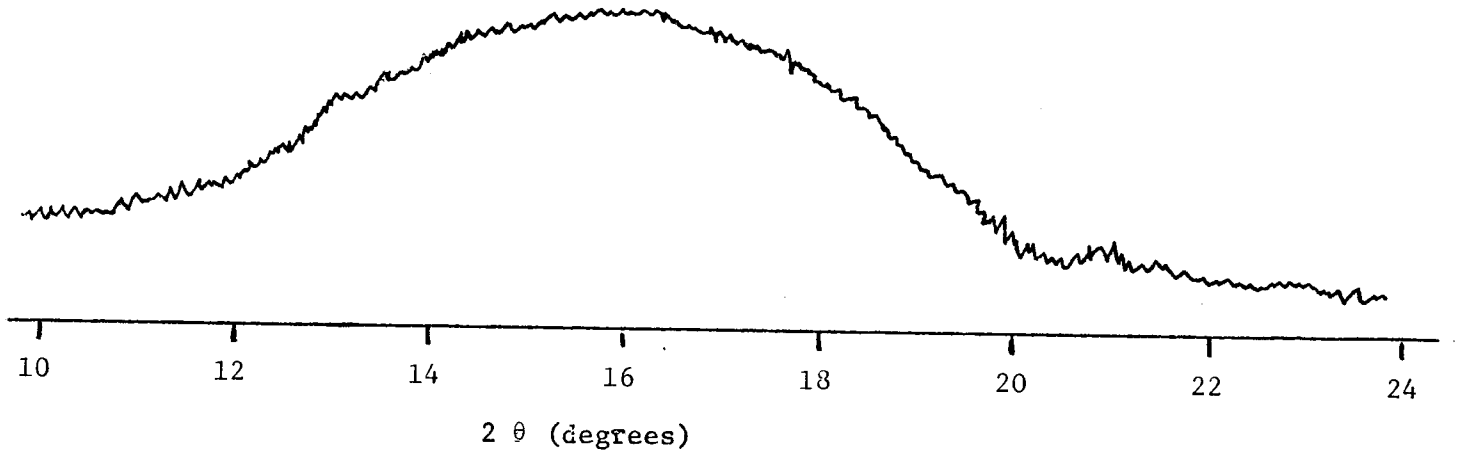


Figure 15. X-ray diffractometer scan of Polyterpene Resin.

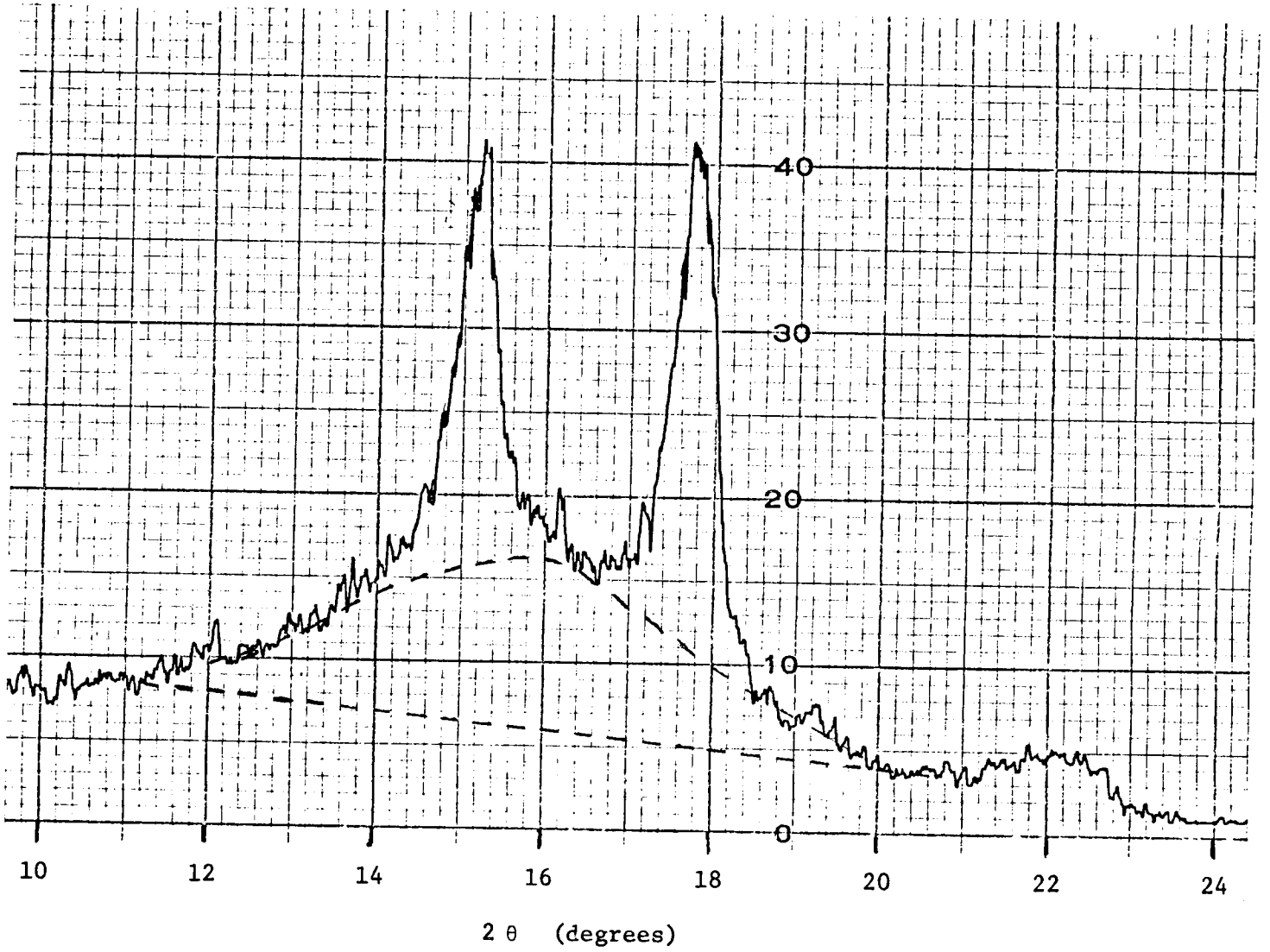


Figure 16. X-ray diffractometer scan of a typical sample of poly(β-pinene) prepared by radiation-induced polymerization.

of the reduction of the areas of the sharp peaks by disorder within the crystalline phase. This problem along with that of the disposition of the defect scattering were present in these methods. Ruland showed that the effect of the intracrystalline defects could be determined.[134] However, the calculations suggested by him are such that the experimental techniques involved therein are too tedious and yet his method does not significantly improve the accuracy obtained, especially when the unit cell is not defined.[133,135] The semi-empirical method, using the correlation of crystallinity intensities with the density or rather the specific volume of the polymer, gives a better value of the degree of crystallinity.[135,136] The manner in which the correlation was carried out is dealt with later in this section, after the density determinations.

The densities of the various samples were determined by both the density gradient column (DCG) using two different mixtures and by the floatation methods. Table XIII gives the densities obtained by both methods.

By soaking a sample of radiation-polymerized of poly(β-pinene) in chloroform, it was possible to dissolve off most of the amorphous regions of the polymer, thus obtaining almost completely crystalline polymer. This is because the poly(β-pinene) prepared by irradiation is only partially soluble in chloroform at room temperature and it was expected that only the amorphous fraction would readily dissolve. By fractionating the polymer prepared by radiation-induced polymerization using β-pinene monomer and chloroform as solvents in this manner, four other polymer samples were prepared with differing densities as seen

TABLE XIII

DENSITIES OF FRACTIONATED SAMPLES OF POLY(β-PINENE)

Sample No.	Fraction	Density ($g\ cm^{-3}$) from D.G.C.*	Floatation@
PTR	#	0.9735	0.975†
RPβP-1	#	1.0460	1.045
RPβP-2	soluble in monomer	1.0220	1.020
RPβP-3	soluble in $CHCl_3$	1.0130	1.015
RPβP-4	insoluble in monomer	1.0605	1.060
RPβP-5	insoluble in $CHCl_3$	1.1125	1.110

*density gradient columns made from ethanol and chloroform; density values significant to ± 0.0005

@density values significant to ± 0.005

#unfractionated samples

†obtained using ethanol-water mixtures.

from table XIII. These samples would be expected to have different crystalline contents if the assumption that only the amorphous fraction dissolves easily at room temperature is right. These fractionated samples are designated "RPβP" while the commercial polyterpene resin is labelled as "PTR" in table XIII. The density gradient curve from which the densities of these samples were determined is shown in figure 17. From the results it is obvious that the density gradient column method and the floatation method give density values which are very close to one another for each of the samples shown in this table.

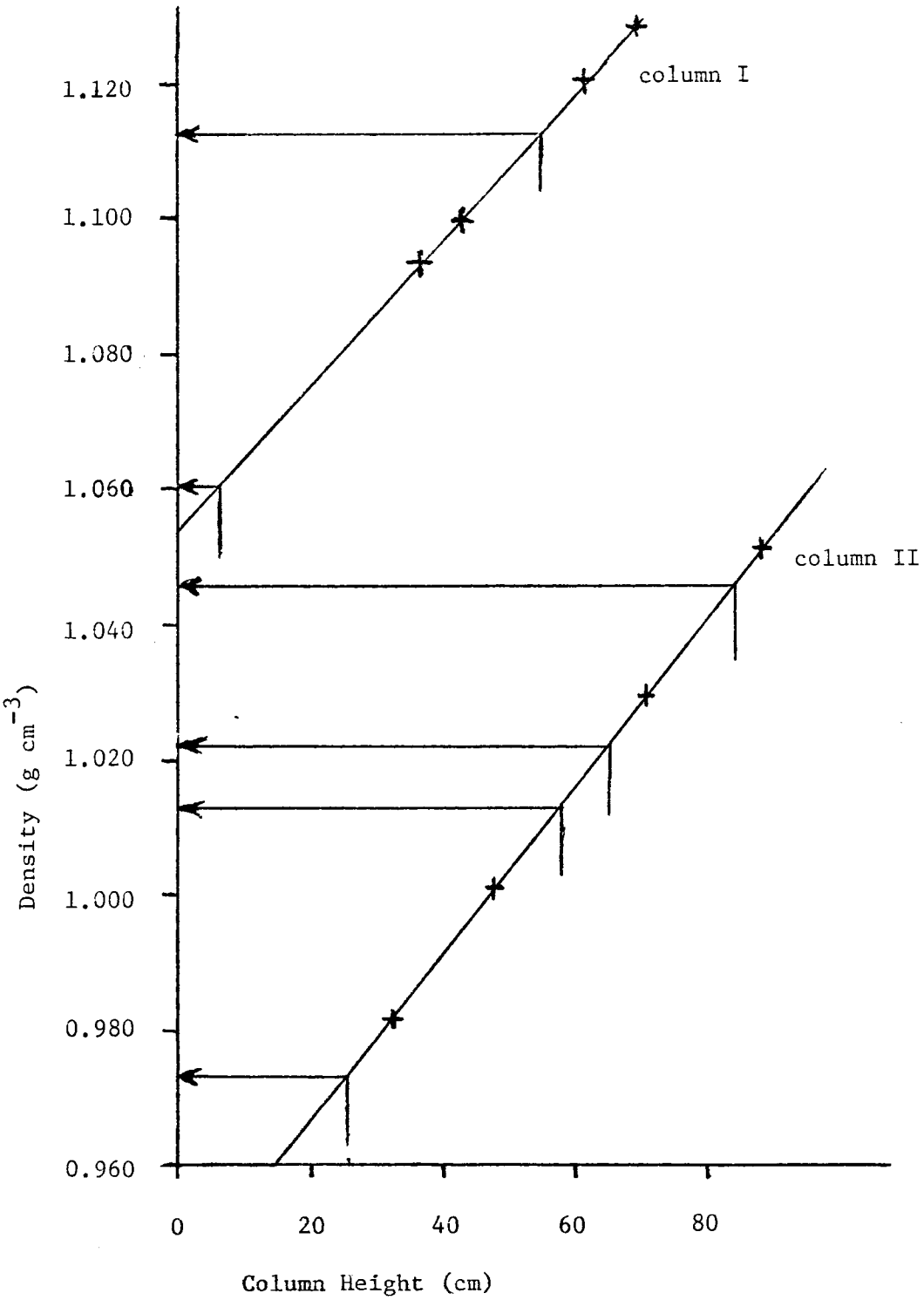


Figure 17. Density gradient curve for determination of densities of poly(β-pinene). The beads with known densities are marked +. Columns made from ethanol and chloroform.

It is known that the degree of crystallinity, X_c, is related to the ratio of the area of the amorphous hump in the X-ray diffractometer scan, A_a, to that of the crystalline peaks, A_c, by the equation,

$$X_c = \frac{1}{1 + x\frac{A_a}{A_c}} \tag{52}$$

where x is a correction factor and is assumed to be constant for each polymer. This constant has been shown to be 0.56 for polyoxymethylene by Hammer, Koch and Whitney.[136] The theoretical basis for this correction factor arises from the need to correct the intensities of the amorphous humps and the crystalline peaks for appropriate Lorentz-polarization, atomic scattering and temperature factors.[132,135,136]

It can be shown that the degree of crystallinity is related to the specific volume of the polymer by the equation,

$$X_c = \frac{V_a - V}{V_a - V_c}, \tag{53}$$

where V_a and V_c are the specific volumes for the amphous polymer and for the 100 % crystalline polymer respectively, and V is the specific volume determined for the polymer whose degree of crystallinity is being determined. Combining equations (52) and (53), one can obtain the relation,

$$\frac{V_a - V_c}{V_a - V} = 1 + x\frac{A_a}{A_c}. \tag{54}$$

which can be rewritten as

$$\frac{1}{V_a - V} = \frac{1}{V_a - V_c} + \frac{x}{V_a - V_c} x \frac{A_a}{A_c} \tag{55}$$

From a plot of $1/(V_a-V)$ against A_a/A_c, as shown in figure 18, one should be able to obtain $1/(V_a-V_c)$ as the intercept on the y-axis, from which V_c, the specific volume of the crystalline fraction can be calculated. Also, from the slope of the straight line graph, the constant x can be evaluated.

From X-ray diffractometer scans of these six samples, the ratios A_a/A_c were calculated. These values along with the calculated specific volumes and the values of $1/(V_a-V)$ are shown in table XIV.

TABLE XIV

DETERMINATION OF CRYSTALLINITY INDICES FOR FRACTIONATED SAMPLES OF POLY(β-PINENE)

Sample No.	A	A_a	A_a/A_c	V	$1/(V_a-V)$	X_c^M	X_c^V
PTR	0	0.4876	∞	1.027	∞	0	0
RPβP-1	0.1521	0.2114	1.39	0.956	14.08	0.418	0.518
RPβP-2	0.1654	0.4730	2.86	0.979	20.83	0.259	0.343
RPβP-3	0.0967	0.3501	3.62	0.986	24.39	0.216	0.292
RPβP-4	0.2145	0.1973	0.92	0.943	11.90	0.521	0.619
RPβP-5	0.3251	0.0244	0.075	0.900	7.87	0.930	0.952

X_c^M obtained from equation (56)

X_c^V obtained from equation (52).

From figure 18 (p 100) the value of the intercept is 7.1 from which V_c, the specific volume of the crystalline fraction is 0.886 $cm^3\ g^{-1}$. It is assumed that the specific volume of the Polyterpene

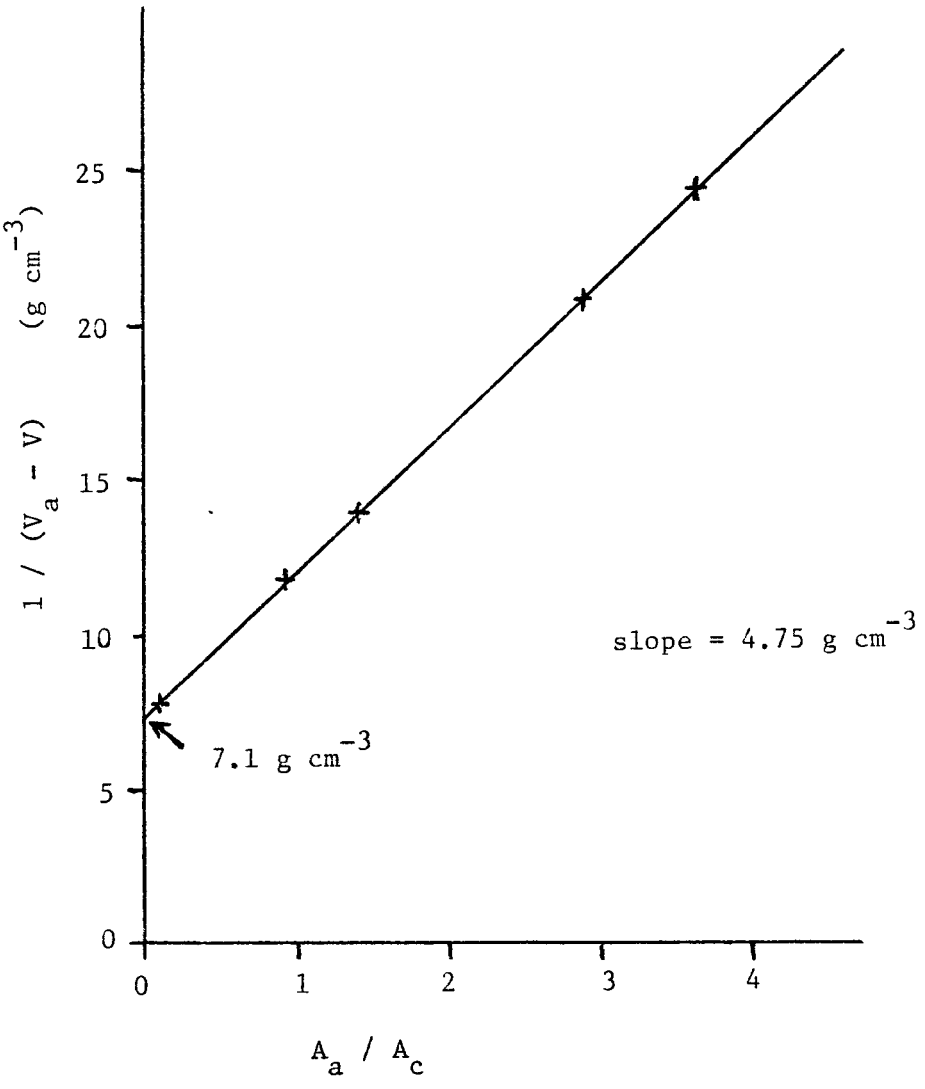


Figure 18. Plot of $1/(V_a - V)$ against A_a/A_c.

sample which gave no crystalline peak on the diffractometer scan as seen from figure 15 (p 93), is the same as the specific volume of the amorphous fraction of the poly(β-pinene) prepared by radiation-induced polymerization. From this value of 0.886 $cm^3\ g^{-1}$ for the specific volume ot the crystalline fraction, the crystalline density can be calculated to be 1.129 g cm^{-3}.

From the slope of the straight-line plot in figure 18 (p 100), the constant x can be calculated to be 0.67. By using this value of x in equation (52), the corrected crystallinity indices, X_c^V, of the fractionated samples of poly(β-pinene) were calculated and are listed in the last column of table XIV (p 99). The crystallinity indices for the same samples calculated using the values for A_a and A_c without any corrections and the equation,

$$X_c^M = \frac{A_c}{A_c + A_a}\ , \qquad (56)$$

are also given in table XIV (p 99).

6. Solubility Characterization

As mentioned earlier, the poly(β-pinene) prepared by gamma irradiation is partially insoluble in all the thirty five solvents tried at room temperature, due to its high crystallinity. It was necessary to carry out a systematic characterization of the polymer's solubility properties. The procedure used for doing this has been described in section D of Chapter III. It was found that the polymer dissolves in chlorobenzene, bromobenzene, β-pinene, and pentachloroethane above 120°C. Because polymer has high susceptibility to autooxidation, it was necessary to keep the solution oxygen-free by bubbling

an inert gas like nitrogen through it. The solvent behavior was classified as belonging to one or more of the classes given in Chapter III, section D. Temperatures above 160°C were not tried because of possible thermal decomposition, although no evidence for thermal degradation was obtained in the absence of air, when the thermal properties were studied. Table XV gives the quantitative data on the

TABLE XV

SOLUBILITY DATA* FOR POLY(β-PINENE) AT VARIOUS TEMPERATURES

Temperature	Bromobenzene (B.P. 156°)	Chlorobenzene (B.P. 132°)	β-pinene (B.P. 165°)	Pentachloroethane (B.P. 162°)
160°	8@	-	10	25
140°	15	12@	21	37
120°	29	37	48	68
100°	130	190	215	#
80°	175	570	#	#

*Amount of solvent needed to keep 1 g of unfractionated radiation-prepared poly(β-pinene) in solution

@data obtained at boiling point of solvent

#polymer starts precipitating from the solution, at a concentration of 1000 ml of solvent per g of polymer.

The solubility classification of all the solvents tried is given in table XVI. This table gives the behavior of both the radiation-prepared polymer as well as that of the Polyterpene Resin B-115. The solvents are arranged in increasing order of their solubility parameters

TABLE XVI

CLASSIFICATION OF SOLVENTS BASED ON THEIR ABILITY TO DISSOLVE POLY(β-PINENE)

Solvent	B.P.	δ-value[@]	Classification[*] PTR[†]	RPβP[†]
n-decane	174°	6.6	N	N
n-pentane	36°	7.0	N	N
n-hexane	68°	7.3	Z	N
n-octane	125°	7.6	Z	N
methyl cyclohexane	101°	7.8	Z	N
cyclohexane	81°	8.2	Z	N
sec-butyl bromide	91°	8.4m	Z	Z
bicyclohexyl	220°	8.5	YZ	Z
n-butyl iodide	130°	8.5m	XYZ	Z
carbon tetrachloride	77°	8.6	OX	Z
cyclopentane	49°	8.7	XZ	N
ethyl benzene	136°	8.8	OXY	Z
o-xylene	143°	8.8	OXY	Z
toluene	111°	8.9	OXY	Z
tetrahydrofuran	66°	9.1	OX	Z
benzene	80°	9.2	OX	Z
trichloroethylene	87°	9.2	OXY	Z
chloroform	61°	9.3	OX	Z
tetrachloroethylene	120°	9.3	OXY	YZ
pentachloroethane	162°	9.4	OXY	YZ
chlorobenzene	132°	9.5	OXY	XYZ

TABLE XVI (CONTINUED)

Solvent	B.P.	δ-value[@]	Classification* PTR†	RPβP†
tetrahydronaphthalene	194°	9.5	OXY	YZ
1,1,2-trichloroethane	113°	9.6	OXY	Z
ethylene bromide	131°	9.7	OXY	Z
methylene chloride	41°	9.7	OX	Z
1,1,2,2-tetrachloroethane	130°	9.7	OXY	YZ
ethylene dichloride	83°	9.8	OXY	YZ
acetone	56°	9.9m	XZ	Z
bromobenzene	156°	9.9	OXY	XY
carbon disulfide	45°	10.0	XZ	Z
o-dichlorobenzene	179°	10.0	OXY	YZ
1,4-dioxane	101°	10.0m	OXY	Z
nitrobenzene	211°	10.0	OXY	Z
1-2-dibromoethylene	109°	10.1	OXY	Z
iodobenzene	187°	10.1	OXY	Z
1,2-dibromoethane	131°	10.4	YZ	N
1-bromonaphthalene	281°	10.6	Z	N
nitroethane	115°	11.1	N	N
acetonitrile	85°	11.8m	N	N

[@]Source: "Polymer Handbook," J. Brandrup and E. H. Immergut, eds., Second edition, John Wiley and Sons, New York, N.Y., 1975, pp. IV-341-348. All the δ-values are for solvents with poor hydrogen-bonding capacity unless they are marked m, indicating medium hydrogen-bonding.

TABLE XVI (CONTINUED)

*Classification according to the following system:
O-dissolves at room temperature in one week or less;
X-dissolves at 80°C (or at its boiling point, if lower) in 24 hours;
Y-dissolves at 160°C (or at its boiling point, if lower) in 24 hours;
Z-swells without dissolving completely at room temperature in 24 hours.
N-does not even swell in 24 hours.

†PTR stands for Polyterpene Resin, B-115, while RPβP stands for radiation-prepared poly(β-pinene).

(δ-values). The solubility parameter is defined as the square root of the cohesive energy density or of the energy of vaporization, ΔE per unit volume, V, so that $\delta = (\Delta E/V)^{1/2}$.[107]

7. Thermal Properties

The thermal properties of the radiation-prepared poly(β-pinene) and the Polyterpene Resin were studied by two techniques: differential scanning calorimetry (DSC) and the hot stage polarizing microscopy.

Differential scanning calorimetry gave one sharp peak at 206-208°C with a heating rate of 10°C min^{-1}, characteristic of a melting transition of its crystalline regions, for the polymer prepared by radiation-induced polymerization. The commercial resin, however, gave a slight change in the slope of its DSC curve at ca. 125°C, probably corresponding to its glass transition temperature, and a melting transition around 170°C.

The results of the hot stage polarizing microscopy are given in table XVII. The results of the hot stage microscopy indicate that the transitions obtained with this technique give slightly higher transition points than with the differential scanning calorimetric technique. This is possibly due to the greater time needed for heat to reach the sample through the microscopic slide made of glass.

8. Studies of Auto-oxidation

The polymer formed by irradiation seemed to turn yellowish after exposure to the atmosphere and room light. Also the infra-red spectra of the sample exposed to air exhibited some extra peaks to oxidation. Hence it was decided to monitor the extent of oxidation and, if possible, to determine the mechanism of the auto-oxidation.

TABLE XVII

OBSERVATIONS OF HOT-STAGE POLARIZING MICROSCOPY

Temperature	PTR[@]	RPβP[*]
135°	softens	loses rigidity somewhat
165°	flows freely	no apparent change
180°	no apparent change	begins to soften under pressure
195°	no apparent change	flows under pressure
210°	no apparent change	flows freely, no birefrigence

[@]Polyterpene Resin, Zonarex B-115 showed no effect with polarizers, even at room temperature. With crossed polarizers, no light passed through the sample.

[*]Radiation-prepared poly(β-pinene) showed birefringence pattern under crossed polarizers up to 210°C.

[†]Heating rate: 10°C min^{-1}.

The extent of auto-oxidation was determined by elemental analyses of samples exposed to air in the presence of room light, for various durations. The results of the analyses are given in table XVIII. All the data corresponds to auto-oxidation at room temperature (21 ± 3°C). The sample stored in the presence of air in the dark showed very little auto-oxidation.

The nature of auto-oxidation was monitored by infra-red spectroscopy. Figure 19 gives the infra-red spectra of the radiation-prepared polymer, unoxidized, after one week's exposure, and after an exposure of 60 weeks to the atmosphere. The polymer becomes very powdery and yellow and the pellet with KI becomes quite opaque causing the infra-red

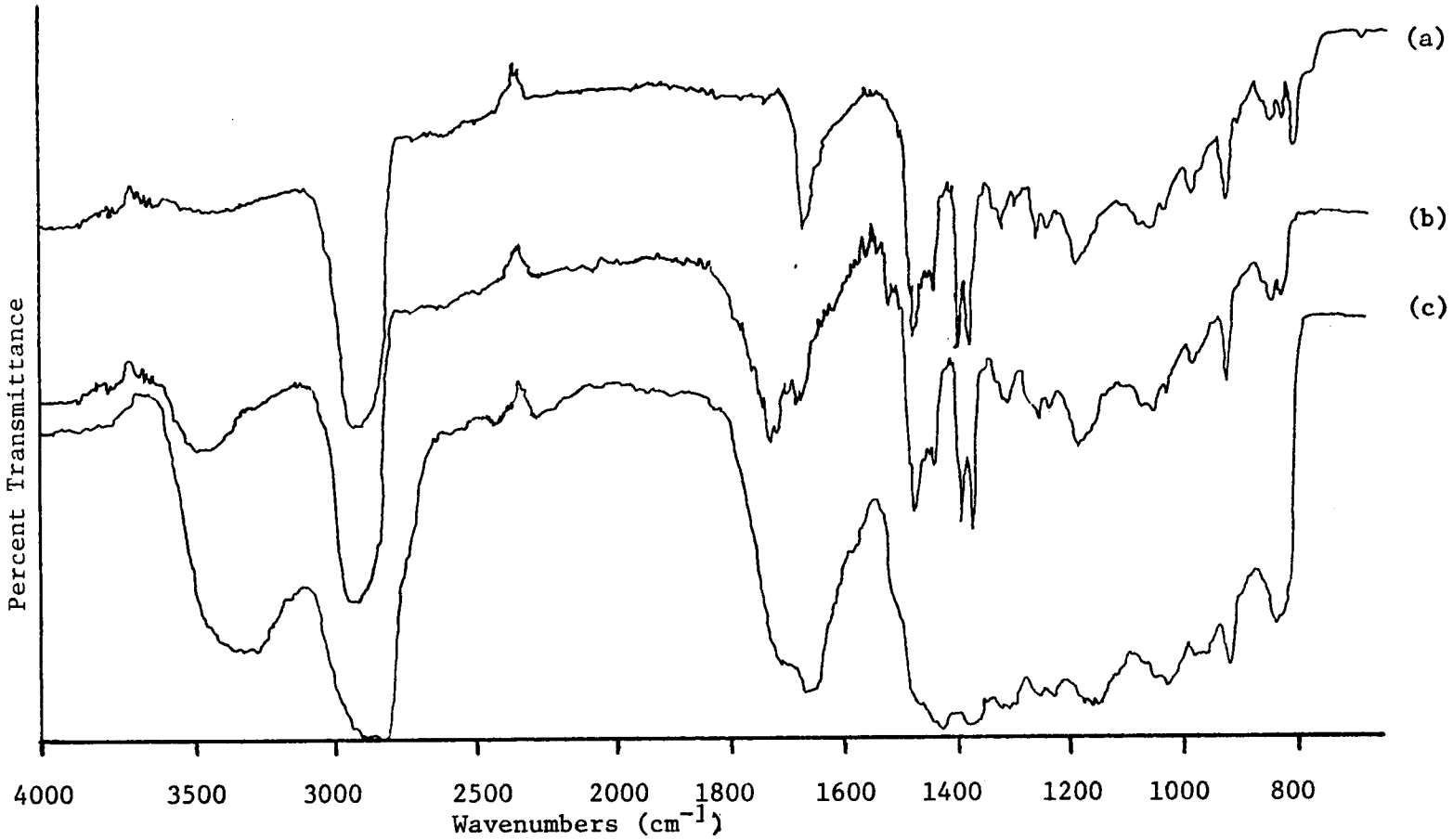


Figure 19. Infra-red spectra of poly(β-pinene) prepared by irradiation: progress of auto-oxidation. (a) unoxidized, (b) after one week, and (c) after sixty weeks.

TABLE XVIII

ELEMENTAL ANALYSES OF AUTO-OXIDIZED SAMPLES OF RADIATION-PREPARED POLY(β-PINENE)

Exposure to atmosphere	% C[@]	% H[@]	% O	No. of O atoms[†] per repeat unit
Freshly prepared	88.15	11.68	0.17[*]	0.0014
24 hours	82.60	11.42	5.79[*]	0.053
72 hours	82.53	10.40	7.00	0.064
1 week	81.16	10.63	7.87	0.073
10 weeks	80.56	10.16	9.28[*]	0.086
60 weeks	79.40	10.11	11.29[*]	0.107
4 weeks (kept in dark)	87.86	11.91	0.23[*]	0.0010

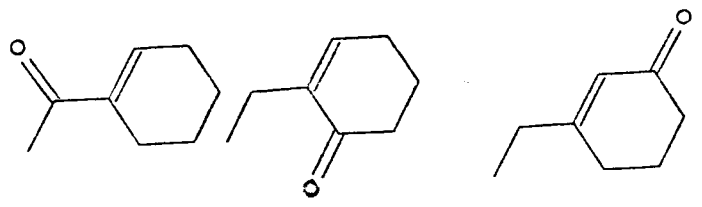
[*]Oxygen content by difference.

[†]Calculated on the basis that the percent C values correspond to 10 atoms per repeat unit.

[@]Theoretical weight percentages for a repeat unit of $[C_{10}H_{16}]$ for carbon and hydrogen are 88.15 % and 11.85 % respectively.

spectrum to lose its resolution. The main differences worth noting at this stage are the two broad bands not present in the unoxidized sample, one at ca. 3200-3400 cm^{-1} and the other in the region 1640-1750 cm^{-1}. The former corresponds to the absorption by a peroxide type group such as -OOH, while the latter corresponds to a conjugated ketone.

The ultraviolet absorption spectra of the unoxidized poly(β-pinene) prepared by irradiation and of the same polymer after exposure to the atmosphere for one week in the presence of light are shown in figure 20. The auto-oxidized sample shows absorptions in the region 230 to 250 nm as well as from 300 to 350 nm. The bands due to groups such



as give absorption maxima at 330, 318, and 340 nm as well as at 233, 235, and 247 nm respectively,[137] which indicates that probably all three of these structures are present in the auto-oxidized polymer.

C. POLY(β-PINENE) PREPARED BY THERMAL POLYMERIZATION

Kennedy and Chou[78] have reported that the polymer formed on heating neat β-pinene in capped glass vials at 160°C for a week was highly crystalline. They made several unsuccessful attempts to increase the rate of polymerization and/or yield of the crystalline polymer by adding various chemicals known to induce cationic or radical polymerizations to neat β-pinene and heating the systems to 160°C for a week. "Cumene peroxide" [2,2'-di(phenylisopropyl) peroxide], a radical initiator and aluminum trichloride, a cationic initiator were tried at concentrations of 0.1 and 1.0 weight percent. Addition of water at the same concentration levels also did not produce any increase or decrease in yield. Simultaneous photoinitiation by ultraviolet light

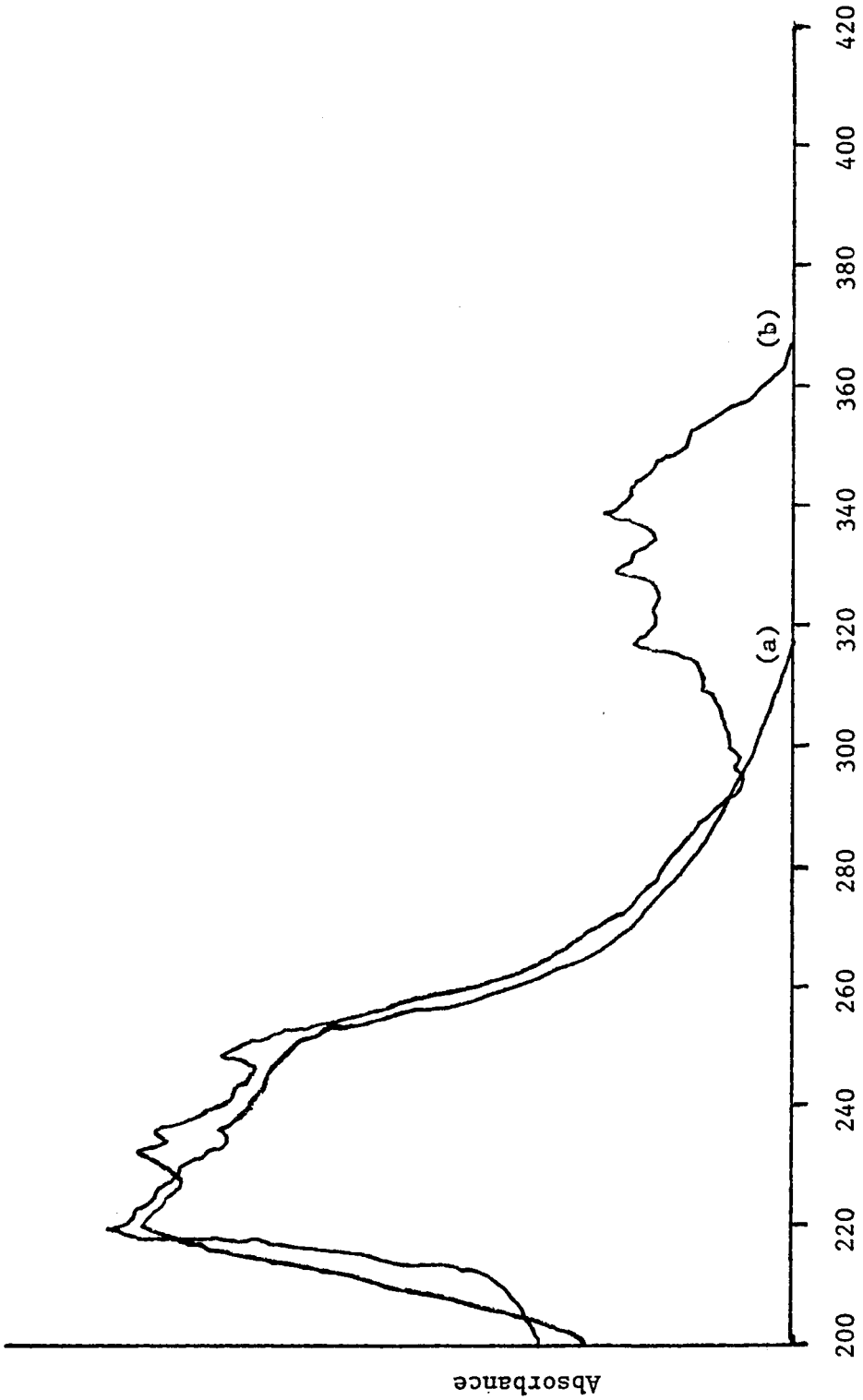


Figure 20. Ultraviolet spectra of (a) unoxidized and (b) auto-oxidized poly(β-pinene).

of 2800-3000 Å in a quartz vial produced a much higher yield but the polymer was a viscous semisolid, which was soluble in chloroform. Possibly the molecular weight of this polymer was very low. No molecular weight measurements were reported by Kennedy et al.[78]

Since this work is the only report of a crystalline polymer of β-pinene other than that produced by gamma irradiation, it was decided to carry out a series of experiments on the thermal polymerization of β-pinene.

1. Preparation of Poly(β-pinene)

The experimental procedure for preparing the polymer has been discussed in Chapter II, section F of this dissertation. The monomer was heated in a three-necked flask at ca. 160°C for a week using a reflux condensor. Various chemicals were added in order to study the effect of inhibiting agents on the thermal polymerization and thereby to obtain information about the mechanism of propagation. The results of these experiments are presented in table XIX. These results indicate that only the free radical inhibitor, 4-tert-butyl catechol, was able to completely prevent the thermal polymerization of β-pinene.

One experiment was carried out to study the effect of a solvent with a higher dielectric constant on the thermal polymerization of β-pinene. Thirty grams of β-pinene was refluxed with 172 g of bromobenzene in a similar set-up to that described above. The temperature was maintained at 160 ± 3°C for a week. This corresponds to a β-pinene concentration of 1.47 moles liter^{-1} or 16.7 mole percent. Nitrogen gas was bubbled through the monomer solution to keep the hot solution oxygen-free. After a week, the mixture was cooled to ambient

TABLE XIX

STUDIES ON THERMAL POLYMERIZATION* OF β-PINENE

No.	Additive	Insoluble Polymer (g)	Soluble Polymer (g)	% Conversion
1	None	2.0387	2.1137	4.1524
2	10^{-2}M dicyclohexylamine	1.1034	1.1970	2.3004
3	10^{-2}M t-Bu catechol	0	0	0
4	10^{-2}M tripropylamine	2.1269	2.2110	4.3379

*100 g β-pinene heated at 160°C for 1 week and then cooled to room temperature. N_2 gas bubbled through monomer while it was being heated.

temperature and added slowly to 650 ml of swirling methanol. The precipitated polymer was filtered off. The yield of polymer was 1.1168 g corresponding to a percentage conversion of 3.723%.

2. Chemical Characterization

The proton nmr spectrum of the soluble fraction of the thermal polymer is shown in figure 21. The spectrum seems to be similar to that obtained from the radiation-prepared polymer. The most prominent signal is at ca. 0.85 ppm (δ) and is due to the methyl protons, the broad peak at about 5.3 ppm is due to the vinylic proton while the other protons are all bunched together in the region from 3.0 to 1.0 ppm.

3. Morphological Studies

The monomer-insoluble fraction was scanned by X-ray

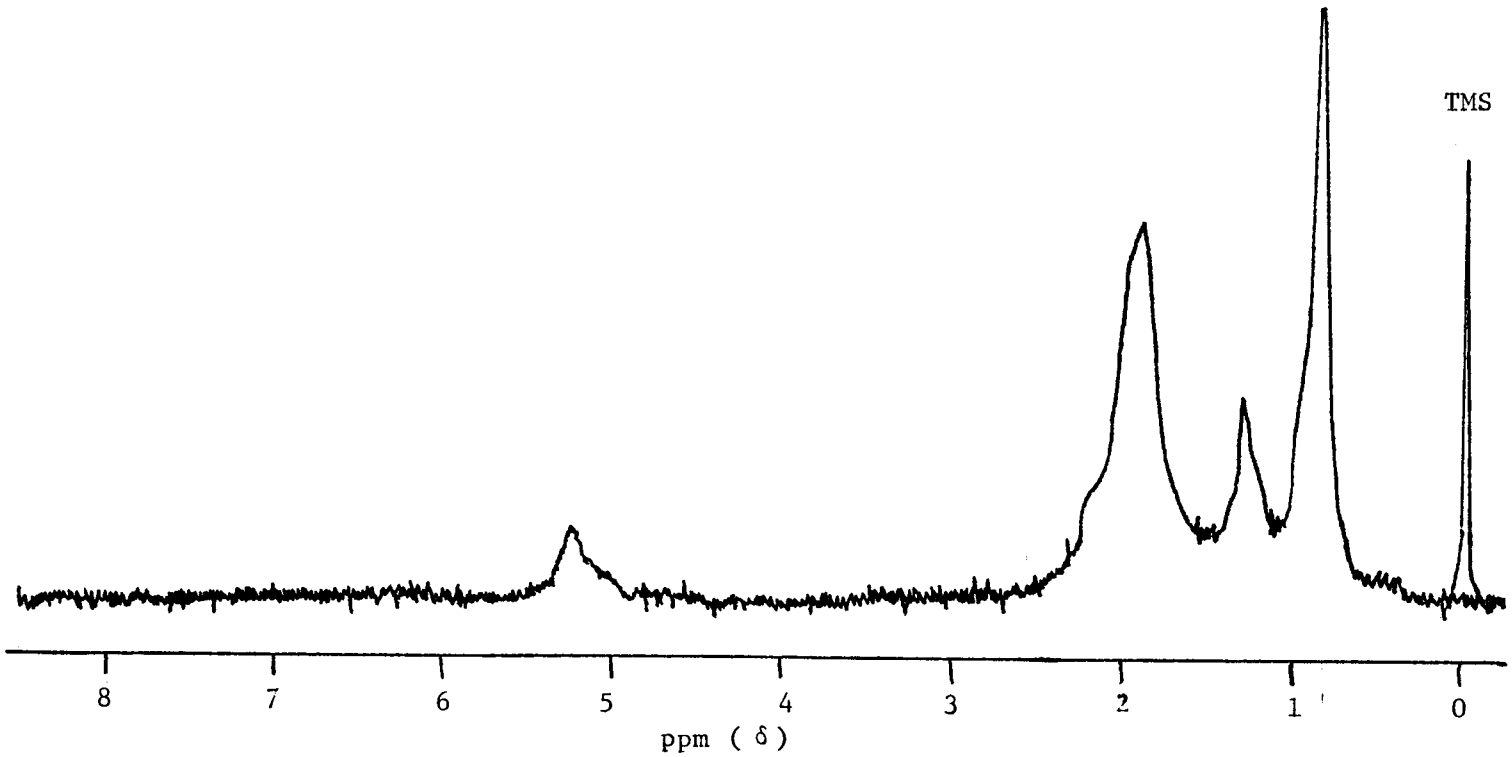


Figure 21. Proton nmr spectrum of thermally-prepared poly(β-pinene) in CCl_4 solution.

diffractometry to find out if it was crystalline. The 2θ scan observed is presented in figure 22. Within experimental error, the diffraction peaks occur at precisely the same 2θ angles observed for the polymer prepared by radiation-induced polymerization, thereby indicating the same crystal structure as that of the latter polymer. No birefringence or WAXS studies were carried out.

4. Other Properties

Thermal properties were not studied and solubility characterization were not carried out on this polymer because Kennedy and Chou[78] have reported preliminary data on these characteristics in their paper, and their data seem to agree well with the data obtained for the radiation-prepared polymer and reported earlier in this chapter. The thermal polymer is also susceptible to auto-oxidation. This was observed by infra-red spectroscopy. These spectra are not presented here, however.

D. DISCUSSION

1. Radiation-induced Polymerization

The results of the preliminary experiments carried out indicate that, unless all the moisture sticking to the glassware is removed by a process such as baking it in an oven, this small amount of moisture is probably sufficient to depress the propagation reaction by degradative chain transfer to water. That water acts as an inhibitor has been demonstrated very well by the experiments of Bates et al.[126] in which they studied the effect of adding small amounts of water to β-pinene on the rate of polymerization. Their results showed that this rate was

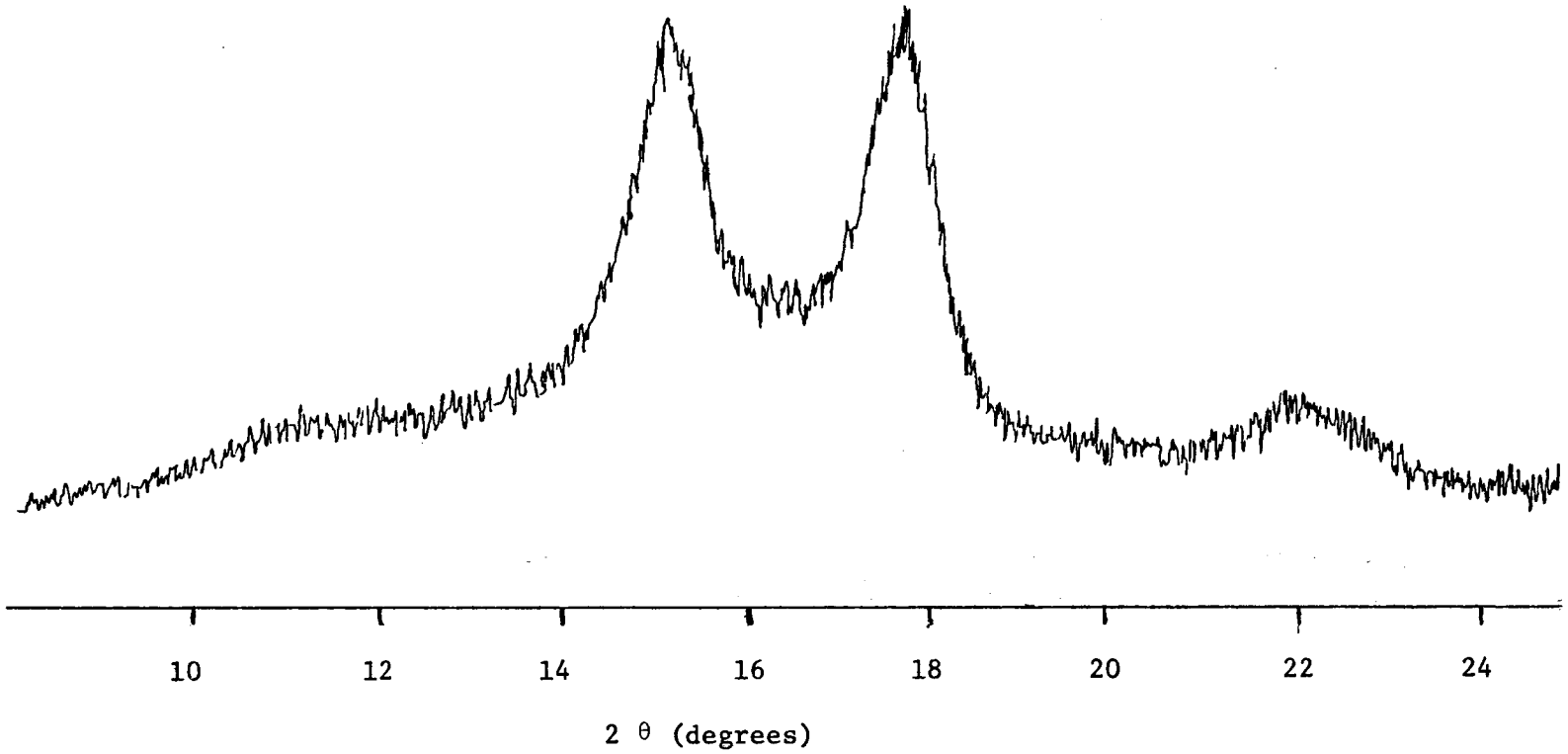


Figure 22. X-ray diffractometer scan of poly(β-pinene) prepared by thermal initiation.

reduced substantially (by a factor of 10 to 100 depending on the concentration of water). The G-values reported by them for β-pinene samples containing 10^{-3} to 10^{-2} M are in the same range as the values reported in table V (p 68) of this dissertation.

The experiments with the bakeout vacuum apparatus gave results with G-values which were comparable with those obtained for well-dried monomer in the previous work.[126] The dessicant-grade silica gel gave irreproducible results with G-values varying from 5.2 to 1182 within the same batch. The reasons for this variance is not known, although very probably it is due to some moisture somehow getting into the system. On the other hand the experiments with the tell-tale indicator grade silica gel gave G-values of 770 to 1236 with a mean value of 1004 and a standard deviation of 125.4. This mean value of 1004 is higher than that of 850 obtained by Bates et al.[26], although they have reported a value of 2230 for an individual sample. The dose rate at which they irradiated their samples of β-pinene was 247 x 10^{-17} eV g^{-1} min^{-1} (0.237 Mrad $hour^{-1}$) which is comparable to the average dose rate used by this author. (The rate of propagation varies inversely as the n^{th} power of the dose rate, where n is between 0.5 and 1.0.)

The percentage of the polymer insoluble in the monomer varied from 49.8 to 53.1 % for a mean value of 51.3 %. The fraction of the polymer that remained insoluble was independent of the irradiation dose and of the percent conversion of monomer to polymer. Bates and Williams[51] reported that their yield of the polymer fraction, which was insoluble in the monomer, was slightly greater than that of the soluble fraction. Hence, the value of 51.3 % agrees with this observation of Bates and Williams.

The mean molecular weight value of 2013, obtained from the data reported in table XI (p 78), is higher than that reported by Bates et al.[126], who obtained values of 494 to 1840 by ebulliometric measurements for the fractions of the radiation-prepared polymer soluble in chloroform, carbon tetrachloride, benzene, and β-pinene. Both their results and those reported here indicate that the molecular weights obtained are almost independent of the total irradiation dose, of the percent conversion, and of the G(-M) value.

From the mean value of 2013, the degree of polymerization can be calculated to be 14.79. Since the average G(-M) value for β-pinene was about 1004 it is clear that considerable chain transfer takes place and that the kinetic chain is sustained by this chain transfer to monomer, because the G (R^+) for initiation is thought to be only ca. 0.1 for hydrocarbon monomers.[25] The alternative explanation in terms of the formation of a large number (ca. 68) of primary initiators is untenable because such high values for primary ion and radical yields are extremely improbable from energetic considerations, as pointed out by Bates et al.[126] Both cation and radical transfers to monomer are possible but the latter would probably generate stable allylic radicals by hydrogen-atom abstraction from the alpha position to the double bond.[138] Also, if radical transfer of this type had taken place, a terminal vinylidene group would be incorporated in the growing polymer after transfer. However, neither the infra-red spectra of Bates et al.[126], nor that shown in figure 11b (p 86) of this dissertation, show the presence of a terminal vinylidene group around 895 cm^{-1}.[139] Besides, the allylic radical if produced by radical transfer would be

expected to be too unreactive to initiate a polymerization chain at room temperature and hence would terminate by dimerization.[126] Hence the chain transfer occurs by proton transfer. The effect of water on the propagation has been explained by Bates et al.[52] on the basis of proton transfer to water, as detailed in section B of Chapter II.

It is now accepted that water acts as a strong inhibitor of both cationic and anionic propagation in radiation-induced polymerization. To be able to distinguish between these two modes of propagation, ammonia and tertiary amines such as trimethylamine have been used by other researchers on the basis that these bases are cationic inhibitors. It has thus been demonstrated, for example, that the addition of these compounds even at concentrations as low as 10^{3}M inhibited or retarded the radiation-induced polymerization of α-methyl styrene,[67,127] isobutylene[58], styrene[56] and cyclopentadiene.[127] These monomers, therefore, were shown to polymerize cationically in the dry state. No such work has been reported on β-pinene.

As mentioned earlier, Bates et al.[52,126] had concluded from their studies on the retardation of the radiation-induced polymerization of β-pinene by small quantities of water that the propagation was ionic and not free radical in character. However, water is known to act as an inhibitor for both cationic and anionic propagation. Based on structural considerations they had suggested it was cationic rather than anionic.

The experiment with the addition of ca. 10^{-2}M tripropyl amine, reported in table IX (p 74) showed that the radiation-induced polymerization of β-pinene was inhibited by the tertiary amine. This result

demonstrates that the poly(β-pinene) formed by gamma-irradiation is produced by cationic propagation rather than an anionic pathway. The result obtained thus corroborates the conclusion of Bates et al.[52] that this polymerization occurs via a cationic propagating species. Williams[24] has argued from the available evidence that these species are free ions and not ion-counterion pairs. There is no evidence in the literature to suggest otherwise. Since the purpose of the experiment was only to determine the effect of the tertiary amine on the polymerization and thus ascertain the nature of the mechanism, no kinetic studies were carried out along the lines of Williams and his group,[56,58,127] who followed the effect of ammonia and amines on the radiation-induced polymerization of cyclopentadiene, isobutylene, styrene, and α-methylstyrene kinetically.

The mean value of the number-average molecular weight of the soluble fraction of the poly(β-pinene), reported by Bates et al.[126], is about 1360. While reviewing this work, Pinner[77] mistakenly took this number as the value of the degree of polymerization. Later in the same article, he reviewed a personal communication by Leese, who had obtained the $\overline{DP}_n$ for the insoluble fraction as being twice that of the soluble fraction. In a subsequent review,[79] Kennedy took this incorrect value of 1360 to be the degree of polymerization of the soluble fraction, multiplied it by 2 to obtain the degree of polymerization of the insoluble fraction as 2720, and thus derived a value of 370,000 as the number-average molecular weight of the insoluble fraction. This value is misprinted in his review[79] as 37,000. It is clear, however, that the correct values of the molecular weight determined

for the soluble and the insoluble fractions are 1360 and 2720 respectively.

Roberts and Day[116] have reported molecular weights of *ca.* 3000 for the polymer obtained with a Friedel-Crafts catalyst. Achon *et al.*[122] have reported $\overline{DP}_n$ values of 2.9, 13, and 17 corresponding to molecular weights of 390, 1770, and 2300 respectively for their poly(β-pinene) prepared with Ziegler-Natta catalysts. Marvel *et al.*[123] have not calculated molecular weights for their polymers prepared with a (*iso* Bu)$_3$Al-TiCl$_4$ complex but only reported inherent viscosity values of 0.02 to 0.12. Huet and Marechal[119] have reported both inherent viscosity values of 0.04 to 0.18 and molecular weights of 2500 to 9000. It must be noted that all these values refer to poly(β-pinene) which is completely soluble in the monomer and in many other liquids at room temperature. The radiation-prepared polymer is only partly soluble and the insoluble fraction probably contains material which has higher molecular weight.[77,126] The values reported in table XI (p 78) are, therefore, generally in the same region as these other values.

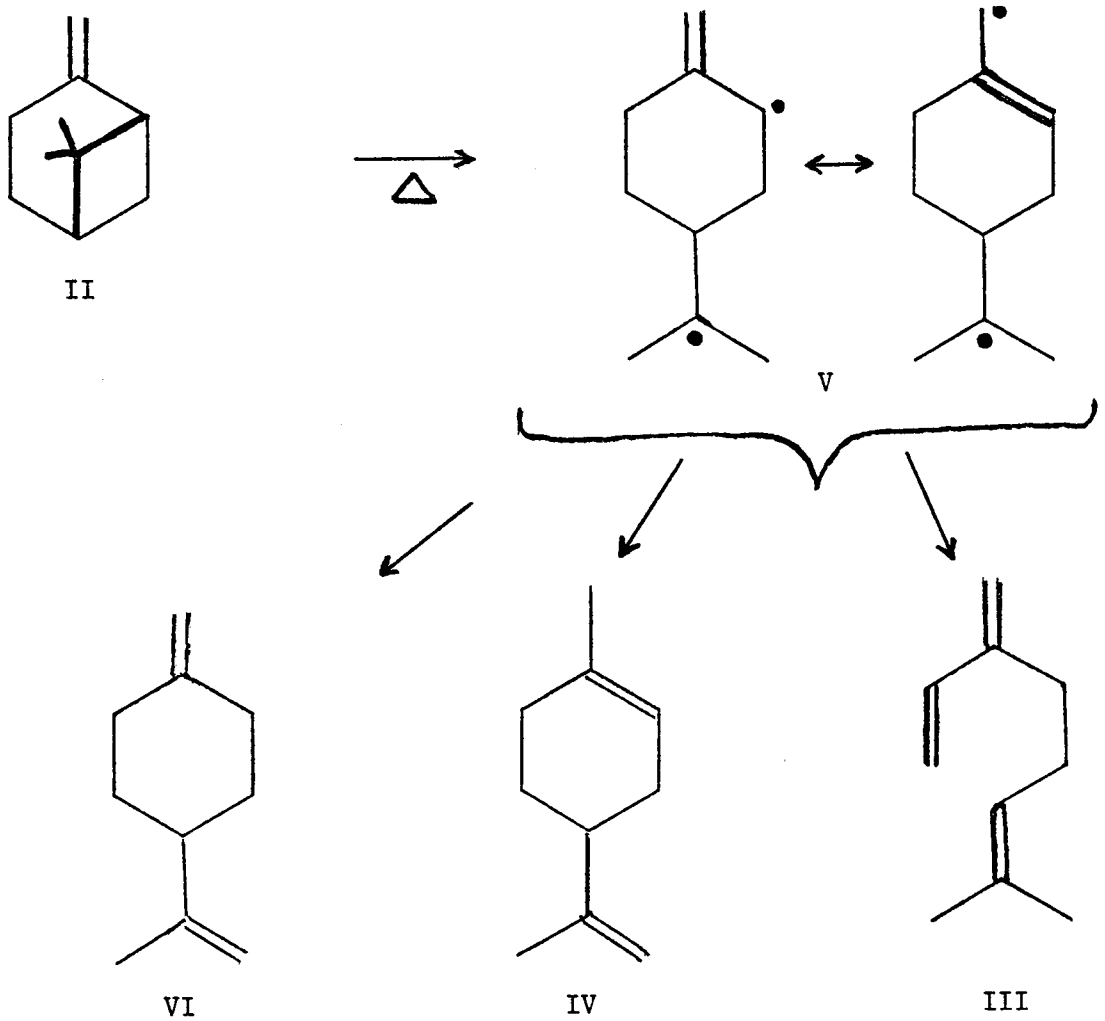
2. Comparison of Thermal Polymerization with Radiation-induced Polymerization

The results of the thermal polymerization carried out by the author and given in table XIX (p 113) indicate very strongly that the thermal polymerization occurs by free radical propagation. This is most clearly substantiated by the experiment in which 4-*tert*-butyl catechol was able to completely inhibit this polymerization because this catechol derivative is a well-known free radical inhibitor. The tripropyl amine did not reduce the yield of poly(β-pinene), showing

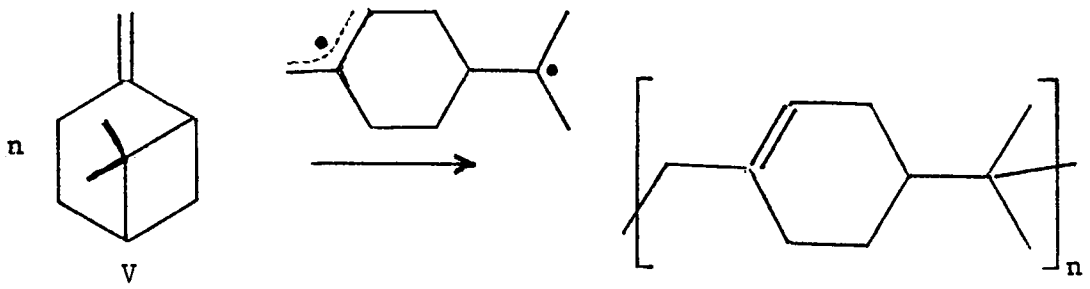
that the thermal propagation does not involve cationic species. The addition of dicyclohexyl amine caused a 50 % reduction in the yield, probably due to this secondary amine reacting with the propagating free radical by a hydrogen atom abstraction reaction to produce a radical with a reactivity too low to initiate further propagation.

Pyrolysis of β-pinene has been studied by several workers. Goldblatt and Palkin[140] reported the vapor phase pyrolysis of β-pinene (II) to myrcene (III) and to limonene (IV), which is also refered to as dipentene. Hawkins and his group[141] studied the kinetics of this isomerization in the liquid state at 219.5 and 234°C. Burwell[142] proposed a mechanism involving the dissociation of the cyclobutane ring to form a biradical (V) as the reaction intermediate, which he suggested could give myrcene (III), limonene (IV), and a third product 1(7),8-p-menthadiene (VI). This mechanism is shown in figure 23(a). Later, this third product was detected by Steinbach et al.[143] using modern gas chromatographic equipment.

Thus, it is reasonable that the free radicals thought to be generated by thermal means could initiate free radical polymerization at 160°C, as shown in figure 23(b). Kennedy and Chon,[78] who first reported the thermal polymerization of β-pinene, observed no increase or decrease in yield by the addition of additives such as cumene peroxide, aluminum trichloride, distilled water, or bis(triphenyl-phosphine) rhodium carbonyl chloride at concentration levels of 0.1 and 1.0 M. That distilled water did not kill the thermal propagating species is suggestive of a free radical rather than an ionic mechanism. The inability of aluminum chloride to increase the yield of the



(a) Formation of free radicals during isomerization, proposed by Burwell [J. Amer. Chem. Soc., 73, 4461(1951)].



(b) Polymerization of β-pinene by free radical initiation.

Figure 23. Proposed mechanism of thermal polymerization of β-pinene.

poly(β-pinene) does not shed much light on the mechanism of the thermal polymerization. $AlCl_3$ is usually used to polymerize monomers such as β-pinene in solvents of high dielectric constant (ca. 4 to 6) and at low temperatures (-50°C to 10°C). Aluminum chloride is not known to induce polymerization of β-pinene in bulk, especially at 160°C. Therefore their rationale of using aluminum chloride as an accelerator of cationic polymerization is questionable, and no conclusion can be drawn from the lack of enhancement in the yield.

The reason cumene peroxide did not increase the polymer yield in their experiments is probably because the alkoxy radical formed does not initiate the propagation of β-pinene at 160°C, although alkoxy radicals are known to be extremely reactive hydrogen-atom abstraction agents.[144]

The work on the thermal isomerization of β-pinene to other isomers[140-143] still leaves open the possibility that at 160°C β-pinene may be isomerizing to one or more of these isomers and these isomers may be undergoing the free radical polymerization to give the crystalline polymer. However, this possibility can be excluded as shown below.

Hunt and Hawkins[141] have reported that the thermal isomerization of β-pinene proceeds as a first order reaction with a rate constant which is unaffected by the addition of small quantities of hydroquinone. Also dilution of β-pinene with limonene did not affect the rate constants. They reported the rate constant for the disappearance of β-pinene to be 2.1×10^{-4} min^{-1} at 219.5°C and that at 234°C to be 9.0×10^{-4} min^{-1}. From these values the activation energy, E_a, can

be calculated using the Arrhenius equation to be 49.8 kcal $mole^{-1}$. Using this value of the activation energy, the rate constant at 160°C can be calculated to be 1.9×10^{-7} min^{-1}. From this rate constant, the total amount of β-pinene isomerizing at 160° in one week can be calculated to be only 0.19 %. However, the percent conversion to poly(β-pinene) was found to be ca. 4.0 %. Hence the thermal polymerization of β-pinene to polymer does not depend on a preliminary isomerization to limonene or myrcene, followed by the polymerization of one or both of these compounds to the crystalline poly(β-pinene). Assuming that the isomerization rate is comparable to the rate of biradical initiation, the results imply a kinetic chain length of ca. 20, which is reasonable. On pyrolysis, β-pinene forms the biradical intermediate, which can either isomerize with an activation energy of E_i, to limonene and myrcene as shown in figure 23(a), or initiate polymerization with an activation energy of $(E_p - 1/2\ E_t)$. If E_i is greater than $(E_p - 1/2\ E_t)$, it is understandable that isomerization becomes relatively more important at the higher temperatures, as observed by Hunt and Hawkins[141] while at relatively lower temperatures (ca. 160°C) the polymerization is about 20 times faster than the isomerization rate.

It is clear from the discussion so far that the thermal polymerization is thought to take place via a free radical mechanism. In the case of radiation-induced polymerization as well as that of thermal polymerization, the poly(β-pinene) formed is crystalline and contains the same crystal lattice spacings. This raises the possibility that if free radical propagation is the predominant mechanism for thermal polymerization at 160°C, the radiation-induced polymerization of

β-pinene at room temperature (ca. 25°C) may also be free radical in nature. However, using the Arrhenius equation it can be shown that the rate constant for the disappearance of β-pinene by isomerization at 25° would only be about 8.8×10^{-16} min^{-1} and that the amount of β-pinene reacting in one week would be 0.60×10^{-5} %. On the other hand, the radiation-induced polymerization produces ca. 2.4 % poly(β-pinene) per hour. Such calculations show that the contribution of the thermal polymerization is negligible in the latter case. The free radicals produced by irradiation also do not appear to propagate at 25°C probably because the energy of activation for propagation is too high. Besides, there is reason to believe that free radical propagation of β-pinene is too slow at room temperature to produce even dimers. Webb[124] has reported that the irradiation of β-pinene with CCl_4 gave a 1:1 addition product produced by opening of the cyclobutane ring. If free radical propagation had been possible at room temperature, telomers consisting of at least dimers and trimers would have been produced. Under the same conditions, the irradiation of styrene containing CCl_4, for example, gives telomers with $\overline{DP}_n$ of ca. 96.[125] Hence it can be surmized that free radical propagation of β-pinene at room temperature does not contribute significantly to the overall rate of polymerization. This conclusion is entirely consistent with the findings discussed earlier in this section regarding the strongly inhibiting effect of water and tripropyl amine in the radiation-induced polymerization of β-pinene.

Hence, the thermal polymerization of β-pinene at 160°C probably occurs by a predominantly free radical mechanism while the

radiation-induced polymerization occurs by a cationic mechanism. However, both these methods yield a crystalline polymer whereas the Lewis acid catalysis and the Ziegler-Natta initiation give rise to an amorphous polymer. The reason for this is not clear. One of the differences in the conditions, under which these reactions are carried out, is that in the case of the thermal and the irradiation methods, β-pinene is polymerized in the bulk state (dielectric constant ca. 2). In the case of the two catalyses, the reactions are carried out in polar solvents which have higher dielectric constants (ε = ca. 4-6). Hence an experiment was carried out to determine if the thermal polymerization of β-pinene in bromobenzene (ε = ca. 4) at a concentration of 1.47 moles liter^{-1} resulted in a crystalline polymer. A crystalline polymer was indeed formed, implying that the solvent effect (or the dielectric constant effect) was minimal.

When the stereochemistry of the propagation step, shown in figure 24, is examined, it is obvious that the stereochemistry of the chiral carbon at 4 position in the repeat unit remains unchanged from that in the monomer unit, inspite of the isomerization. The monomer is the laevorotatory isomer and has the absolute S configuration. Thus it can be shown that the stereochemistry of the propagation is independent of the mode of initiation, whether it is free radical or cationic.

In their paper,[78] Kennedy et al. state that, considering the complicated repeat unit of poly(β-pinene), it is of interest that this material crystallizes. From the discussion above it is clear why the thermal and the radiation-prepared polymers crystallize: they are stereoregular.

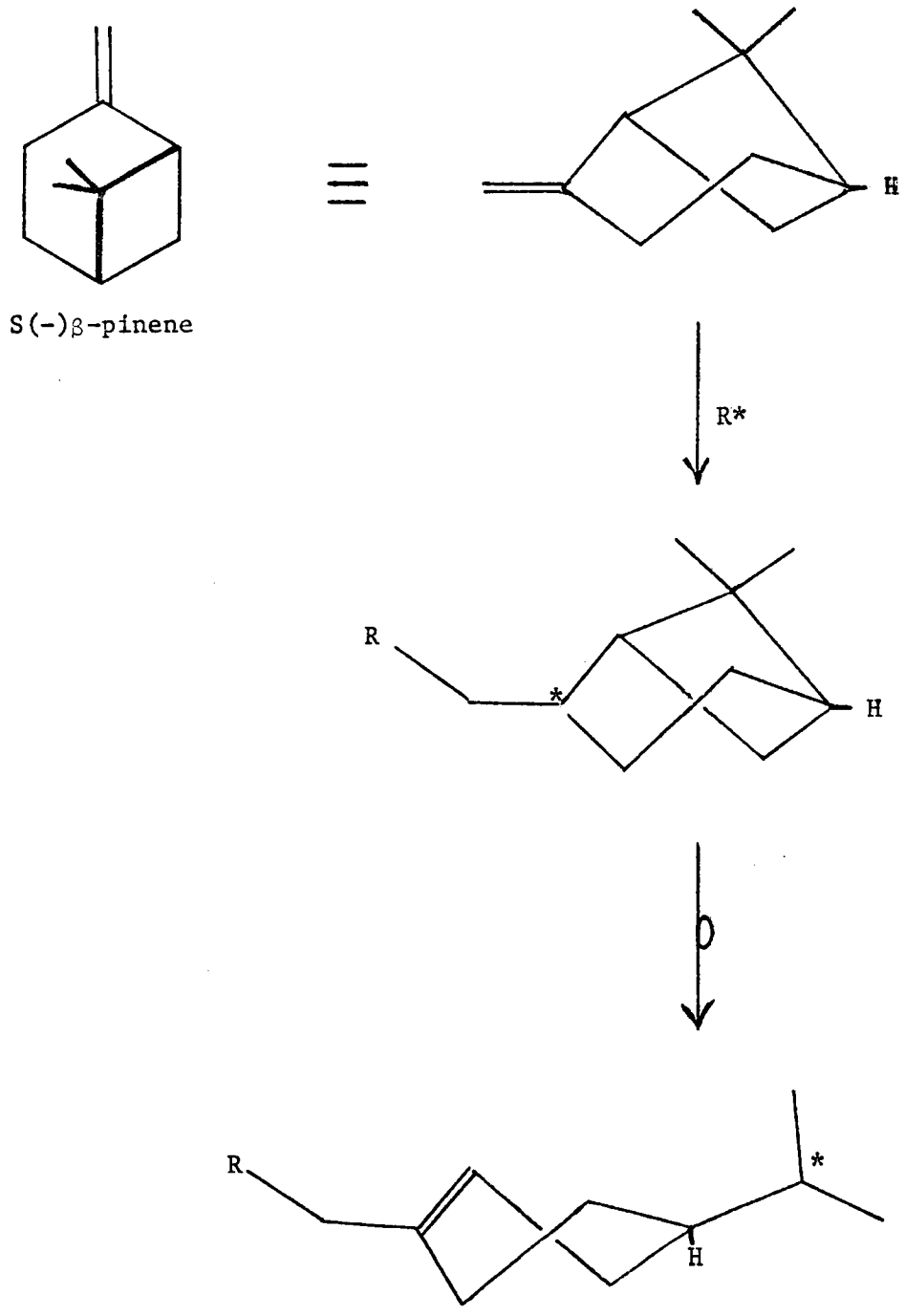
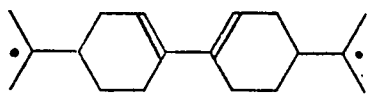


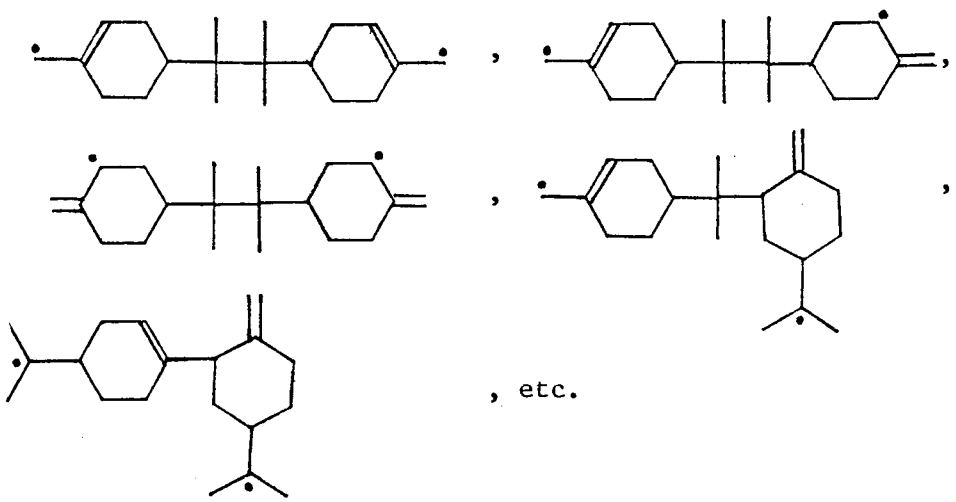
Figure 24. Stereochemistry of propagation during polymerization of β-pinene.

This conclusion raises the question of why the polymers formed by the catalytic methods do not crystallize. Possible deviations from the stereoregularity in these polymerizations could be the answer. Deviations could possibly arise from head-to-head addition reactions during propagation or from the presence of a small proportion of other isomeric units in the macromolecular chain. Either of these possibilities would disrupt the stereoregularity of the polymer, preventing it from crystallizing. The presence of some isomeric units among the majority of the repeat units will be dealt with in the next subheading of this section.

There is little or no possibility of head-to-head addition in the case of the cationic propagation. In the case of free radical propagation, several conceivable reactions, such as diradical-monomer reactions to give dimer diradicals like



and diradical-diradical coupling reactions to give dimerized diradicals of the type shown below could be written.



, etc.

Such structures could then be incorporated in the polymer chain. However, diradical-monomer reactions of the type shown above are unlikely to occur because the radical which needs to attack the exo-double bond of the β-pinene monomer is allylic and therefore very unreactive. The diradical-diradical reaction is very unlikely because the diradicals would be too few for this to happen and consequently the probability of two diradicals coming together to couple is negligible. Hence the thermal polymerization of β-pinene by free radical propagation does not involve head-to-head addition reactions to any significant extent.

3. The Nature of the Repeat Unit

Elemental analysis showed that the unoxidized poly(β-pinene) prepared by irradiation conformed to the theoretical carbon-hydrogen ratios within experimental error. Hence the repeat unit of this polymer is $\dagger C_{10}H_{16}\dagger$. The proton magnetic resonance spectra of the radiation-prepared polymer, the commercial resin, and the thermal polymer are shown in figures 8 (p 82), 9 (p 83), and 21 (p 114) respectively. The assignments for the nmr peaks in these spectra are given in table XX. The spectra, all obtained at ca. 23°C are similar. The main difference is that the spectrum of the commercial resin is less sharply resolved than that of the other two polymers, especially in the region from 0.6 to 3.3 ppm (δ). This could be attributed to either differences in chain length or in regularity of the repeat units. The molecular weights are about the same, as shown earlier in this chapter. Hence the difference in the resolution of the spectra is probably due to the greater regularity of the polymer chains in the poly(β-pinene) prepared by thermal and radiation-initiation. Another possible

TABLE XX

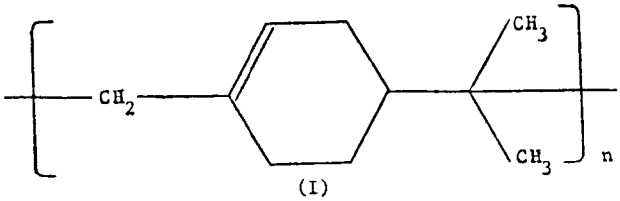
ASSIGNMENT OF PROTON NMR PEAKS

Region (ppm) δ	Relative Peak Intensity PTR*	RPβP*	TPβP*	Assignment of protons
5.0 to 5.5	1	1	1	vinylic
1.2 to 3.3	9	9	9	other methylene and methine
0.9 to 1.2	6	6	6	geminal dimethyl

*PTR, RPβP, and TPβP refer to the Polyterpene Resin, the radiation-prepared poly(β-pinene), and the thermally prepared poly(β-pinene) respectively.

explanation for the difference in the shape of the spectral peaks in the region of 0.6 to 3.3 ppm is that the commercial poly(β-pinene) prepared by Lewis acid catalysis contains the same repeat unit as that in the crystalline polymer (prepared by irradiation and by thermal means) as well as some other repeat units, which are isomeric, in its macromolecular chain. Such an explanation would explain why the commercial resin is amorphous whereas the polymer prepared by irradiation and thermal initiation is highly crystalline.

The β-pinene polymers prepared by Lewis acid catalysis by Roberts and Day[116] and other workers[117-120] as well as that prepared by Ziegler-Natta initiation[121-122] are all reported to have the structure (I).



(I)

However, these workers seem to have come to this conclusion from only a cursory examination of their polymer. Ruckel et al.[111] carried out a more detailed characterization of the poly(β-pinene) prepared by Lewis acid catalysis. From their infra-red absorption spectral data, they have shown that their polymer contained the geminal dimethyl doublet at 1365 and 1383 cm^{-1} as well as a methyl singlet at 1375 cm^{-1} and that the ratio of the dimethyl doublet to the single methyl is 85:15. In other words the Lewis acid polymer contains another type of repeat unit in its polymer chain in addition to that in structure (I) and roughly 15 % of the repeat units of the polymer chain contain this isomeric unit. The nature of the latter unit will be discussed later in this discussion. The presence of this singlet at 1375 cm^{-1} seems to have been overlooked by the earlier workers.[116-122]

The infra-red spectra of the commercial polymer prepared by Lewis acid catalysis, and of the polymer prepared by radiation-induced polymerization have been shown in figure 11 (p 86) and the assignments for the absorptions in these spectra are shown in table XXI. The commercial polymer does show the presence of the methyl singlet at 1375 cm^{-1}. This is absent in the spectrum of the radiation-induced poly(β-pinene). The latter spectrum shows a prominent peak at ca. 1660 cm^{-1}. This peak is not very pronounced in the commercial resin. This peak occurs in the same region as the peak expected for the C=C stretching of the cyclohexene ring.[139] All the other peaks seen in the spectrum of the radiation-induced polymer are present in that of the commercial resin, although some of them are not as prominent. Once again, the spectral resolution of the polymer prepared by irradiation is much

TABLE XXI

ASSIGNMENTS OF INFRA-RED SPECTRAL ABSORPTIONS OF POLY(β-PINENE)

Absorptions cm^{-1}	Presence in PTR†	Presence in RPβP*	Assignment
2820-3000	strong	strong	C-H stretching
1650-1670	not prominent	medium	C=CH- nonconjugated stretching
1430-1460	strong	strong	$-CH_2$ deformation
1375	medium	absent	$-C-CH_3$ assymetric deformation
1365 and 1383	strong	strong	$-C\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$ symetric deformation
1140-1180	medium	medium	$-C\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$ stretching
1010	medium	medium	-CH=C<
920	weak	medium	-C=C
890	medium	absent	non-cyclic CH_2=C<
900			
1750	absent	absent	CH_2=C< in β-pinene and other cyclic systems
3070			
970	absent	absent	cyclobutane ring deformations and stretching
850-870			

†PTR refers to Polyterpene Resin; spectra taken by spotting a drop of the polymer solution in CCl_4 onto a NaCl plate, followed by drying off the solvent.

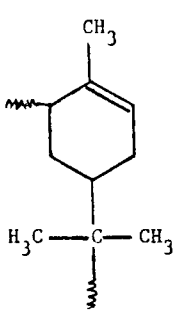
*RPβP refers to the poly(β-pinene) prepared by radiation-induced polymerization; spectra taken by pelletizing polymer with anhydrous KI.

higher than that of the commercial poly(β-pinene). This can be attributed to the greater regularity of the chains in the polymer prepared by radiation-induced polymerization. The commercial polymer also contains some vinylidene groups seen around 890 cm^{-1} which are absent in the radiation-prepared polymer. Thus, from infra-red spectral analysis, the presence of vinylidene groups at 890 cm^{-1} and the $-C-CH_3$ assymetric deformation at 1375 cm^{-1} were detected in the commercial polymer and which did not exist in the polymer prepared by gamma-irradiation. This does indicate that the commercial resin contains some isomeric repeat units. Hence it is proposed that Lewis acid and Ziegler-Natta catalysis give rise to an amorphous polymer from β-pinene because of the presence of other isomeric units in the polymer chain.

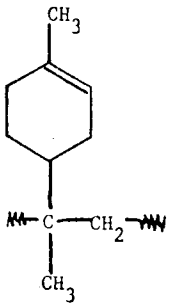
The nature and the origin of these units are not known. The nature of these structures could not be positively identified by ultraviolet spectroscopy since their respective absorptions overlap considerably.

The origin of these isomeric units could be possibly explained by either rearrangement of the repeat unit during propagation to give other units, or by the incorporation of the repeat units of limonene and/or of α-pinene in the macromolecular chain. Rearrangement of the repeat unit by Wagner-Meerwein reactions would lead to a camphenic cation which would not propagate as noted by Ruckel and his coworkers.[111] Also the presence of camphenic units would not give rise to the asymetric methyl deformation singlet observed at 1375 cm^{-1} in the infra-red spectra. On the other hand, the other possibility, namely that of the incorporation of units due to α-pinene, and especially limonene, could explain the occurrence of the single peak at 1375 cm^{-1}

in the commercial polymer. The units that would be incorporated from α-pinene and limonene are



and



respectively. Low molecular weight polymers containing these repeat units are produced in the homopolymerization of α-pinene and limonene respectively. However, α-pinene has much lower reactivity than β-pinene and limonene because of the double bond in α-pinene is part of the cyclohexene ring while β-pinene and limonene contain more reactive double bonds, which are exo to the ring.[111]

If such structures are present in the polymer chain in the commercial polymer, the next question that needs to be answered is how limonene and α-pinene are present in the β-pinene monomer during its Lewis acid polymerization. α-Pinene and limonene along with myrcene are the common impurities present in β-pinene. The β-pinene used by the author after fractional distillation on a Nester-Faust column showed such impurities to be below 0.1 %, whereas the commercial polymer was made from the drum grade of β-pinene, which usually contains 98 % β-pinene. It is assumed that the other 2 % of the constituents are limonene, α-pinene, and myrcene. The cationic polymerization of myrcene has been shown to lead to the formation of oligomers of $\overline{DP}_n$ of 4 to 6 with the same chemical repeat unit as that of β-pinene.[145] The myrcene, if present in β-pinene would lead to the disruption of the

stereoregularity in the polymer chain since the myrcene would not be expected to form stereoregular units, but would not explain the occurrence of the peak at 1375 cm^{-1}.

The presence of less than 2 % limonene and α-pinene in the commercial drum grade monomer would not explain the methyl singlet to gem dimethyl doublet ratio of 15:85. It can be speculated that limonene and α-pinene are produced by isomerization of β-pinene induced by Lewis acid catalysis. No work on the isomerization of β-pinene by aluminum chloride has been reported in literature. However, isomerization of β-pinene to α-pinene, limonene, and other terpenic isomers has been reported with acidic solid catalysts such as $AlPO_4$, $NiSO_4$, $ZnSO_4$, $Al_2O_3 \cdot SiO_2$, TiO_2 saturated with H_2SO_4, Zeolite which is protonated, or even with water, etc.[146] as well as by acids such as H_3PO_4 and H_2SO_4 in aqueous and non-aqueous solutions.[147]

The experiments to determine unsaturation by the reaction of iodine monochloride or bromine resulted in the consumption of more than one halogen molecule per repeat unit for both the commercial resin and the radiation-prepared polymer. However this does not necessarily indicate the presence of more than one double bond in each repeat unit. Some substitution reaction, probably of the allylic hydrogen atoms could have occurred. This is substantiated by the proton nmr data, which confirms the presence of only one vinylic proton per repeat unit, and by infra-red spectroscopy by which no double bonds of the type, $R_2C=CR_2$ are present. Only the presence of such double bonds could give higher halogenation results which are consistent with nmr spectra and with no substitution reactions taking place. It may be

pointed out that the detection limits in the two spectroscopic techniques for determination of these particular species were not ascertained.

4. Morphological Considerations

The morphological characterization carried out on the various poly(β-pinene) samples shows that the commercial resin is amorphous while the thermally-prepared polymer and the polymer prepared by irradiation are crystalline. The latter polymers show X-ray diffraction peaks at approximately the same 2θ angles of 15.2 and 17.7°. These angles correspond to lattice spacings of 5.83 and 5.01 Å respectively. The chemical repeat unit distance was determined using models to be 6.5 Å with the cyclohexene ring in a half-chair conformation and with the isopropyl-type group in its most stable conformation, which is with this group being equitorial to the cyclohexene ring. It has been shown earlier in section B that the density, D_c, of the 100 % crystalline poly(β-pinene) would be 1.128 g cm^{-3}. From this value, the volume of the unit cell can be calculated using the formula,

$$\text{volume of unit cell } V\ (\text{Å}^3) = \frac{\text{Mol. wt. of Repeat Unit (g mole}^{-1})}{D_c\ (\text{g cm}^{-3})} \times \frac{10^{24}\ (\text{Å cm}^{-3})}{6.023 \times 10^{23}\ (\text{mole}^{-1})} \qquad (57)$$

to be 200 $Å^3$, assuming there is only one chemical repeat unit per unit cell.

If the unit cell had been isometric, with its three sides equal (a = b = c) and with equal angles (α = β = γ = 90°), then the volume of the unit cell would have been $a^3 = (6.5)^3 = 275\ Å^3$. Since the volume

of the unit cell is 200 $\mathring{A}^3$, the unit cell of poly(β-pinene) is not isometric.

If the unit cell had been tetragonal with $a = b \neq c$ and $\alpha = \beta = \gamma = 90°$, the volume of the unit cell would have been $V = a^2c = 221\ \mathring{A}^3$ if $a = 5.83\ \mathring{A}$ and $V = 163\ \mathring{A}^3$ if $a = 5.01\ \mathring{A}$. Hence the unit cell is not tetragonal.

If the unit cell had been orthorhombic with $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90°$, V, the calculated volume of the unit cell and the d spacings do not match with the experimental values.

Using similar calculations, it can be shown that the unit cell is also not hexagonal. Hence the unit cell is either monoclinic ($a \neq b \neq c$ and $\alpha = \beta = 90° \neq \gamma$) or triclinic ($a \neq b \neq c$ and $\alpha \neq \beta \neq \gamma$). If the unit cell is of either of the monoclinic or the triclinic system, the number of known quantities such as the two values of d spacings, the volume of the unit cell, and the chemical repeat unit distance are less than the number of unknowns, making a definition of the unit cell impossible. In general, the method of determining the unit cell parameters needs more d spacings to be determined experimentally from X-ray diffractometry. To be able to do this it is necessary to produce some orientation in the polymer. This is usually done by converting the powdery polymer to either a film or a fiber, which is then stretched. However, every attempt to cast a film from solution failed. It was not possible to melt spin or to cast a film from the molten polymer because of degradation and auto-oxidation problems. Wet spinning the polymer from solution also failed. The reason for this probably is that to be able to form a good film or fiber it is necessary

that the polymer have moderately high molecular weight (over ca. 10,000) and/or a relatively high polydispersity ratio. Obviously neither of these criteria are met by this polymer. Hence it was not possible to determine the dimensions and the angles of the unit cell of the crystalline poly(β-pinene).

Although the crystalline polymers made by the two methods, namely by irradiation and by thermal means, show the crystalline peaks at the same Bragg angle, one small but significant difference in their X-ray diffractometer scans can be seen from figures 16 (p 94) and 22 (p 116). The thermal polymer shows peaks which are much broader than those of the polymer prepared by radiation-induced polymerization. This indicates that the crystallite size in the radiation-prepared polymer is larger than that in the thermal polymer since the width at half-maximum intensity is inversely proportional to the crystallite size according to the Scherrer equation,[148]

$$L \approx \frac{0.9\ \lambda}{B\ \cos\theta} \qquad (58)$$

where L is the crystallite size in Å, λ is the wavelength of the X-ray beam in Å, θ is the Bragg angle of the diffraction peak and B is the observed diffraction peak width in radians at half-maximum intensity. In the case of the radiation-prepared polymer, the crystallite size approximately 75 Å while that of the thermally-prepared polymer is about 50 Å.

The crystallites are formed during the polymerization stage. The simultaneous polymerization and crystallization taking place is different from the more common crystallization from macromolecular

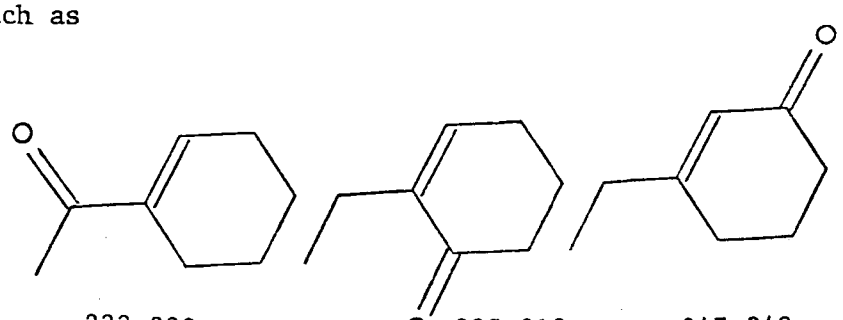
melt or solution. In the latter cases, the polymer formed by the chemical reaction is not crystalline just after formation but needs to be raised to temperatures above the glass transition temperature so that chain folding of the random chains can take place.[149,150] The occurrence of crystallization during polymerization is quite rare. The formation of poly(p-xylylene), formed by polymerizing the monomer is also known to be a case of crystallization during polymerization.[151] In this case the monomer is produced in 100 % yield by vapor phase pyrolysis of di-p-xylylene at 550-600°C. The solid polymer has been observed only on surfaces cooled below 30°C.[152] The solid state polymerization of trioxane to polyoxymethylene is a topochemical reaction and therefore a special case of crystallization during polymerization. Wunderlich et al.[153] have shown that increased crystal perfection results from the direct transformation of monomer to the macromolecular crystalline state.

5. Auto-oxidation

The auto-oxidation taking place in poly(β-pinene) is induced by ultraviolet light in the wavelength range of 230 to 280 nm (absorption by the double bond) which is the region in which the polymer absorbs light as seen from figure 12 (p 88). Very little auto-oxidation took place when the sample of poly(β-pinene) was kept in the dark or in the absence of oxygen as seen from the elemental analysis data in table XVIII (p 109).

The progress of auto-oxidation was followed by infra-red spectroscopy. This is shown in figure 19 (p 108). As auto-oxidation increases, two peaks corresponding to the peroxy group and to the ketonic

carbonyl group become prominent. Ultraviolet spectra of the auto-oxidized polymer seen in figure 20 (p 111) shows the presence of groups such as



The corresponding absorption maxima are indicated below these structures, which suggests that the ultraviolet absorptions corresponding to these peaks are present in the spectra of the auto-oxidized poly(β-pinene) sample. Similar conjugated ketones have also been reported in auto-oxidized samples of polyisoprene[154] and polybutadiene.[155]

A possible general mechanism, consistent with the overall results of the auto-oxidation of poly(β-pinene), has been suggested by Ranby[156] for the auto-oxidation of other polymers containing olefinic double bonds. This involves the formation of the relatively stable allyl radical by hydrogen abstraction by singlet oxygen, which can react with atmospheric oxygen to give peroxy radicals and linkages such as R-O-O-H. These can further react to form ketones, the formation of which is aided by the fact that the ketones formed have the carbonyls conjugated to the double bond of the cyclohexene ring.

5. Other Properties

All the other properties such as solubility and thermal behavior are related ultimately to the chemical nature of the repeat unit and to the manner in which the repeat units of the polymer are arranged

morphologically. Due to the high crystallinity, the crystalline fraction is very difficult to dissolve at room temperature. The crystalline melting point of 206-208°C is quite sharp and is quite high for a hydrocarbon with no aromaticity.

CHAPTER V

COPOLYMERS OF β-PINENE WITH STYRENE AND WITH α-METHYL STYRENE

A. INTRODUCTION

In Chapter IV, the homopolymerization of β-pinene has been dealt with. It was shown there that the radiation-induced polymerization of β-pinene occurs predominantly by a cationic mechanism. Copolymerization of β-pinene has been carried out by catalytic methods using Lewis acid and Ziegler-Natta catalyst systems. Almost all the work has been patented since the copolymers are widely used for the preparation of adhesives and coatings.[111] Procedures for the preparation of copolymers of β-pinene with vinyl chloride, isobutylene, formaldehyde, and several other comonomers have been described in the patent literature[157] for preparing copolymers of β-pinene.

Very little literature is available in non-patent form on copolymers of β-pinene. Marvel and his group prepared terpolymers of β-pinene with ethylene and propylene using Ziegler-Natta catalysts.[158] Kennedy and Chou[159] have reported that the copolymerization of β-pinene with isobutylene using Lewis acid catalysts gives random copolymers. Pietila *et al.*[119] have prepared polymers of β-pinene with styrene and α-methyl styrene using similar catalysts. Copolymers of β-pinene with styrene and with α-methyl styrene have also been reported in a Tenneco Chemicals patent,[160] again using Lewis acid catalysts.

No work has been reported on the radiation-induced copolymerization of β-pinene with any other monomer. Hence it was decided to study such copolymerizations with styrene and with α-methyl styrene,

since both of them are also known to polymerize by irradiation via a free cationic mechanism.

B. COPOLYMERS OF β-PINENE WITH STYRENE

1. Preparation

Using the procedure described in Chapter II of this dissertation, five sample vials were prepared so as to obtain monomer feed ratios of approximately of 0 %, 25 %, 50 %, 75 %, and 100 % β-pinene. The exact compositions of the comonomers were determined by polarimetry. Table XXII gives the percent compositions of the samples.

TABLE XXII

DETERMINATION OF MONOMER COMPOSITIONS OF SAMPLES OF β-PINENE-STYRENE MIXTURES

No.	Approximate Composition*	Polarimeter Reading Observed	Polarimeter Reading Corrected	Percent Volume	β-Pinene Mole Percent
1	100 % St	-0.05	-0.00	0.0	0.0
2	100 % βP	-4.20	-4.25	100.0	100.0
3	50 % βP	-2.20	-2.25	47.6	52.9
4	75 % βP	-3.25	-3.30	73.7	77.6
5	25 % βP	-1.05	-1.10	22.1	25.9

*As determined from the height of the liquid in the sample vial. St refers to styrene while βP refers to β-pinene.

These vials were irradiated for a total dose of 5.478 Mrads. The irradiated samples were processed and the results of the copolymer preparation are given in table XXIII.

TABLE XXIII

RESULTS OF COPOLYMERIZATION OF β-PINENE-STYRENE MIXTURES

No.	Mole Percent β-Pinene	Monomer (g)	Polymer (g)	Percent Conversion	G-value
1	0.0	13.540	4.487	33.14	561
2	100.0	17.067	8.387	49.14	636
3	52.9	25.354	9.521	37.55	552
4	77.6	20.721	7.817	37.73	513
5	25.9	25.690	8.602	33.48	533

Irradiation dose 5.478 Mrad at 25°C at a dose rate of 0.166 Mrad $hour^{-1}$.

2. Molecular Weight Studies

The number-average molecular weights of these polymers were determined by vapor pressure osmometry, except the sample with 100 % styrene. This sample was beyond the range of the osmometer and viscometry was resorted to. Toluene was used as a solvent to prepare solutions of various concentrations. The Ubbelohde viscometer was immersed in a constant temperature bath kept at 30°C and t, the time required for each of these solutions to flow through the capillary of the viscometer between the two graduated marks, was determined. From these values of t, the viscosities of the solutions were calculated using the equation

$$\frac{\eta}{\eta_o} = \frac{t}{t_o} \qquad (59)$$

where η and η_o are viscosities of the solution and toluene respectively

and t_o is the time required for toluene to flow between the same marks. The ratios of $(\eta-\eta_o)$ to η_o C was plotted against the concentration C, as in figure 25. The intercept value directly gives the intrinsic viscosity, $[\eta]$. In this case $[\eta]$ = 26.9 cp. Using the Mark-Houwink equation,

$$[\eta] = K (\bar{M}_v)^a \qquad (60)$$

and the parameters K and a as 9.2×10^{-3} and a = 0.72 respectively,[102] the value of $[\bar{M}_v] = 6.5 \times 10^4$ is obtained.

Solutions of the three copolymers were prepared by dissolving them in carbon tetrachloride. These solutions were then inserted into the syringes of the vapor pressure osmometer and readings obtained. In the case of each of the copolymers, from the plot of the ratios of the readings to the concentrations against the concentrations of the solutions, the intercept ratio was determined by extrapolation to zero, similar to the procedure used for determining this intercept value for the soluble fraction of poly(β-pinene) in figure 5 (p 77). The intercept values obtained were used to calculate the number-average molecular weights of these copolymers as described in chapter III of this dissertation. The copolymers containing 52.9 %, 77.6 %, and 25.9 % β-pinene gave molecular weights of 3.46×10^3, 3.30×10^3, and 3.93×10^3 respectively.

3. Chemical Characterization:

The proton nmr spectra of these samples are shown in figure 26. As the percentage of β-pinene decreases, so do the contribution of the peaks from its monomer units in the spectra. At the same time the peaks due to the aromatic protons around 7 ppm (δ) are observed to increase with increasing styrene content.

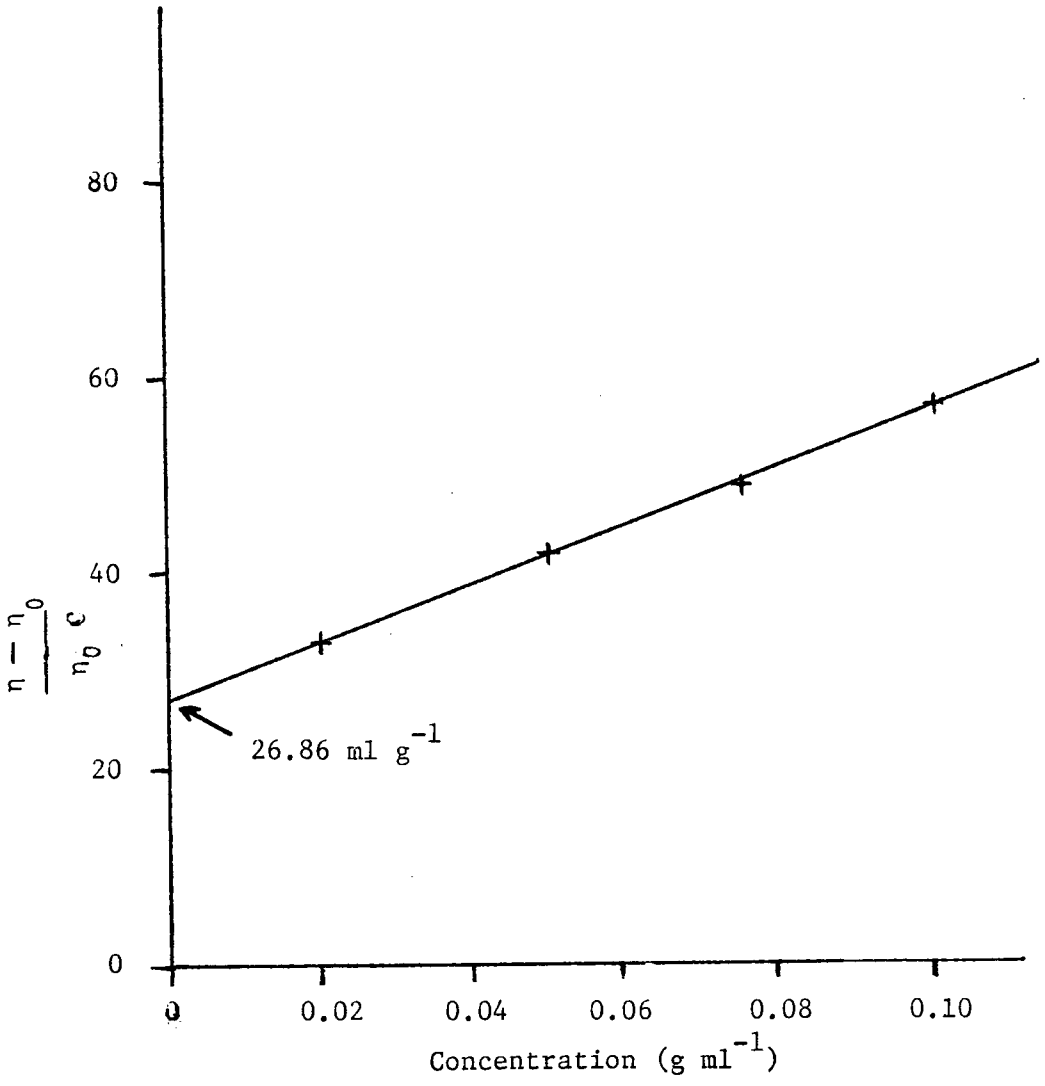


Figure 25. Plot of specific viscosity against concentration for polystyrene sample prepared by irradiation.

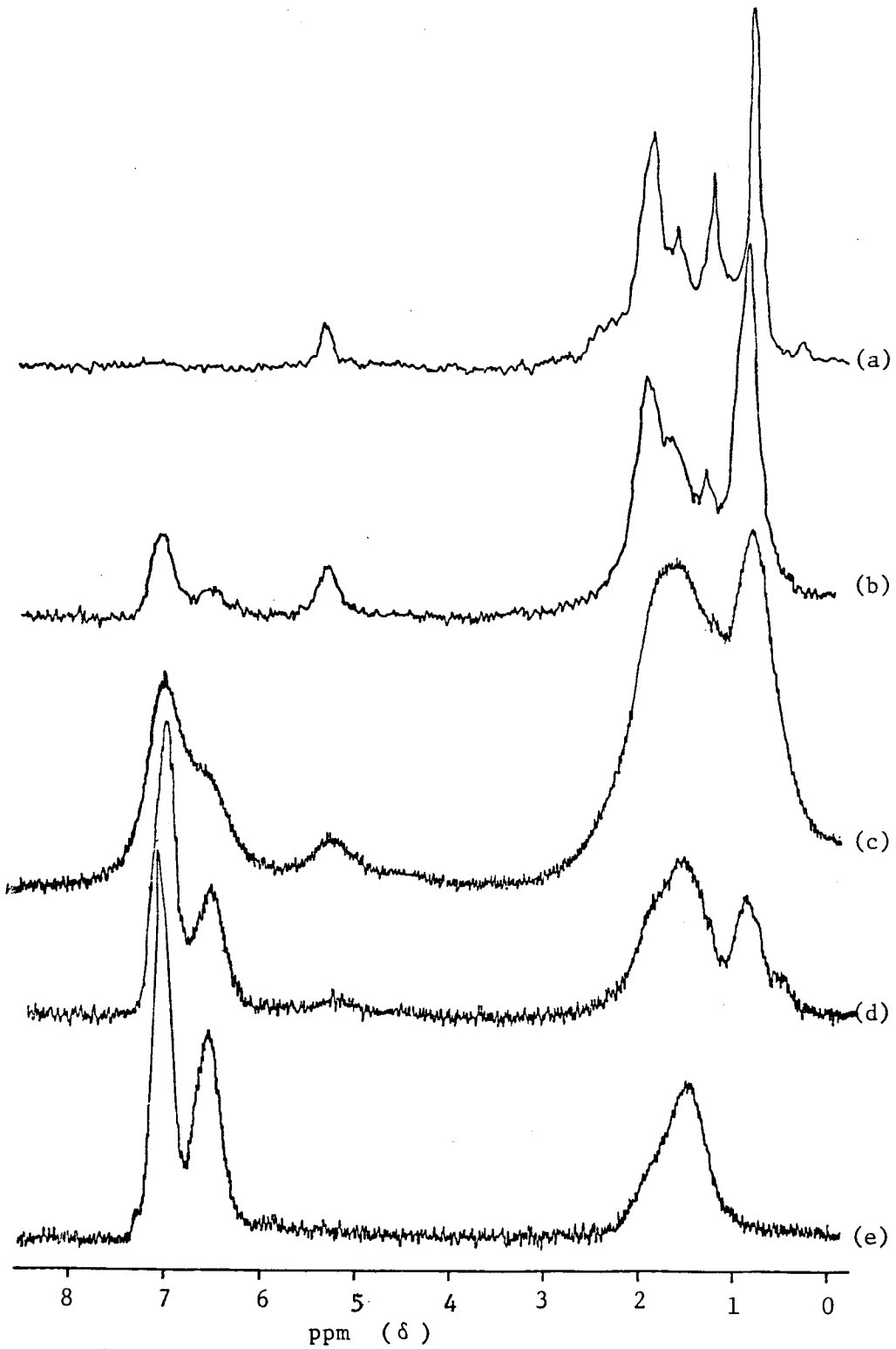


Figure 26. Proton nmr spectra of copolymers of β-pinene and styrene containing (a) 0 %, (b) 24 %, (c) 47 %, (d) 77 %, and (e) 100 % styrene.

The infra-red spectra of these samples are similarly shown in figure 27. Again, as the percentage of one of the components increases, the contribution of its absorption peaks increase. This is quite prominently seen for the 1601 cm^{-1} peak and for the bond at ca. 760-800 cm^{-1}, both of which are present in the polystyrene sample.

No elemental analyses of these copolymer samples were carried out. Also the amount of unsaturation in the copolymers by chemical reactions was not determined.

No attempt was made to fractionate the copolymers by differences in solubility, although repeated reprecipitations from carbon tetrachloride and methanol did not affect the comonomer composition of the polymer significantly. This indicated that little, if any, homopolymer was formed.

4. Other Properties

Except for the polymer sample that had 100 % β-pinene content, the others were determined to be amorphous by X-ray diffractometry. The diffractometer scans were very similar to the amorphous humps seen for the Polyterpene Resin and shown in figure 15 (p 93).

The solubility characteristics of these samples were studied. The copolymers were soluble in most solvents in the solubility parameter range 8.4 to 10.1. Systematic characterization of the solubility properties of the type carried out on poly(β-pinene) was not attempted.

The thermal properties were studied by both differential scanning calorimetry (DSC) and by hot-stage microscopy. The data obtained are shown in table XXIV.

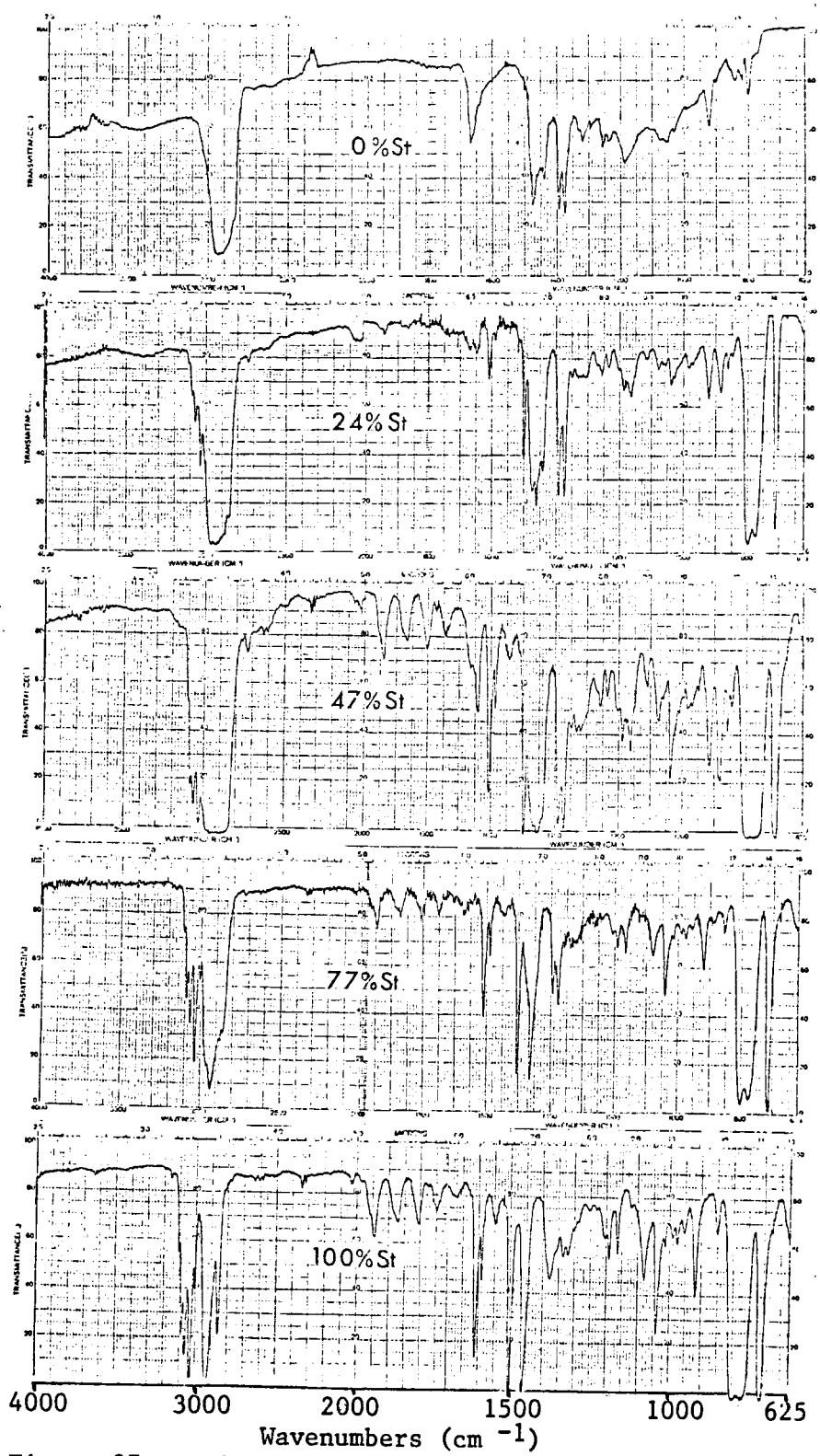


Figure 27. Infra-red spectra of copolymers of β-pinene and styrene.

TABLE XXIV

THERMAL PROPERTIES OF COPOLYMERS OF STYRENE AND β-PINENE

Mole Percent β-Pinene	DSC Transition*† Temperature (deg C)	Exothermic/ Endothermic	Hot-stage Microscopy Temperature (deg C)	Observation@
0	95-100	exothermic	97	softens
	202-205	endothermic	205	flows freely
25.9	98-103	exothermic	99	softens
	171-175	endothermic	175	flows freely
52.9	103-109	exothermic	105	softens
	179-182	endothermic	180	flows freely
77.6	106-111	exothermic	110	softens
	181-184	endothermic	185	flows freely
100.0	206-208	endothermic	135	loses rigidity somewhat
			180	begins to soften under pressure
			195	flows under pressure
			210	flows freely, no birefrigence

*An exothermic transition could indicate the glass transition temperature while an endothermic transition indicates the melting point.

†Heating rate in both cases was 10°C min^{-1}.

@Softening is indicative of a glass transition while the melting point is indicated by the temperature at which the polymer flows freely.

C. COPOLYMERS OF β-PINENE WITH α-METHYL STYRENE

1. Preparation

Monomer mixtures of β-pinene and α-methyl styrene were prepared using the procedure detailed in Chapter II of this dissertation. The composition of each mixture was determined by polarimetry, as for the β-pinene-styrene mixtures described in section B of this chapter, by taking advantage of the fact that β-pinene is optically active while α-methyl styrene is not. The results of these determinations are shown in table XXV. Three batches of poly(α-methyl styrene-co-β-pinene) were prepared. The first batch was prepared using the dessicant grade of silica gel as the drying agent. The tell-tale indicator type of silica gel was used for the other two batches of these copolymers.

The irradiated samples were processed and the results of the copolymer preparation are given in table XXVI. During the processing of the first sample of the first batch, the polymer that was precipitated from methanol was filtered as usual and then evacuated in a dessicator. However, after just five hours of pumping to remove residual methanol, no polymer was left in the beaker. Instead a liquid was obtained. Proton magnetic resonance spectroscopy showed that this liquid was the α-methyl styrene monomer, along with a little methanol. Hence for all the other copolymer samples containing α-methyl styrene, the samples were not evacuated or heated to prevent any depolymerization. Instead any residual monomer was washed off with repeated washings of methanol and the methanol was removed by air drying in the absence of any light (to prevent auto-oxidation). Only

TABLE XXV

DETERMINATION OF MONOMER COMPOSITIONS OF β-PINENE-α-METHYL STYRENE MIXTURES

Sample No.	Polarimeter Reading† Observed	Corrected	Percent β-Pinene Mole Percent
I-1	+0.30	0.00	0.0
I-2	+0.30	0.00	0.0
I-3	-3.40	-3.70	87.1
I-4	-3.15	-3.45	81.1
I-5	-2.60	-2.90	68.2
I-6	-3.95	-4.25	100.0
II-1	+0.05	0.00	0.0
II-2	-2.55	-2.60	61.2
II-3	-1.25	-1.30	30.6
II-4	-1.75	-1.80	42.4
II-5	-1.55	-1.60	37.6
II-6	-4.15	-4.20	98.8
III-1	+0.10	0.00	0.0
III-2	-0.35	-0.45	10.6
III-3	-1.05	-1.15	27.1
III-4	-0.50	-0.60	14.1

†Significant up to ± 0.51.

TABLE XXVI

RESULTS OF COPOLYMERIZATION OF β-PINENE-α-METHYL STYRENE MIXTURES

No.†	Mole Percent β-Pinene@	Monomer (g)	Polymer (g)	Dose Rate Mrad hour^{-1}	Dose Mrad	Percent Conversion	G-value
I-1	0.0	13.413	*	0.1623	5.348	*	*
I-2	0.0	13.073	6.307	0.1623	5.420	48.24	726.8
I-3	87.1	21.177	12.452	0.1623	5.481	58.80	772.5
I-4	81.1	16.325	0.133	0.1623	5.481	0.81	10.8
I-5	68.2	17.711	0.566	0.1623	5.481	3.20	43.1
I-6	100.0	14.049	6.469	0.1623	5.481	46.05	595.0
II-7	0.0	5.292	1.050	0.1602	5.500	19.84	294.5
II-2	61.2	13.732	2.573	0.1602	5.500	18.74	254.4
II-3	30.6	19.583	4.133	0.1602	5.500	21.11	299.2
II-4	42.4	22.225	7.649	0.1602	5.500	34.42	479.8
II-5	37.6	7.199	1.084	0.1602	5.500	15.06	211.7
II-6	98.8	24.132	15.918	0.1602	5.500	65.96	850.9
III-1	0.0	13.431	9.050	0.1579	4.553	67.38	1210
III-2	10.6	22.396	7.670	0.1579	5.698	34.25	483.1
III-3	27.1	22.145	8.627	0.1579	5.795	38.96	481.0
III-4	14.1	21.342	10.270	0.1579	5.684	48.12	676.8

†Dessicant grade silica gel was used for batch I while Indicator grade silica gel was used for batches II and III.

*The polymer formed gave only monomer after evacuating the sample. Hence for the rest of the samples, no evacuation was carried out.

@In monomer feed.

in the case of the mixture containing ca. 87 % β-pinene, a small fraction of the polymer precipitated from the irradiated mixture prior to the addition of methanol.

2. Molecular Weight Studies

The number-average molecular weights of some of these copolymers were determined by vapor pressure osmometry. The results obtained are shown in table XXVII. The molecular weight of poly(α-methyl styrene)

TABLE XXVII

MOLECULAR WEIGHTS OF COPOLYMERS OF β-PINENE AND α-METHYL STYRENE

Sample No.	β-Pinene Content*	Dose (Mrad)	Percent Conversion	G-value	$\bar{M}_n$ @ x 10^3
I-2	0	5.42	48.2	727	16.4
III-2	10.6	5.70	34.3	488	2.36
II-3	30.6	5.50	21.1	299	2.56
II-4	42.4	5.50	34.4	480	2.15
I-5	68.2	5.48	3.2	43	2.94
I-3	87.1	5.48	58.8	773	2.66
I-6	100.0	5.48	46.1	595	2.15

*β-pinene content in the monomer feed, expressed as mole percentage.

†Only for the soluble fraction.

@Determined by vapor pressure osmometry.

was determined both by vapor pressure osmometry, which gave a value of

1.65×10^4, and by viscometry. The latter method gave a molecular weight of 1.68×10^4 from an intrinsic viscosity [η] of 5.28 and Mark-Houwink parameter values of $K = 2.2 \times 10^{-3}$ and $a = 0.80$.[103]

3. Chemical Characterization

The proton nmr spectra of some of the copolymer samples are shown in figure 28 while the infra-red spectra are shown in figure 29. As the percentage of β-pinene decreases, the contributions of the peaks due to this monomer also decrease. At the same time, in the region around 7 ppm (δ) in the case of the nmr spectra and around 800 cm^{-1} for the infra-red spectra the peaks due to the aromatic protons and bonds increase with increasing α-methyl styrene content.

No elemental analyses of any of these copolymer samples were carried out. Also chemical reactions of these polymers for determination of the chemical repeat unit were not carried out. Again, no attempt was made to fractionate the copolymers by differences in solubility, although repeated reprecipitation from carbon tetrachloride and methanol did not affect the comonomer composition of the polymer significantly in the case of comonomer ratios from 15:85 to 85:15. Outside this range, some homopolymers were probably produced. However the solubility differences were so low that easy significant fractionation was not possible.

4. Other Properties

Almost all the samples tested by X-ray diffractometry were amorphous because they did not give any sharp crystalline peaks but gave amorphous humps similar to that observed for the Polyterpene

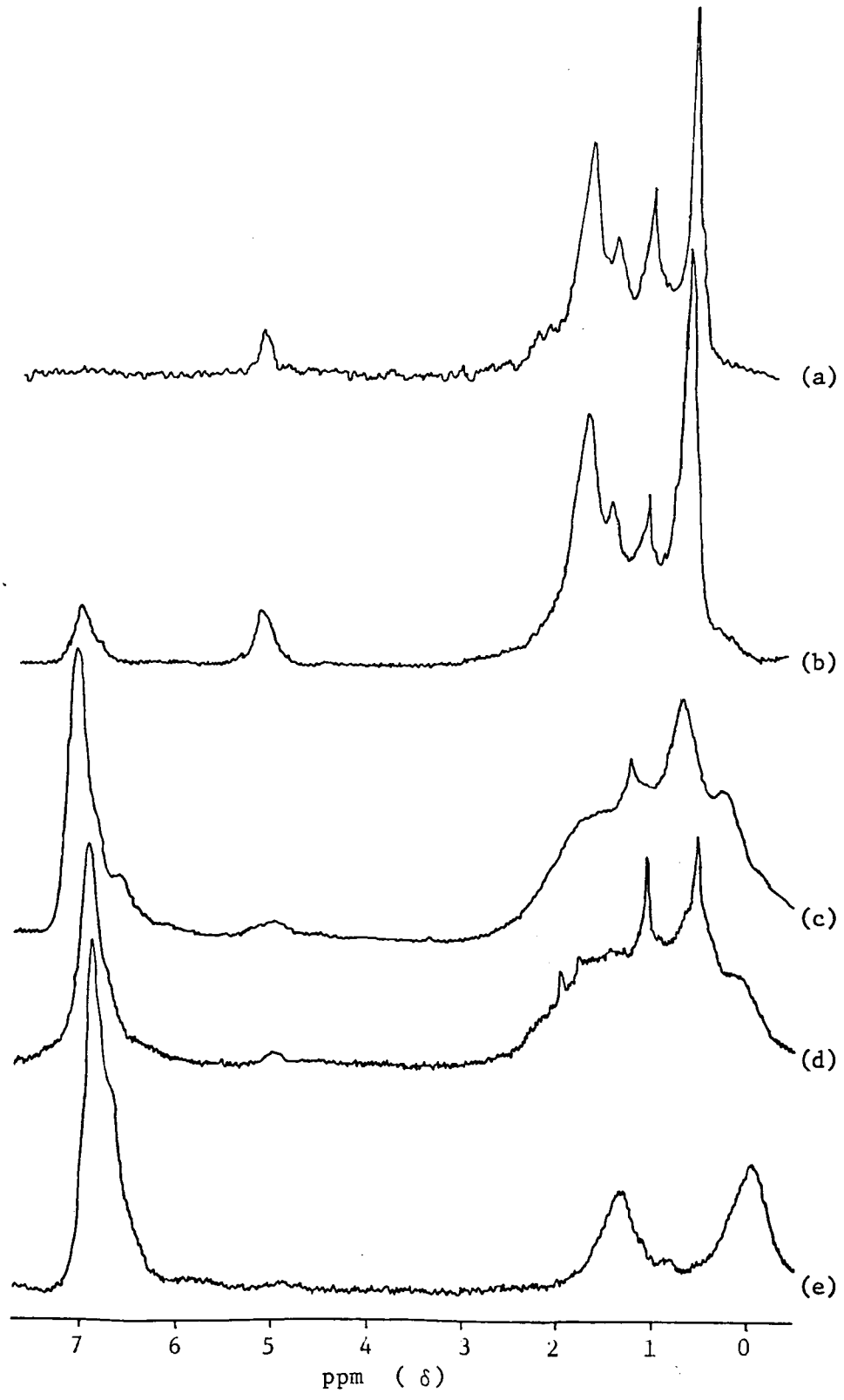


Figure 28. Proton nmr spectra of copolymers of β-pinene and α-methyl styrene containing (a) 0 %, (b) 12 %, (c) 38 %, (d) 58 %, and 100 % α-methyl styrene.

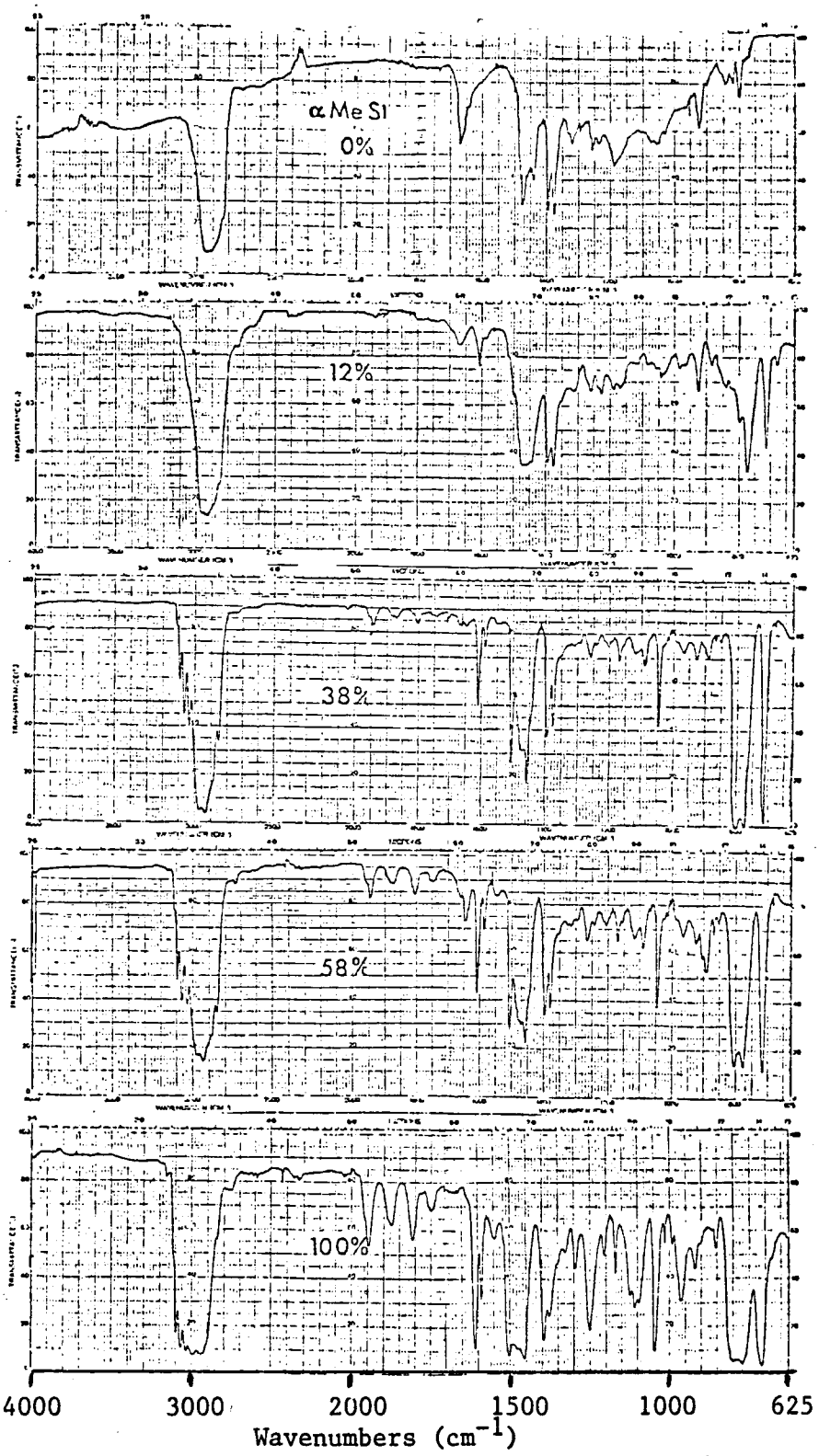


Figure 29. Infra-red spectra of copolymers of β-pinene and α-methyl styrene.

Resin. However, the copolymer containing 88 % β-pinene showed small peaks at 15.2 and 17.7° indicating that some crystalline homopolymer was present in this irradiated sample. This result is consistent with the observation that a small fraction of the polymer had precipitated from the irradiated monomer mixture prior to the addition of methanol.

The solubility characteristics of these samples were studied. The copolymers were soluble in most solvents in the solubility parameter range 8.4 to 10.1. Systematic characterization of the solubility parameters of the type described in Chapter IV for poly(β-pinene) homopolymer was not attempted.

The thermal properties were studied by both differential scanning calorimetry (DSC) and by hot stage microscopy. The data obtained is shown in table XXVIII. The samples with high α-methyl styrene content decomposed (depolymerized).

D. DISCUSSION

1. Copolymerization

The G(-M) values obtained for these copolymers are generally lower than those reported for the homopolymerization of β-pinene in table VII (p 71) of this chapter, and much lower than those reported elsewhere for the homopolymerization of styrene[55-57] and α-methyl styrene.[54,67] As pointed out earlier, the main thrust of the work was not to try to attain the highest reported yields, but instead to prepare copolymers with adequately high G-values and then to characterize the polymers formed. Two greased stopcocks needed to be used in the manifold glassware during sample preparation in order to dispense

TABLE XXVIII

THERMAL PROPERTIES OF COPOLYMERS OF β-PINENE AND α-METHYL STYRENE

Mole Percent β-Pinene	DSC Transition*† Temperature (deg C)	exothermic/ endothermic	Hot-stage Microscopy† Temperature (deg C)	Observation*
0	45	highly exothermic	48	starts bubbling (decomposition)
10.6	86	highly exothermic	86	starts bubbling (decomposition)
42.4	92-99	exothermic	98	softens
	170-175	endothermic	175	flows freely
61.2	100-106	exothermic	103	softens
	174-181	endothermic	180	flows freely
100	206-208	endothermic	135	loses rigidity somewhat
			180	begins to soften under pressure
			195	flows under pressure
			210	flows freely, no birefringence

*At the glass transition temperature an exothermic transition is observed and the polymer begins to soften. At the melting point the transition is endothermic and the polymer begins to flow freely.

†Heating rate was 10°C min^{-1}.

varying amounts of the two monomers into each of the sample ampules. The glassware at and close to the stopcocks could not be dried either by baking it in the oven or by flaming it. This possibly introduced minute quantities of water, which were sufficient to reduce the

G-values. The use of the dessicant grade silica gel, used for the first batch for preparing copolymers of β-pinene and α-methyl styrene, gave very irreproducible results, paralleling the results of the homopolymerization of β-pinene.

There does not seem to be much difference between the G-values obtained in the styrene series and in the α-methyl styrene series, showing that these two reactive monomers showed similar reactivities towards β-pinene in copolymerization. This is possibly because the net rate of the copolymerization is more dependent on the reactivity of the β-pinene monomer than either of the two aromatic monomers. Rapid homopolymerization of styrene and α-methyl styrene is probably hampered by chain transfer to β-pinene, so that the copolymerization is favored over homopolymerization of these monomers. This appears to be supported by the fact that the G-values do not seem to depend on the percent composition of the monomer mixture. Similar results have been reported for the radiation-induced copolymerization of isobutylene and isoprene.[73]

The poly(α-methyl styrene) samples decomposed to form monomer, when they were evacuated. This observation implies that somehow the polymer unzips to monomer at room temperature at reduced pressure. No similar studies have been reported, although it has been shown that the ceiling temperature, T_c of poly(α-methyl styrene) is reported to be quite low (ca. 70°C) at atmospheric pressure.[3] As the pressure is increased, it has been reported that the ceiling temperature increases, probably because the monomer-polymer equilibrium is shifted towards the formation of the polymer.[161] It is plausible that as the polymer sample

is evacuated, the finite quantity of the monomer present is pumped out, shifting the equilibrium towards depolymerization.

The molecular weights of the homopolymers of styrene and α-methyl styrene obtained here were about 65,000 and 17,000 respectively. These values are in the same range as those reported by other workers. For instance, Metz et al.[87], report molecular weight values of about 6.64×10^4 to 8.85×10^4 while Ueno et al.[57,63] report values around 50,000 for polystyrene prepared by radiation-induced polymerization under ultradry conditions. Similarly the poly(α-methyl styrene) prepared by gamma irradiation had molecular weights in the range of 1880 to 5100.

The plot of molecular weights of all the copolymers against the mole percentage of β-pinene in the monomer feed is shown in figure 30. The molecular weights of the homopolymers of styrene and α-methyl styrene are much higher than those of any of the copolymers. This is because the degree of polymerization is probably governed by chain transfer from the growing cationic species and especially from the carbocation of the β-pinene repeat unit. This can explain why the copolymers have approximately the same molecular weights as that of poly(β-pinene) and also why these molecular weights are almost independent of the monomer concentration as long as there is sufficient β-pinene to give adequate chain transfer.

In a series of papers, Higashimura et al.[163] found that the molecular weights of the copolymers of isobutylene, prepared by Lewis acid catalysis, fall off rapidly in the presence of even modest amounts of styrene or α-methyl styrene. Further, they found that the molecular

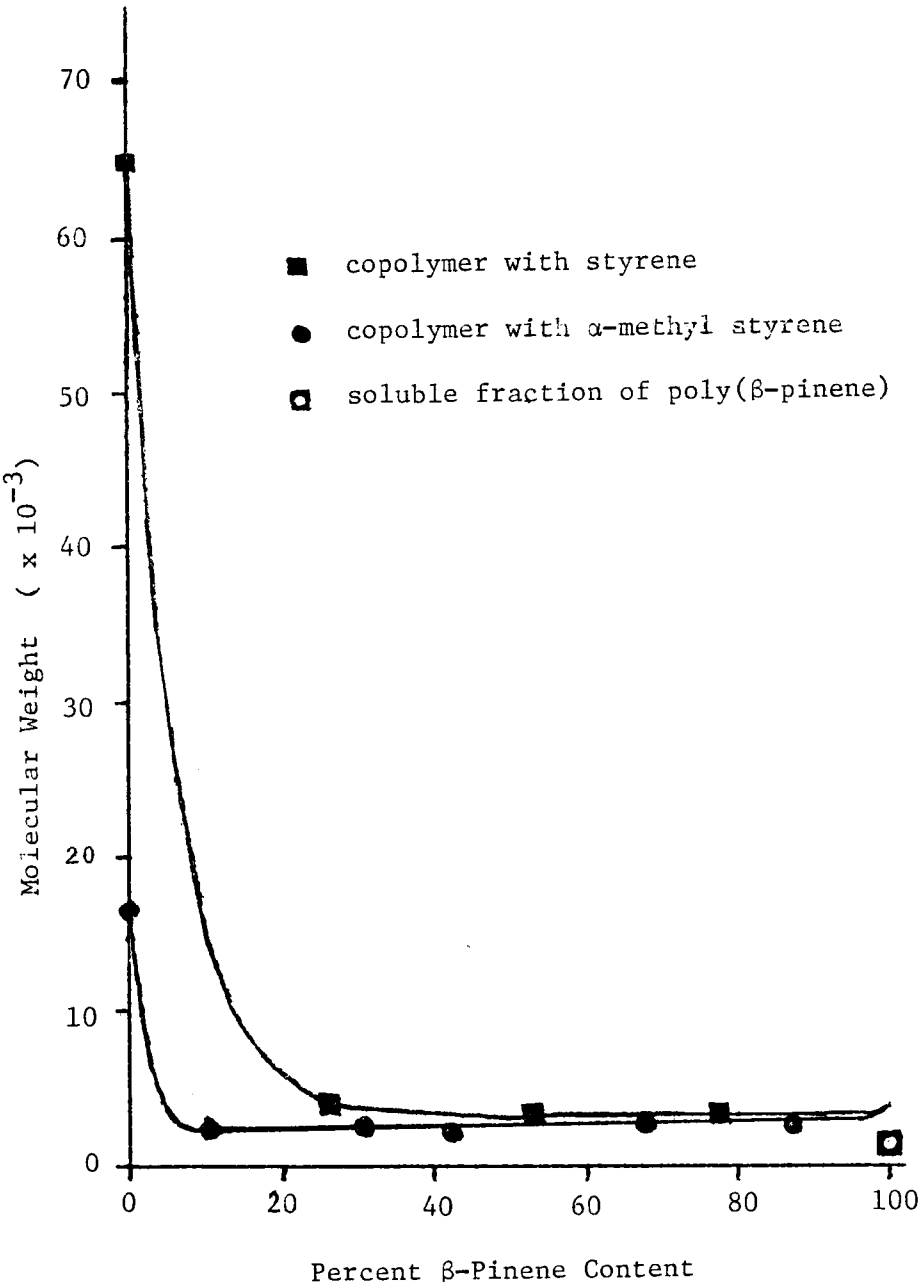


Figure 30. Plot of molecular weights of copolymers of β-pinene with styrene and with α-methyl styrene against mole percent β-pinene in the monomer feed.

weights of the copolymers containing appreciable amounts of either components were always lower than those of the respective homopolymers. They developed a kinetic treatment based on the fact that molecular weights of cationally produced polymers are by and large determined by chain transfer to the less reactive monomer, hereafter called cross-transfer, to explain their observations.

Similar results were obtained by Kennedy and Chou[159] for the cationic copolymerization of β-pinene with isobutylene. They expanded on Higashimura's treatment and showed that the rate of cross-transfer increases more than that of cross-propagation. If k_p and k_{tr} are the rate constants for the propagation transfer reactions respectively and if the subscripts 1 and 2 stand for the first and the second monomers respectively, then k_{p12} refers to the rate constant for propagation from the cation derived from monomer 1 to add a molecule of monomer 2, $k_{tr_{21}}$ refers to the rate constant for transfer from the cation derived from monomer 2 to a molecule of monomer), etc. Since the molecular weight of the copolyemr is determined by the competition between the cross-propagation (rate constants k_{p21} and k_{p12}) and the cross-transfer reactions (rate constants $k_{tr_{21}}$ and $k_{tr_{12}}$), the presence of appreciable quantities (greater than ca. 5 %) of the second monomer in the mixture would result in decreased molecular weights. The cross-transfer reaction would be faster than either of the homo-propagation reactions (i.e. $k_{tr_{21}} > k_{p22}$ or k_{p11}). Hence the molecular weights of a random copolymer produced by a carbenium ion mechanism in which the energy of activation for transfer is slightly lower than that for propagation, will be lower than that of the respective homopolymers

under identical conditions. This conclusion seems to be true in the case of the radiation-induced copolymerizations of β-pinene with styrene and with α-methyl styrene. This is because the number-average molecular weights of the copolymers are much lower than those for the polystyrene and the poly(α-methyl styrene) samples.

If monomer 2 is assumed to be more reactive than monomer 1, $k_{p_{22}} >> k_{p_{11}}$ and $k_{tr_{12}}$ and $k_{tr_{22}}$ can be neglected since these two rate constants are very low. On similar reactivity considerations, one can expect the values of $k_{p_{12}}$, $k_{p_{11}}$, $k_{tr_{11}}$, and $k_{tr_{12}}$ to be comparable. Similarly, $k_{p_{22}} \approx k_{p_{21}}$. Kennedy *et al.*[159] have shown that $k_{tr_{21}} \geq k_{p_{22}} \approx k_{p_{21}}$, implying that the molecular weight of the copolymer is primarily governed by the value of the rate constant for transfer from the cation of the more reactive monomer to a molecule of the less reactive monomer. Hence, this phenomenon of a decrease in the molecular weight of the copolymer would be small, if one of the copolymerizable monomers produced low molecular weight homopolymers, because in such a system the activation energy difference between propagation and transfer would be small.[159] This last conclusion is probably true in the cases studied by the author since the difference between the molecular weights of the copolymers and the homopolymer of β-pinene is not very high.

β-Pinene, styrene, and α-methyl styrene are all thought to homopolymerize by a cationic mechanism--an ion-pair type of propagation when Lewis acid catalysis is employed and by a free ion propagation process by radiation-induced polymerization when the monomer is super-dry. There is no reason to believe that the copolymerization of

β-pinene with styrene and with α-methyl styrene induced by gamma irradiation does not occur predominantly via a free cationic propagating mechanism.

2. Repeat Units in the Copolymers:

The proton nmr spectra of the copolymers of β-pinene with styrene and with α-methyl styrene are shown in figure 26 (p 148) and 28 (p 157) respectively. As mentioned earlier, the contributions of the peaks due to β-pinene repeat units decrease as those of the other comonomers increase. This observation can be used to quantitatively estimate the percent β-pinene content of the copolymers as follows.

Figure 31 shows a typical proton nmr spectrum of a styrene-β-pinene copolymer. In the region of 6 to 8 ppm (δ) the resonance peaks are due to the five aromatic protons, which are present in each repeat unit of styrene in the copolymer. All the other three should exhibit peaks in the region from 0 to 3 ppm. Hence the area due to styrene units in the copolymer, A_1, is one-fifth the area of the resonance in the region from 6 to 8 ppm. Each β-pinene repeat unit contains one olefinic proton, which is observed in the region from 5 to 5.5 ppm. The other fifteen protons show resonance peaks in the region from 0 to 3 ppm. This means that the region from 0 to 3 ppm shows peaks due to both the monomers. Of the total area in this region, that due to the styrene is three-fifth of the area of the peaks in the region from 6 to 8 ppm since each styrene unit contains five aromatic protons (6 to 8 ppm) and three non-aromatic protons (0 to 3 ppm). Hence the area of the peaks due to β-pinene units in the copolymer, A_2, is given by

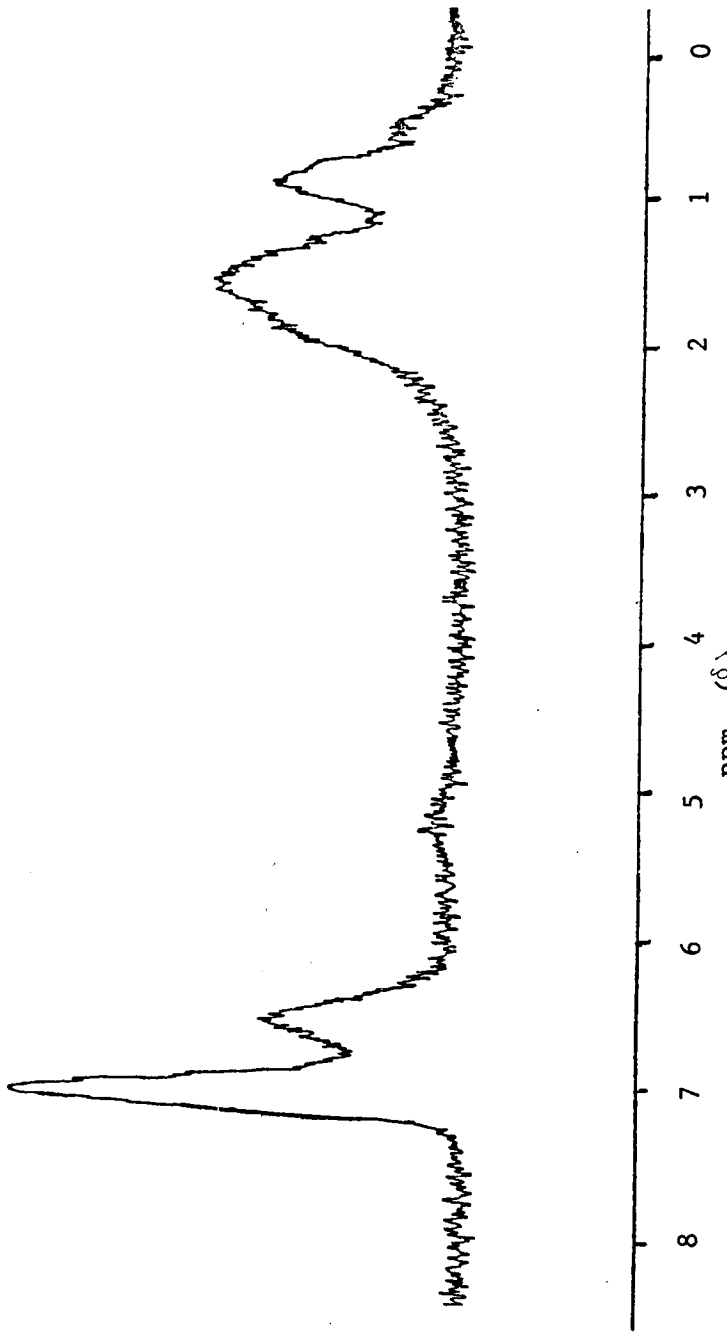


Figure 31. Proton nmr spectra of a typical copolymer of β-pinene with styrene.

$$A_2 = \frac{1}{15}\left[(\text{Area of Peaks from 0 to 3 ppm}) - \frac{3}{5}(\text{Area of Peaks from 6 to 8 ppm})\right] \quad (61)$$

From the areas due to styrene and β-pinene units in the copolymer, A_1 and A_2 respectively, the percent β-pinene units in the copolymer can be calculated as being

$$\frac{A_2}{A_1 + A_2} \times 100.$$

Figure 32 shows a typical proton nmr spectrum of a β-pinene-α-methyl styrene copolymer. The repeat unit of α-methyl styrene contains 5 aromatic protons, exhibiting peaks in the region 6 to 8 ppm, and 5 non-aromatic protons, which show peaks in the region -0.5 to 3 ppm. Using similar arguments as those above, it can be shown that the area due to the α-methyl styrene units in the copolymer, A_3, is given by one-fifth of the area of the peaks in the region from 6 to 8 ppm. Also the area due to the β-pinene units in the copolymer, A_4, is given by

$$A_4 = \frac{1}{15}\left[(\text{Area of Peaks from -0.5 to 3 ppm}) - (\text{Area of Peaks from 6 to 8 ppm})\right] \quad (62)$$

The percentage of β-pinene units in the copolymer is given by

$$\frac{A_4}{A_3 + A_4} \times 100.$$

Using such calculations the percentage of β-pinene content in each copolymer of both sets of copolymers was calculated. These calculated β-pinene contents were plotted against the β-pinene contents of the monomer feed determined earlier by polarimetry. Such a plot for the poly(styrene-co-β-pinene) samples shown in figure 33 while the similar plot for the poly(β-pinene-co-α-methyl styrene) samples is

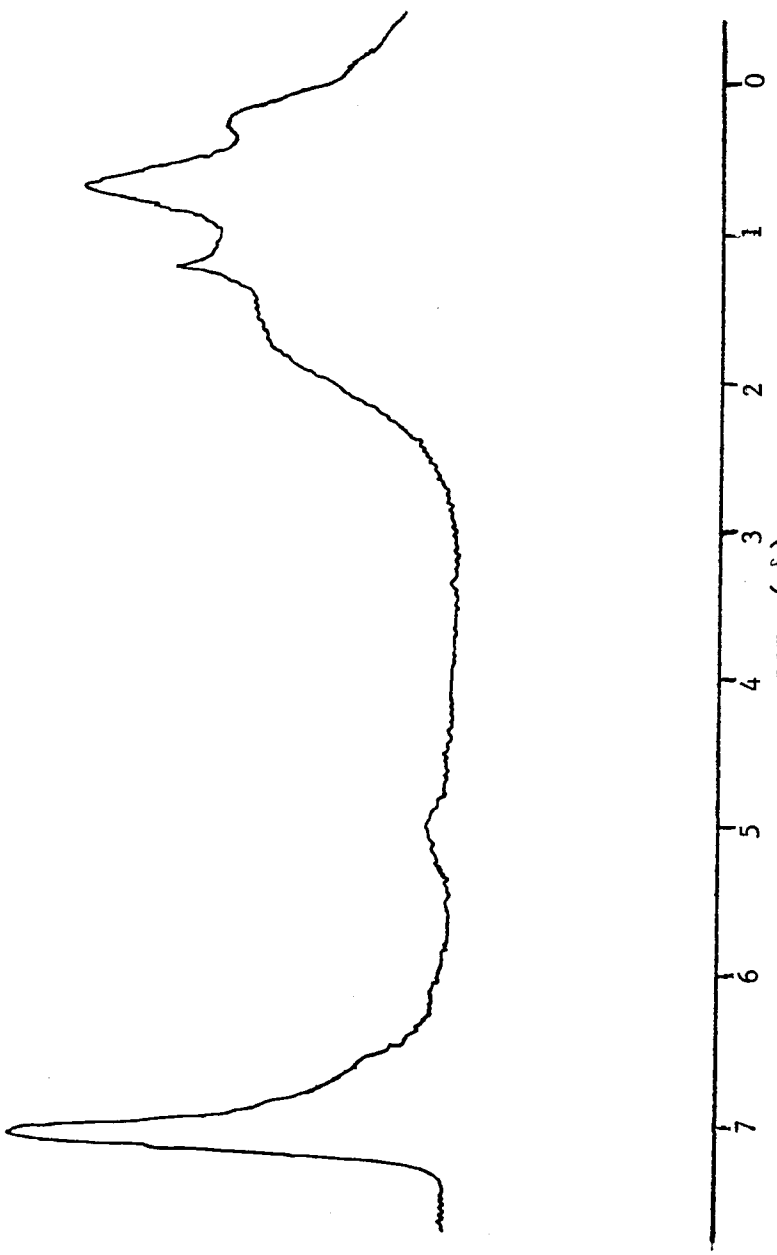


Figure 32. Proton nmr spectra of a typical copolymer of β-pinene with α-methyl styrene.

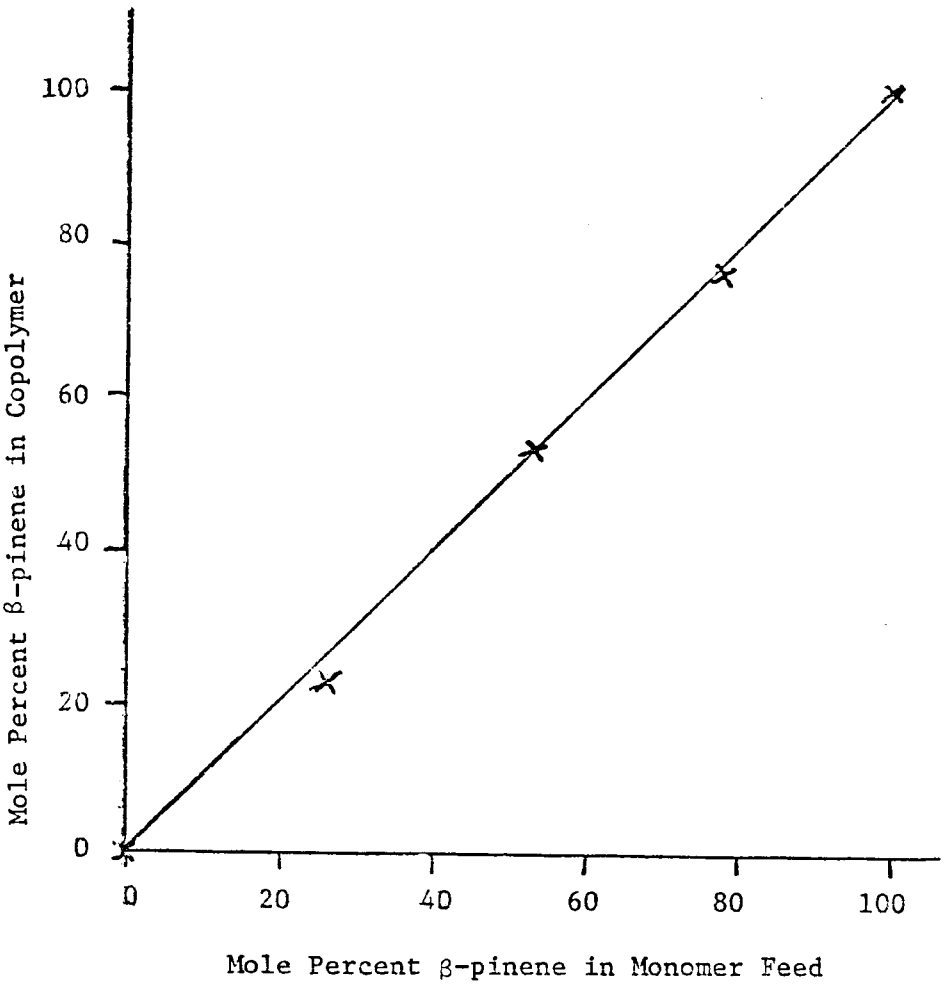


Figure 33. Plot of estimated β-pinene content in poly(β-pinene-co-styrene) samples against β-pinene content in the monomer feed.

shown in figure 34. Both the curves are straight line plots with their slopes equal to unity. This indicates that the copolymerizations are random and probably azeotropic. Similar results were also obtained by Kennedy et al.[159] for the copolymerization of β-pinene with isobutylene initiated by Lewis acid catalysis.

However, this conclusion of random copolymerization of β-pinene and styrene does not necessarily correlate with the pmr spectra of the copolymer samples containing 47 and 77 % styrene, which are shown in figure 26 (p 148). By the splitting of the aromatic resonance into two peaks, these spectra indicate that these copolymer samples either contain some homopolymer of styrene or a significant number of blocks of styrene repeat units.[164] A completely random copolymer, at least in the 47 % case, would have shown a single aromatic peak. No attempt was made to fractionate the homopolymer, if present, from the copolymer since the two would be expected to have very similar solubility characteristics.

Sequence distribution analysis of these copolymers was not carried out because this requires a high resolution (220 or 300 MHz) nuclear magnetic resonance spectrometer. However 100 MHz proton nmr analysis of the poly(α-methyl styrene) prepared by radiation-induced polymerization gave insight into the microtacticity of this homopolymer. Figure 35 shows the high resolution obtained for the methyl peak of the proton magnetic resonance spectrum of this polymer. The ratio of the isotactic to heterotactic to syndiotactic triad placement is 3:28:69. Previous results of Brownstein et al.[165] and of Hubmann et al.[67] for radiation-prepared poly(α-methyl styrene) were 5:32:63 and 0:30:70

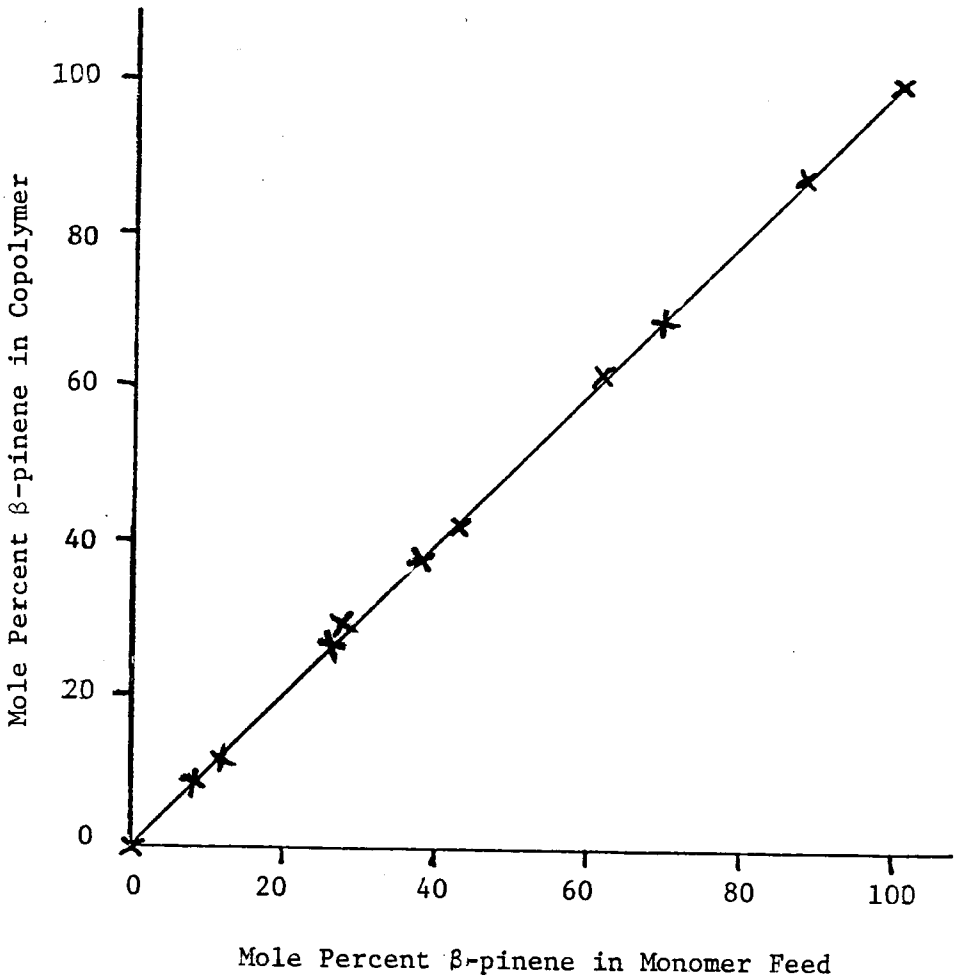


Figure 34. Plot of estimated β-pinene content in copolymers of β-pinene with α-methyl styrene against β-pinene content in the monomer feed.

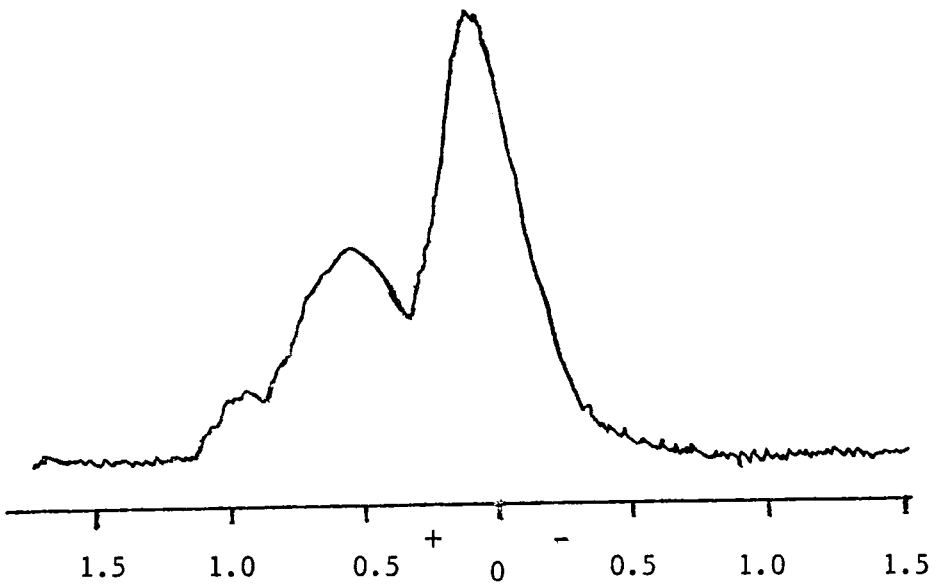


Figure 35. 100 MHz proton nmr spectra of poly(α-methyl styrene) prepared by gamma irradiation: resolution of the methyl peak.

respectively. The result obtained by this author was used to calculate σ, the probability that the growing polymer chain will add a monomer unit to give the same configuration as that of the last repeat unit on the chain. In this case σ = 0.17. This ratio, obtained for the polymer prepared by radiation-induced polymerization of α-methyl styrene is different from that of the poly(α-methyl styrene) samples prepared by catalytic methods, either by cationic or anionic propagation.[164,165]

Infra-red spectroscopic analysis of the copolymers showed that no additional peaks, besides those present in the spectra of the homopolymers, were present.

Most of the copolymers did not show any crystallinity peaks. The copolymer of β-pinene and α-methyl styrene, containing 88 % β-pinene showed a little crystallinity probably due to the formation of some homopolymers as suggested in section C, subheading 4 of this chapter. It is clear that the presence of the bulky aromatic units in the co-polymers sterically hinders the crystal formation, besides destroying the regularity of the polymer chain.

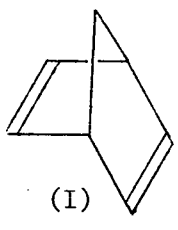
The thermal characterization techniques for both sets of copolymers shows that only one Tg is observed for the copolymers, indicating that there are very few segments of the β-pinene molecules bunched together. This leads to the conclusion that true copolymers are formed and that the result of the copolymerization is not the formation of a mixture of the two homopolymers. The samples containing ca. 100 % and 90 % α-methyl styrene content started depolymerizing at ca. 45°C and 86°C respectively, probably because even in the latter polymer the α-methyl styrene there would be expected to be lengthy segments of this repeat unit.

CHAPTER VI

POLY(2,5-NORBORNADIENE)

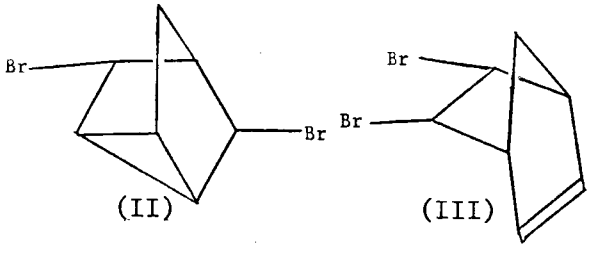
A. INTRODUCTION

Bicyclo[2.2.1]hepta-2,5-diene, which is commonly known as 2,5-norbornadiene, is a liquid (b.p. 90°C and f.p. -24°C) with the structure,



(I)

It was first synthesized by the Diels Alder reaction from cyclopentadiene and acetylene.[166] It has also been synthesized by Hine et al.[167] by dechlorination of trans-5,6-dichloro-2-norbornene with MgI in ether. Schmerling and his coworkers[168] used the latter method, though independently, and studied many of its reactions as well. They found, for instance, that on bromination 2,5-norbornadiene gives a mixture of dibromonortricyclenes(II) and dibromonorbornenes(III)



under free-radical conditions whereas the ionic reaction is more specific and tends to give almost exclusively 3,5-dibromonortricyclene

(II). These results were independently confirmed by Winstein and Shatavsky[169] and later by several other workers.[170-172] However, as the size of the added group increased the amount of tricyclene-type product was found to increase.[172]

It is relatively easy to distinguish between the nortricyclene structure and the norbornene structure on the basis of infra-red spectroscopy. All nortricyclene structures show a characteristic bond at ca. 807 cm^{-1} [173-174] attributed by Lippincott[175] to "cage-breathing" deformation. 1-Substituted nortricyclenes however absorb in the region 840 to 850 cm^{-1} [174,176]. Moreover, absorption doublets, appearing in each adduct approximately at 1457 and at 1300 cm^{-1}, are characteristic of 3-substituted nortricyclene derivatives.[175] Norbornene derivatives, on the other hand, do not absorb in these regions at all but do so at 707 cm^{-1} (C-H deformation) and 1570 cm^{-1} (C=C stretching)[175,177].

Free radical homopolymerization and copolymerization of norbornadiene was initially disclosed in publications by Kargin, Plate and Dudnik[178] and by Kolesnikov and co-workers.[179] Kargin et al.[178] used the diene synthesis to form a polymer that was insoluble in common organic solvents, had a softening point above 350°C, and was stable to 400°C. Kolesnikov and his group[179] studied the preparation of homopolymers and copolymers of 2,5-norbornadiene with styrene, vinyl acetate, and 1,1,2-trichloro-1,3-butadiene using benzoyl peroxide and other free radical catalysts. Resins have been made from copolymers of 2,5-norbornadiene with cyclic and aliphatic olefins.[180] Several other researchers have also studied the free radical polymerization of norbornadiene. Graham, Buhle and Pappas[181] have carried an excellent

study on the transannular polymerization of a derivative of 2,5-norbornadiene, viz. 2-carboxy-bicyclo[2.2.1.]-2,5-heptadiene, as a 50 % benzene solution with azodiisobutyronitrile (AIBN) as the free radical catalyst. They obtained a polymer containing structures due both to transannular addition and reaction through only one double bond of the molecule. Similar results were obtained by Zutty[182] who carried out the homopolymerization of 2,5-norbornadiene and its co-polymerization with vinyl chloride, vinylidene chloride, acrylonitrile, ethyl acrylate, and methyl methacrylate. He also determined monomer reactivity ratios for these copolymerizations. Researchers at American Cyanamid have polymerized norbornadiene and also copolymerized it with vinyl acetate and with p-chlorostyrene using various free radical initiators.[183] The homopolymer contained both nortricyclene and norbornene units.

Coordination polymerization was first reported in an Australian patent by Dupont.[184] Sulfur-curable elastomers from alpha olefins and methyl-substituted 2,5-norbornadiene have been prepared using coordination polymerization catalysts.[185] Researchers at Dupont copolymerized ethylene with bicyclo[2.2.1]hepta-2,5-diene using $TiCl_4$ and $(iso\text{-}Bu)_3Al$ as co-catalysts.[186] The copolymer formed was such that one of the double bonds of the diene was not used up during polymerization and was available for crosslinking. The crosslinked product showed excellent elastomeric properties and yet was very tough.[186] Norbornadiene has been reported to undergo ring-opening polymerization by vanadium and titanium-based catalysts by Italian scientists in a paper on ethylene-propylene-dicycloheptadiene terpolymerization.[187] The polymer

structure has been elucidated from its ir spectrum and found to possess an appreciable level of trans-vinylene unsaturation. Extremely active polymerization catalysts are those derived from WCl_6 with or without an organo-aluminum derivative co-catalyst.[188] The polymers obtained were found to be virtually insoluble due to an extensive degree of gelation, thus prohibiting detailed structural analysis.

Norbornadiene has also been polymerized by cationic methods. M. Fefer copolymerized it with unsaturated petroleum feeds by means of Friedel-Crafts catalysts to increase the softening points of the petroleum resins.[189] Copolymerization with $C_{10}H_{16}$ terpenes with Lewis acid catalysts has also been reported.[190] Kennedy et al.[191] have made a completely nortricyclene polymer by homopolymerizing bicyclo[2.2.1]-2,5-heptadiene dissolved in C_2H_5Cl using $AlCl_3$ as catalyst at 40°C. At lower temperature (-123°C and -78°C) this polymer contained norbornene units as shown by infra-red and proton magnetic resonance spectroscopy. This work has been reviewed by Cotter and Matzner[192] and by Kennedy and Makowski.[193] The thermomechanical behavior of the polymer has also been studied.[194]

Thus, 2,5-norbornadiene has been polymerized by cationic initiation, by free radical initiation, and by Ziegler-Natta coordination catalysts. It has also been polymerized by gamma radiation. Wiley et al.[195] have reported that a white, solid homopolymer was formed on irradiation of the diene. This polymer contained both nortricyclene and norbornene units. However, the work reported is of a preliminary nature, the G-values obtained are too low and does not make a conclusive structural analysis of the polymer formed. A few experiments

had also been carried out by Martin et al.[196] It was, therefore, thought worthwhile to investigate the radiation-induced polymerization using ultra-drying techniques described earlier in this dissertation in the solid and liquid phases and to characterize the polymers formed.

B. PREPARATION

1. Monomer Sample Preparation

The monomer, bicyclo[2.2.1]-2,5-heptadiene, was distilled and the fraction boiling at 89-90°C was collected. Gas chromatographic analysis indicated better than 99.5 % purity. Samples of the monomer were prepared using the ultra-dry technique described in Chapter II of this dissertation. These samples were oxygen-free as well as free from water. No quantitative measurements were, however, carried out to determine the actual concentrations of oxygen and of water.

2. Liquid State Polymerization

The irradiated samples were weighed, cracked open, and the insides of the vials washed with a minimum amount of solvent, such as chloroform, tetrahydrofuran, or carbon tetrachloride to remove all traces of polymer after which the cracked vials were dried in air and weighed. The difference in the two weights is obviously the weight of the monomer. The polymer solution contained some unreacted monomer as shown by pmr. It was, therefore, repeatedly reprecipitated from chloroform and methanol and finally evaporated to constant weight in a vacuum dessicator and the polymer weight obtained. Precipitation in methanol has been reported to form an adduct complex $(C_7H_8)_n \cdot CH_3OH$.[14,30] However, this was not a serious problem if the samples were evacuated

more than six hours. From the amount of polymer formed from the monomer, the percent conversion and the G-value were calculated. Table XXIX shows the results of the polymerization in the liquid state at 25 ± 1°C.

TABLE XXIX

LQUID STATE RADIATION-INDUCED POLYMERIZATION OF 2,5-NORBORNADIENE AT 25°C

Sample No.	Monomer (g)	Polymer (g)	Dose Rate Mrad $hour^{-1}$	Dose Mrad	Percent Conversion	G-value
1	5.314	0.285	0.190	9.056	5.37	63.2
2	6.106	0.338	0.190	9.120	5.55	64.9
3	7.302	0.856	0.190	21.153	11.72	59.1
4	29.568	2.181	0.183	10.309	7.38	76.3
5	30.591	2.266	0.183	10.309	7.41	76.7
6	15.985	4.019	0.166	46.563	25.14	57.6

3. Solid State Polymerization

In the solid state at -78°C, however, polymerization takes place much faster, as seen from the results in table XXX. The samples of poly(2,5-norbornadiene) which were isolated invariably showed traces of monomer in them. It was necessary to repeatedly dissolve (or suspend) the irradiated samples in chloroform and precipitate the polymer with methanol. At least six redissolutions and reprecipitations were necessary to rid the polymer of any residual monomer. Proton nmr was used to check for monomer content.

TABLE XXX

SOLID STATE RADIATION-INDUCED POLYMERIZATION OF 2,5-NORBORNADIENE AT -78°C

No.	Monomer (g)	Dose Rate Mrad $hour^{-1}$	Dose Mrad	Polymer (g)	Percent Conversion	G-value
1	16.888	0.166	3.29	1.654	9.79	317
2	15.770	0.148	5.18	2.544	16.13	332
3	15.528	0.166	5.48	2.660	17.13	333
4	14.653	0.166	6.28	2.857	19.50	331
5	13.598	0.166	8.80	3.510	25.81	313
6	13.543	0.166	8.80	3.500	25.84	313
7	17.522	0.166	9.46	5.113	29.18	329

To determine if post-irradiation had anything to do with higher rates, experiments were carried out with interrupted irradiation doses. Two samples of 2,5-norbornadiene were irradiated at -78°C for 8.8 Mrads. One of these (sample no. 5 in the table) was continuously irradiated while the other (sample no. 6) was also irradiated for a total dose of 8.8 Mrads but the sample was warmed up to room temperature for intervals of six hours between each six hour irradiation period. Warming the sample to room temperature between the irradiation periods showed no effect on the total amount of polymer produced. In fact the two samples gave identical polymer yields. This experiment indicated that no polymer was produced by post-irradiation effects.

Experiments were also carried out to determine if any free

radicals were present in the frozen matrix. Electron paramagnetic resonance (EPR) spectroscopy was used for this purpose. A sample of 2,5-norbornadiene was prepared in an EPR tube and irradiated for a dose of 1 Mrad at -78°C. The choice of -78°C was determined by the polymerization temperature. The sample tube was then immediately placed in the cavity of the EPR spectrometer and the signals observed. The total intensity of the signals was very low by comparison with those in other irradiated hydrocarbons in the frozen state. Even the small signal obtained was structureless, and as such it could not be definitely attributed to any radical formed from 2,5-norbornadiene. This experiment seems to prove that no significant amounts of free radicals were present, trapped in the irradiated frozen monomer.

Another important observation in the case of the solid state polymerization was that gelation seems to occur beyond a conversion of ca. 18 %. The polymer formed would dissolve only partially in a solvent such as carbon tetrachloride or tetrahydrofuran, which dissolved the polymer prepared in the liquid state as well as that formed below a conversion of 19 %. Occurrence of gelation indicates that crosslinking of the polymer chains begins around a conversion of 18 %. This will be further discussed later in this chapter.

C. MOLECULAR WEIGHT STUDIES

The number-average molecular weights of all the polymer samples were determined by vapor pressure osmometry as described in Chapter III, section B of this dissertation. Beyond the gelation point, the polymers formed from solid-state polymerization did not dissolve

completely. The non-gel fraction was soluble in carbon tetrachloride and the molecular weights of these solutions were determined. Figure 36 shows the molecular weights obtained plotted against the radiation dose. The gel fraction was insoluble in any solvent. The almost vertical dotted line on this graph represents the roughly estimated increase in the molecular weight of the gel fraction based on its swelling. The other dotted line represents the extrapolation of the curve if no gelation had taken place.

D. CHEMICAL CHARACTERIZATION

Figure 37 shows the infra-red spectra of the poly(2,5-norbornadiene) samples prepared by solid-state (pre-gelation) and liquid state irradiations. The infra-red spectrum of the gel fraction, obtained by pelletizing the sample with anhydrous KI, is also shown in figure 37.

Figure 38 shows the proton nmr spectra of the polymer prepared at room temperature, while that of the polymer prepared by irradiation at -78°C prior to gelation is shown in figure 39. The difference in the two spectra appears to be a larger number of vinylic protons in the polymer prepared by liquid-state irradiation. This will be used to determine the nature of the repeat unit in the two cases.

Elemental analyses of the samples of unoxidized poly(2,5-norbornadiene) gave carbon and hydrogen weight percentages of 91.17 and 8.69 % respectively which are very close to the theoretical values calculated from a repeat structure of $\dagger C_7H_8\dagger$ of 91.24 and 8.76 %.

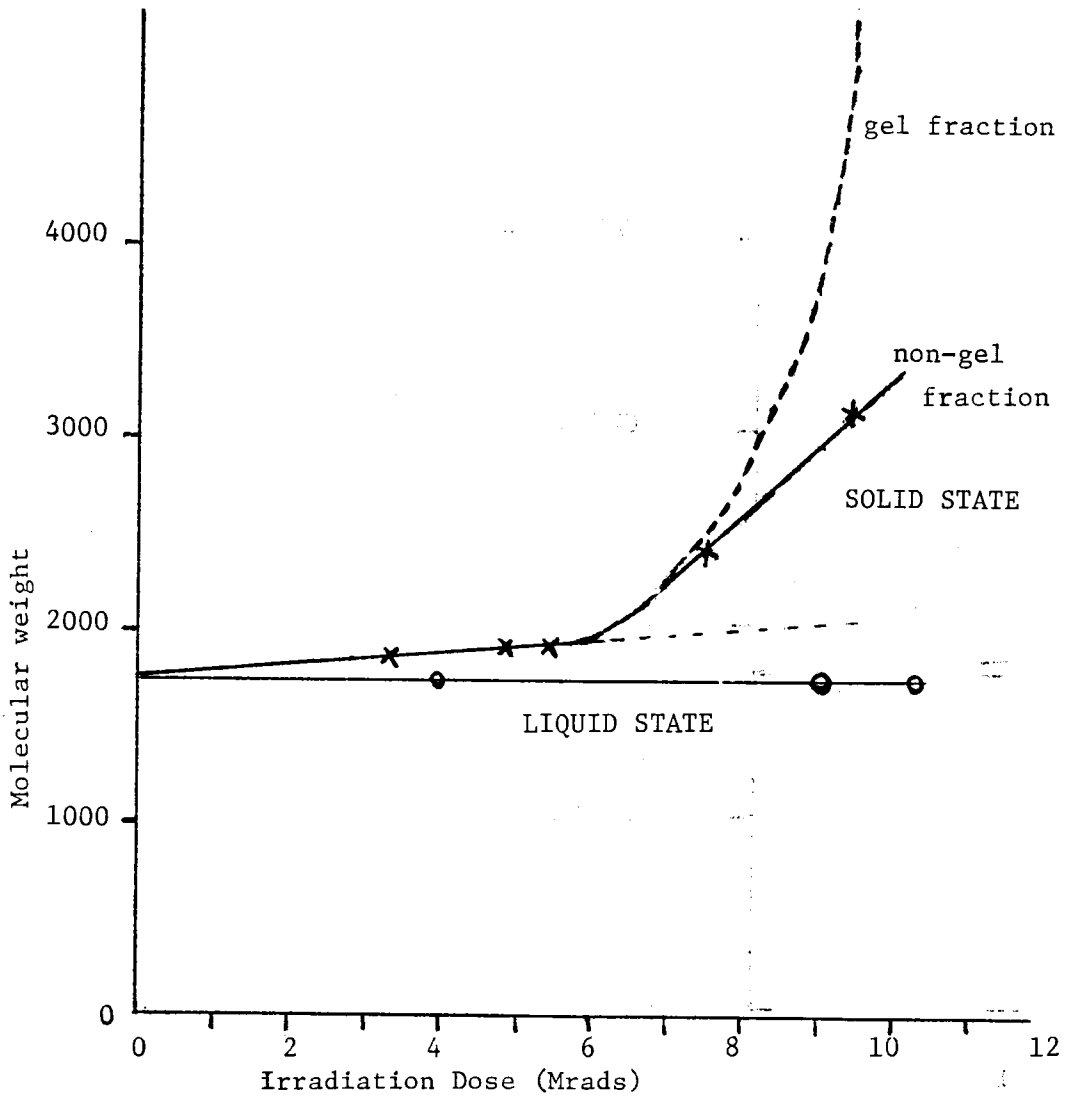


Figure 36. Plot of molecular weights against irradiation dose for poly(2,5-norbornadiene) samples.

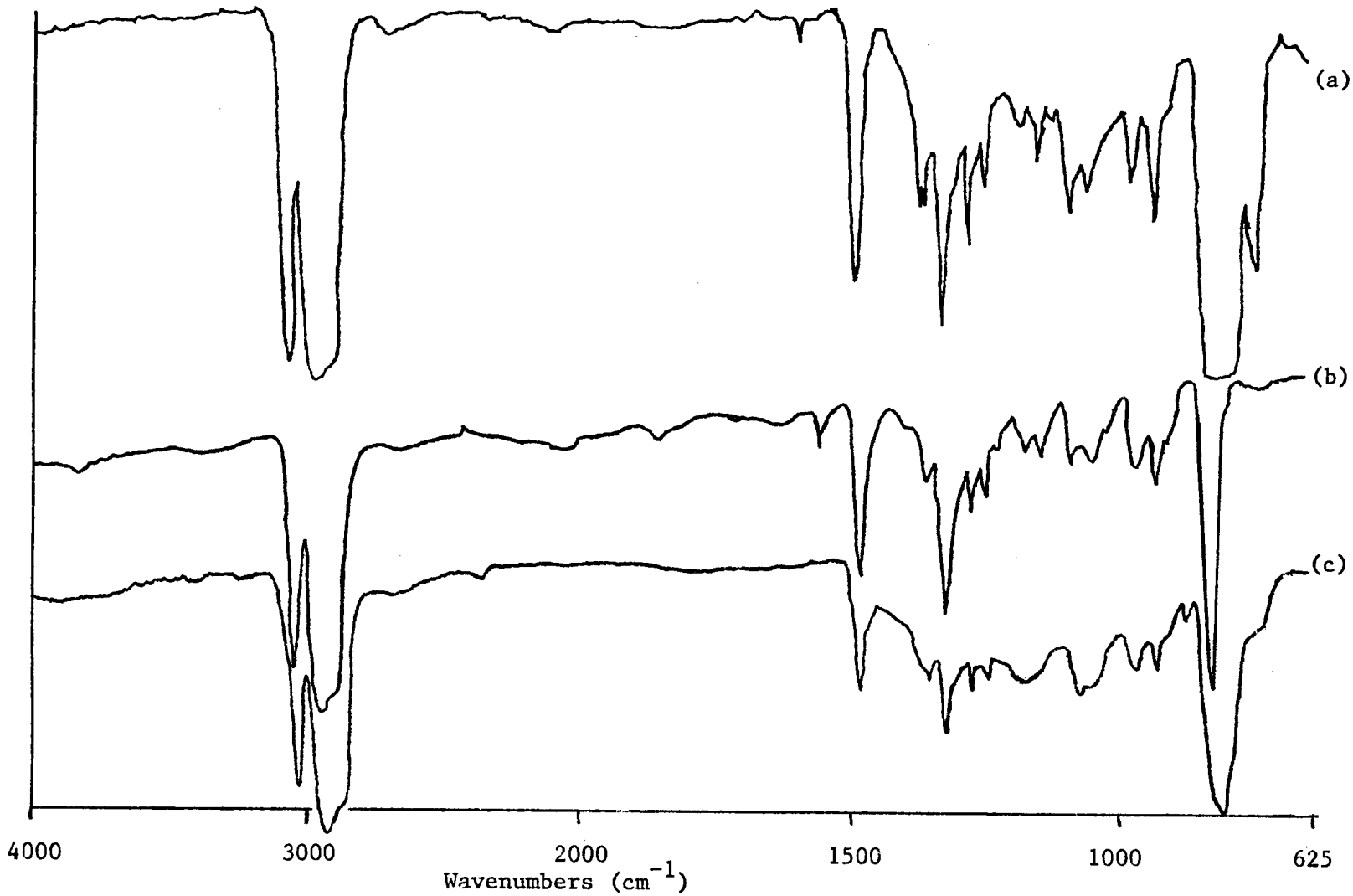


Figure 37. Infra-red spectra of poly(2,5-norbornadiene) prepared by (a) polymerization in the liquid state at ca. 25°C, (b) polymerization in the solid state at -78°C: pregelation, and (c) polymerization in the solid state at -78°C: insoluble gel fraction.

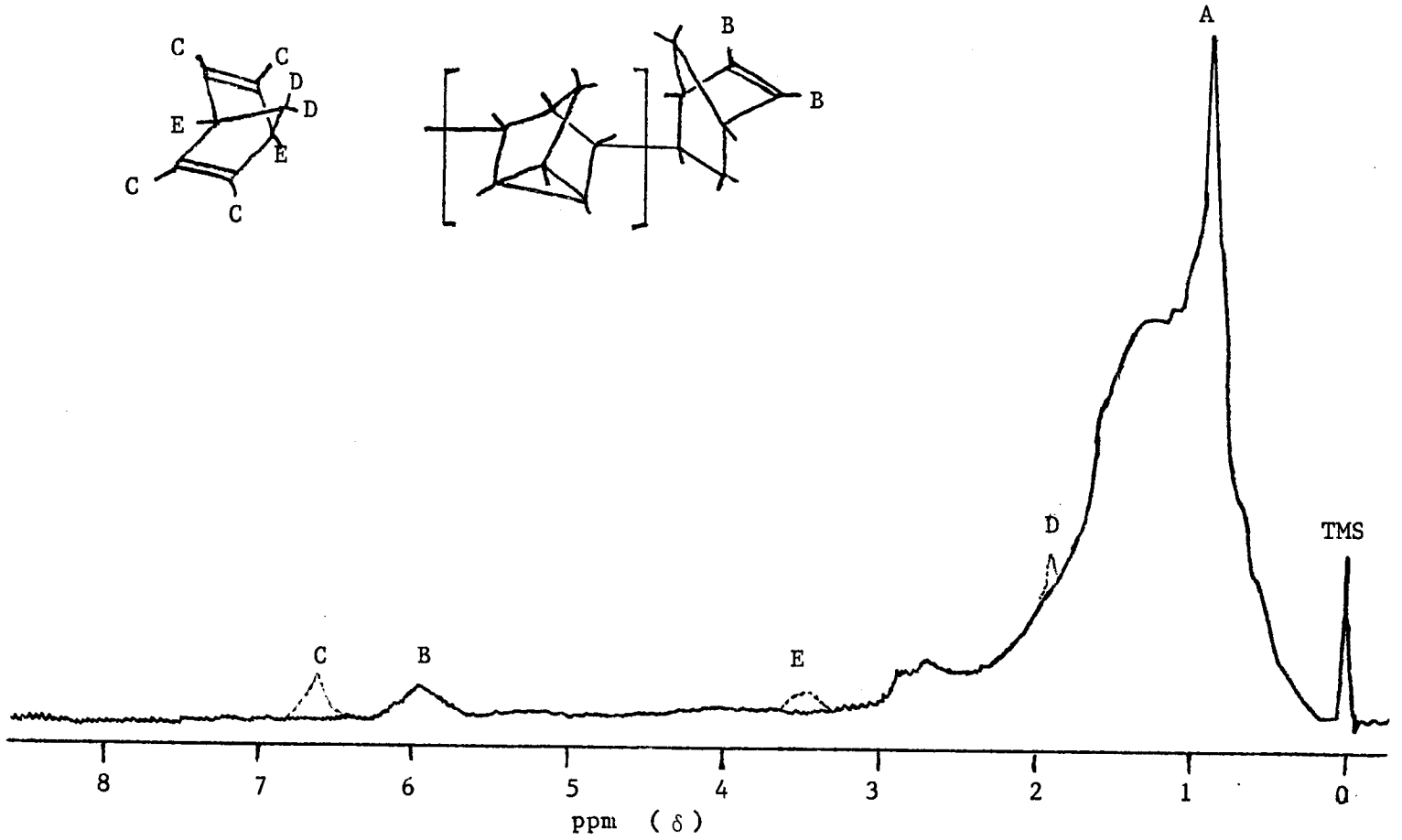


Figure 38. Proton nmr spectra of poly(2,5-norbornadiene) prepared by irradiation in the liquid state at 25°C. The dotted curve shows the polymer still containing some monomer.

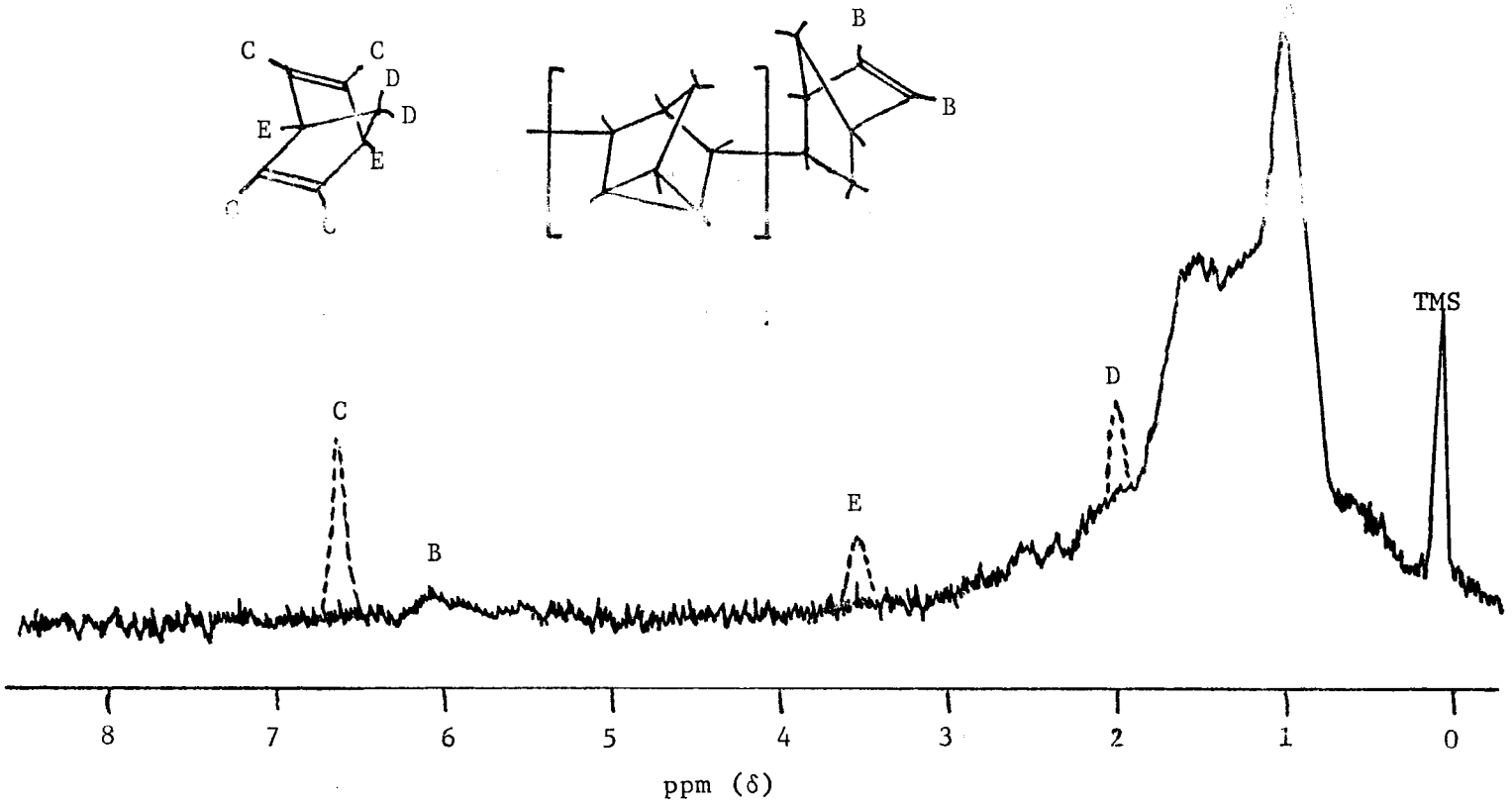


Figure 39. Proton nmr spectrum of poly(2,5-norbornadiene) sample prepared by irradiation at -78°C prior to gelation. The dotted line indicates the presence of some monomer in the unpurified sample.

C. MORPHOLOGICAL STUDIES

The polymer samples prepared by irradiation in the liquid state were not birefringent since no light passed through the crossed polarizers. One of the samples, which had been in the solid state for a total of 8.8 Mrads, allowed some light to pass through it. However this was found to be due to unevenness of the sample in the microscopic slide.

Figure 40 shows the typical X-ray diffractometer scans of poly(2,5-norbornadiene) samples prepared by (a) irradiation at about room temperature in the liquid state, and (b) solid-state irradiation at -78°C. The scans do not show any crystalline peak.

F. OTHER PROPERTIES

The samples of poly(2,5-norbornadiene) whether prepared by irradiation in the liquid or the solid state were very sensitive to atmospheric oxygen. The changes in the structure of the former polymer due to auto-oxidation were followed by infra-red spectroscopy. Figure 41 shows the infra-red spectrum of the unoxidized liquid state-prepared polymer as well as those of the same polymer auto-oxidized in the presence of room light after one week and ten weeks.

The solubility characteristics of the polynorbornadiene samples were studied. The poly(2,5-norbornadiene) samples, prepared by irradiation at room temperature, as well as those which were prepared by irradiation at -78°C prior to the occurrence of gelation, dissolved easily in several common organic solvents such as carbon tetrachloride (δ = 8.6), o-xylene (8.8), toluene (8.9), tetrahydrofuran (9.1),

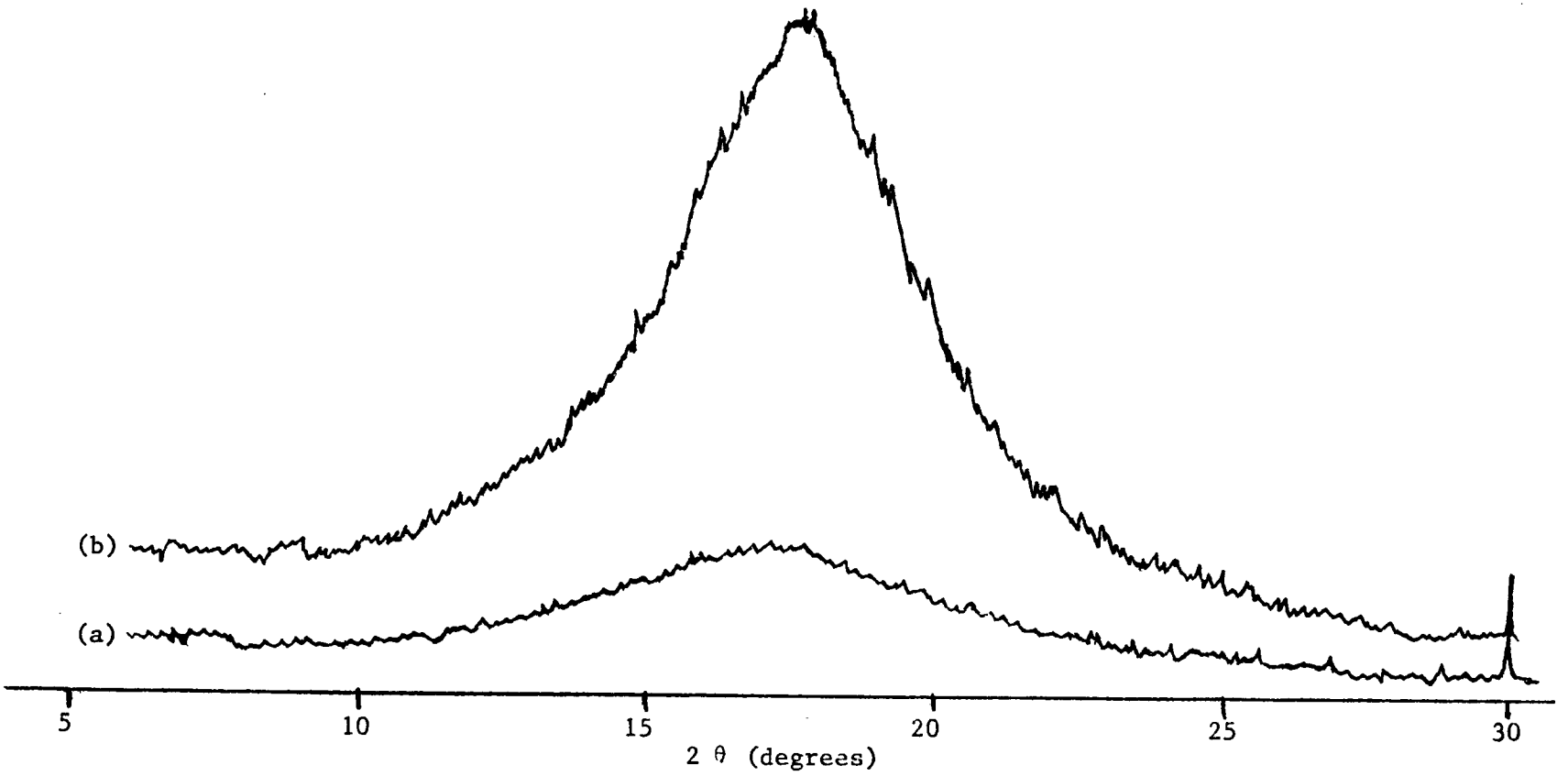


Figure 40. X-ray diffractometer scan of poly(2,5-norbornadiene) samples (a) prepared by irradiation in the liquid state at 25 °C, and (b) prepared by irradiation in the solid state at -78°C.

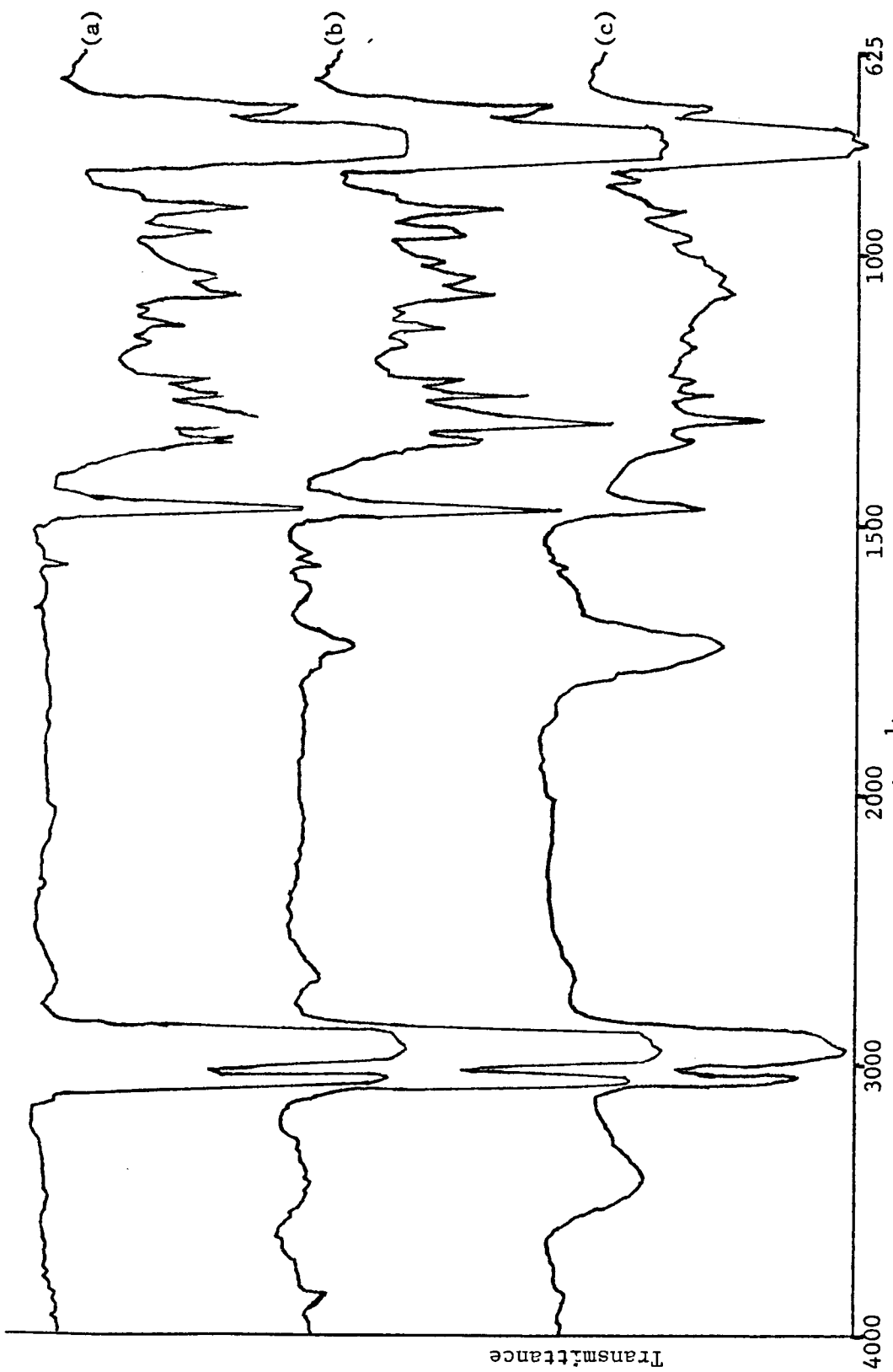


Figure 41. Infra-red spectra of poly(2,5-norbornadiene) prepared by irradiation at 25°C: effect of auto-oxidization. (a) unoxidized, (b) auto-oxidized in one week. and (c) in ten weeks.

benzene (9.2), trichloroethylene (9.2), chloroform (9.3), tetrachloroethylene (9.3), pentachloroethane (9.4), chlorobenzene (9.5), methylene chloride (9.7) and bromobenzene (9.9). However the polymer that had gelled did not dissolve completely in any solvent but showed limited swelling characteristics at elevated temperatures typical to a cross-linked polymer.[197] The fraction that did dissolve showed solubility behavior almost similar to the polymer prepared by liquid state irradiation.

The thermal properties of poly(2,5-norbornadiene) were studied by hot-stage microscopy. There was no change in the sample until ca. 220°C. At this point the polymer started turning yellow. It started flowing around 240°C. Beyond this temperature there was no physical change observed except for a steady darkening of the color from yellow to orange, red, brown and finally black. The polymer turned black at ca. 450°C.

G. DISCUSSION

1. Polymerization

Figure 42 shows the effect of increasing the irradiation dose on the percent conversion of 2,5-norbornadiene to polymer for the liquid and the solid state irradiations. In the liquid state polymerizations (at 25 ± 1°C), the percent conversion is linear with the dose even up to 46.56 Mrads with G-values ranging from 57 to 77. These values are slightly higher than Martin's unpublished data[196] (G-value were 44, 49 and 67 for his three samples) and very much higher than Wiley's data[195] (G ca. 15) in spite of the fact that all three sets of data

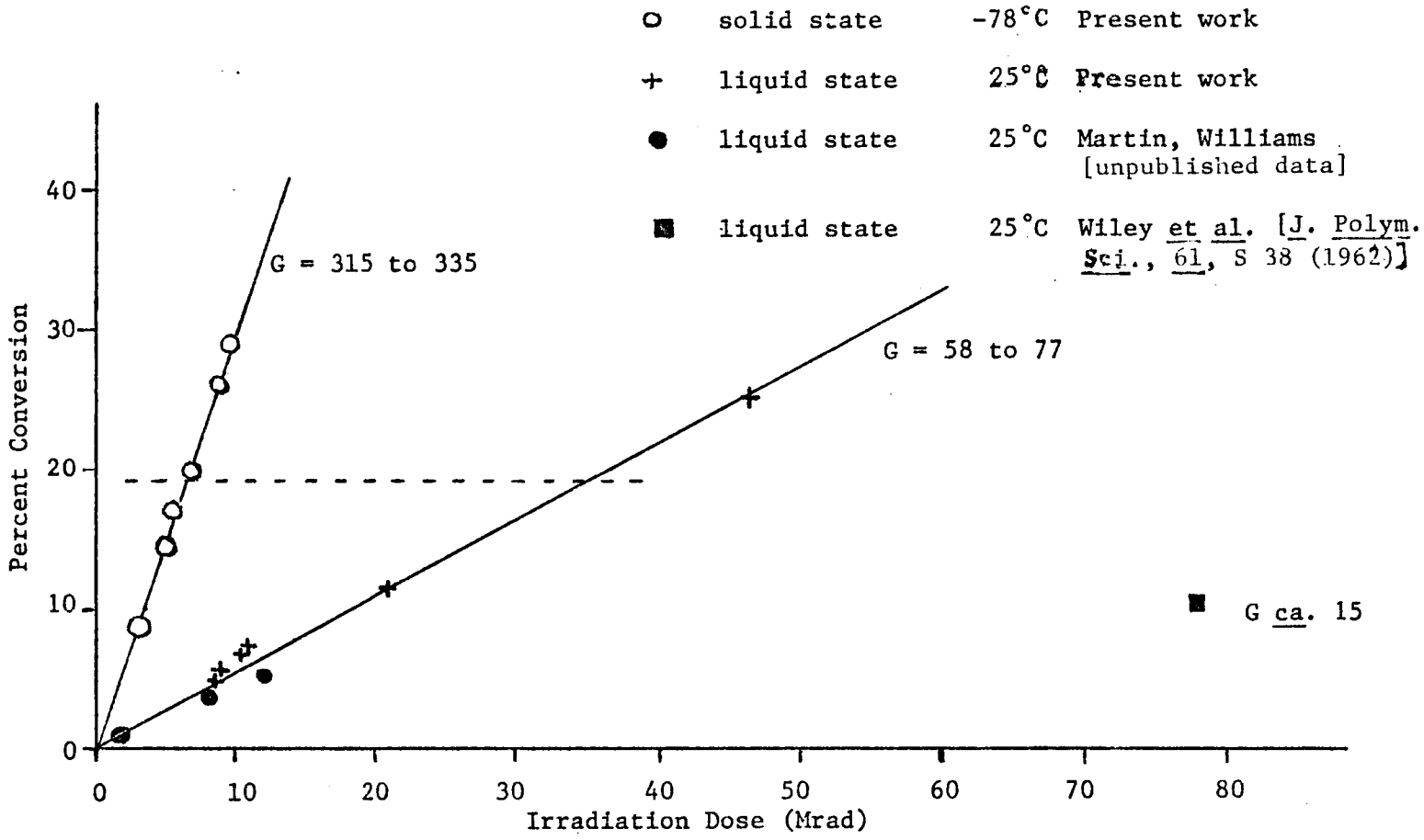


Figure 42. Plot of percent conversion of 2,5-norbornadiene against irradiation dose. The dotted line indicates the start of gelation in the case of the irradiation at -78°C.

are in the same dose rate and temperature range. It is likely that the low values obtained by Wiley et al. are due to impurities in their system. If this polymerization occurs via free radical intermediates, it is possible that some impurities might have been present. However, this is unlikely as these authors have reported distillation of their monomer prior to irradiation. On the other hand, if the polymerization of 2,5-norbornadiene occurs by a cationic mechanism, the lower values obtained by these workers could be easily explained by the effect of small quantities of water, since their paper[195] does not mention any special drying procedures. The retarding/inhibiting effect of water in very low concentrations on the radiation-induced cationic polymerization of olefins has been dealt with in considerable detail in Chapters I and II. The catalytic polymerizations of 2,5-norbornadiene described in section A of this chapter are known to occur by both free radical propagation, using initiators such as benzoyl peroxide and azobis-isobutyronitrile, and by cationic propagation with Lewis acid catalysts. Hence it is reasonable to suggest propagation by a cationic species. No experiments were carried out to determine the mechanism of radiation-induced polymerization of 2,5-norbornadiene. However, a cationic mechanism is supported by the correlation of the repeat unit structures of the poly(2,5-norbornadiene) samples prepared by irradiation in this work with those prepared by these catalytic methods. The nature of the repeat unit obtained is dealt with later in this discussion.

One of the reasons for the low G-values obtained as compared to other monomers such as styrene, isobutylene, methyl methacrylate, and β-pinene might lie in the structural characteristics of

2,5-norbornadiene. The two double bonds are part of a bicyclic ring system and are expected to be therefore less reactive than the double bond in a more reactive monomer like β-pinene, which has exo double bonds. Also the two double bonds in norbornadiene are almost close enough to one another for some conjugation. This is usually refered to as a transannular conjugation.[99,191] The distance between the carbon atoms 2 and 6 and between those at the 3 and 5 position is reported to be 2.37 Å, which is close to the length of a single bond.[198] This transannular conjugation might account for the sluggish reactivity of this monomer. Other conjugated dienes are also less reactive. Butadiene and isoprene give very low G-values as shown by Burlant and Green[41] and by Anderson.[44] However, cyclopentadiene which has conjugated double bonds is very reactive.[59]

The two straight line plots obtained for the liquid state and solid state irradiations respectively are indicative of the difference in the rates of polymerization in the two phases. The G-values for the solid state polymerizations are at least four to five times higher than those obtained for the corresponding polymerizations in the liquid state. This could be attributed either to differing propagation mechanisms, to post-irradiation polymerization in the solid-state irradiations, or to lower rates of termination in the solid phase. The epr experiment to determine if any free radicals were trapped after irradiation at -78°C indicated that very few such radicals could be detected. This probably rules out the possibility of post-irradiation propagation in the case of solid state polymerization by trapped free

radicals. The third explanation for the increased rate namely, the reduction in the rate of termination in the frozen system appears more attractive than the other possibilities.

The formation of a polymer by solid state polymerization of 2,5-norbornadiene is a novel development. This monomer had not been polymerized in the solid state by radiation or by any other method. Other monomers such as trioxane, acrylamide, methyl acrylate, and hexamethyl cyclotrisiloxane have been polymerized in the solid state by gamma radiation, u.v. irradiation, and catalyst systems. Several reviews of this field of solid state polymerization have been published.[199]

The molecular weight dependence on the irradiation dose for poly-(norborbornadiene) has been shown in figure 36 (p 184). The molecular weight of the polymer prepared by irradiation in the liquid state was independent of the dose and was soluble in several solvents even at room temperature. On the other hand, the polymer samples prepared by irradiation at dry ice temperature were completely soluble only up to a percent conversion of about 19 % corresponding to an irradiation dose of ca. 7 Mrads. The molecular weight of the polymer produced by irradiation at -78°C increased slightly with dose, being linear up to ca. 6 Mrads. Beyond the limit of 7 Mrads, the polymer obtained was only partially soluble. The soluble fraction showed a much faster increase in its molecular weight as the irradiation was continued, indicating that beyond the limit of 19 % conversion, some chain extension and possibly crosslinking also takes place. The insoluble gelled fraction is obviously sufficiently crosslinked to undergo only

swelling in solvents that dissolve the polymer prepared at lower doses. An explanation for the occurrence of crosslinking for the solid-state polymerization of 2,5-norbornadiene will be offered later in this discussion.

2. Nature of the Repeat Unit

Elemental analysis showed that the repeat unit consisted of $\{C_7H_8\}$. The monomer structure contains two double bonds. If one of these double bonds reacts, a norbornene unit is produced and if both double bonds react, a nortricyclene unit is produced as mentioned earlier in this chapter. Figure 43 shows the mechanistic pathways to the formation of these units. For catalyst systems it has been shown that Lewis acid initiation leads to the formation of the nortricyclene unit via the Wagner-Meerwein rearrangement of the non-classical carbocation,[191] while the Ziegler-Natta initiators give the norbornene repeat unit almost exclusively, probably due to the ability of the catalyst to be attached to the double bond as a complex, thus preventing interaction with the other double bond.[187] Free radical initiation with benzoyl peroxide, however, gives a polymer containing both repeat units.[182,183] Since the radiation-prepared polymer contains the same nortricyclene units without significant numbers of the norbornene unit as those in the polymer prepared with Lewis acids, this suggests that the radiation polymerization occurs predominantly by a cationic mechanism.

Wiley et al.[195] have reported that the poly(2,5-norbornadiene), prepared by radiation-induced polymerization at room temperature, contained some units of norbornadiene and of norbornene besides the

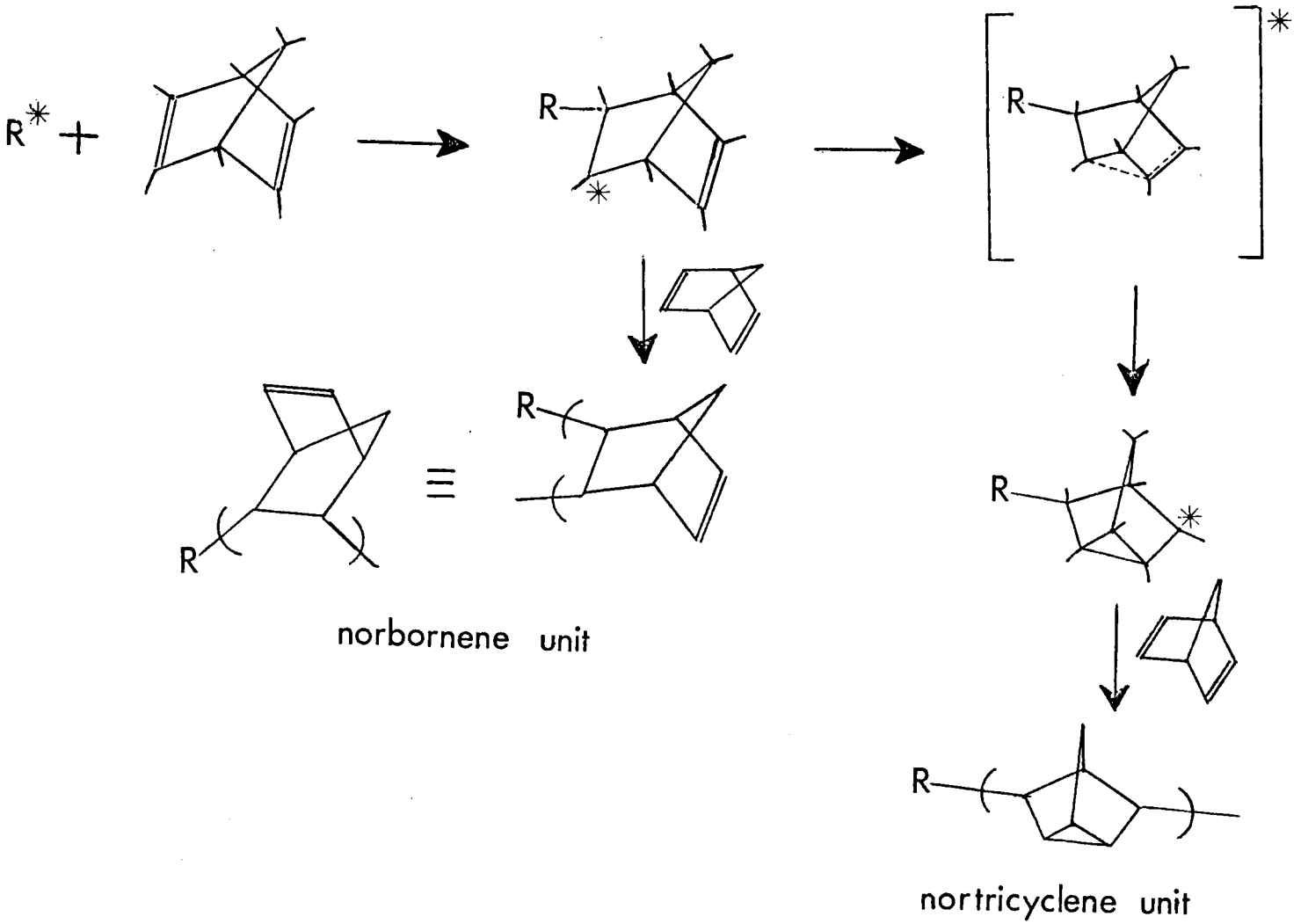
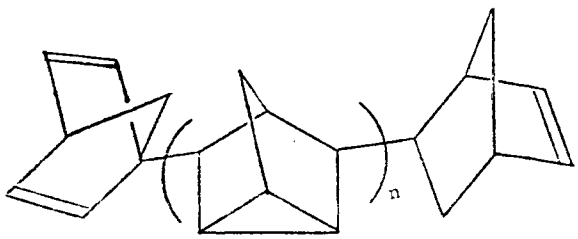


Figure 43. Mechanistic pathways to the formation of a norbornene unit and of a nortricyclene unit.

nortricyclene units, on the basis of their proton magnetic resonance spectra. Consequently they argued that the polymer chain consists of one norbornene unit and one norbornadiene unit as the two end-groups as shown below:



Similar conclusions could have been drawn by the author from his proton nmr spectra of the impure poly(2,5-norbornadiene) samples, which contained some unreacted monomer. This monomer was removed only after repeated reprecipations. The peak obtained by Wiley et al.[195] at about 6 ppm (δ), which they attribute to the norbornadiene unit in the end group, was also observed by the author in the spectra of these impure samples but was absent in the purified samples. In fact, the other peaks due to the presence of the monomer at ca. 3.5 ppm and ca. 2.0 ppm were also observed by Wiley et al. in their spectra. From the spectra of the polymers prepared in the liquid and the solid states and shown in figures 38 (p 186) and 39 (p 187) respectively it is clear that there are no peaks corresponding to any norbornadiene units.

The presence of norbornene units is seen in both these spectra, the peak at about 6.0 ppm being assignable to the norbornene unit. A cursory observation of this peak might lead one to conclude that a small number of norbornene units were present in the polymer along with the nortricylene units, which are more predominant. However,

quantitative analysis of these peaks in the spectra of the liquid-state polymer showed that the ratio of the area of the peaks in the region 0 to 3.3 ppm (δ) to that in the region around 6.0 ppm was ca. 110 : 1.4, which corresponds to a degree of polymerization of 20, if we assume that one end group of each polymer chain is a norbornene unit. The degree of polymerization calculated in this manner agress very well with that calculated from molecular weight measurements by vapor pressure osmometry. This implies that all the norbornene units, present in the polymer prepared by liquid-state irradiation, are due to each polymer chain containing only one end group. Similarly, for the polymer prepared by solid-state irradiation, the corresponding spectral area ratio is 130 : 1. A degree of polymerization of ca. 30 can be calculated from this ratio. This $\overline{DP}_n$ value is very close to that obtained from vapor pressure osmometry measurements. The other end-group is probably a hydrogen atom, which is reasonable from general radiation chemistry considerations. Once again, it can be concluded that all the norbornene units present in the polymer prepared by irradiation at -78°C are present only as the end-groups of the macromolecular chain.

Figure 37 (p 185) shows the infra-red spectra of (a) the polymer prepared by irradiation at room temperature, (b) the polymer prepared by irradiation of 2,5-norbornadiene at -78°C, before the gelation starts taking place, and (c) the insoluble fraction of the gelled polymer prepared by solid-state irradiation. The absence of significant amounts of norbornene units in the polymer beyond that expected from one end group per polymer chain supports the conclusion drawn earlier from nmr spectroscopy that the polymerization is exclusively transannular,

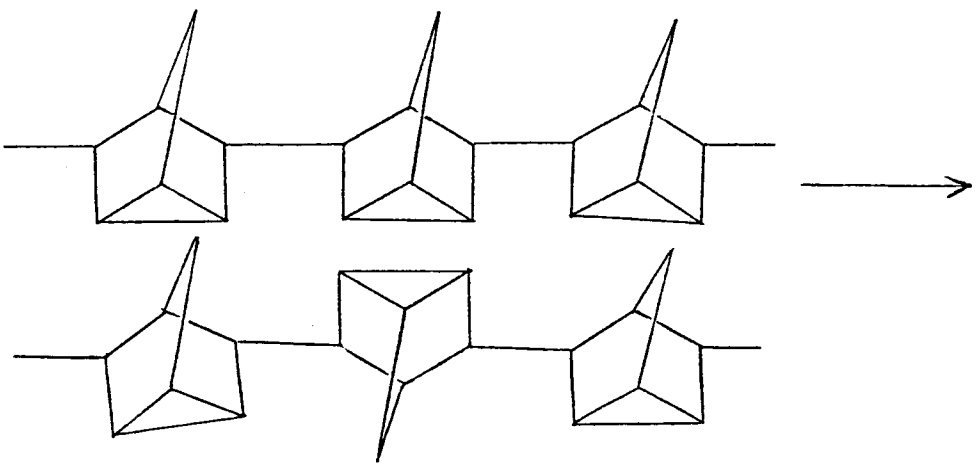
both in the liquid and in the solid states. As mentioned in the introduction to this chapter, the characteristic absorptions of the norbornene and the nortricyclene units are at ca. 710 cm^{-1} and at ca. 810 cm^{-1} respectively seen in the infra-red spectra of 5-methyl-2-norbornene[200] and nortricyclene[175] respectively. Since no double bonds are present in the repeat unit, crosslinking probably occurs by intermolecular reactions via the opening of the cyclopropane ring. Such reactions have been shown to occur slowly in the presence of $AlBr_3$.[201]

3. Morphological Considerations

None of the X-ray diffractometry scans showed a crystalline peak. The slight pointedness of the amorphous peak shown in curve (b) of figure 40 (p 189) was due to running the scan at lower ranges. At the same ranges for pelletized samples of the same thickness, the scans were almost identical. Hence no crystallinity is present even in the polymers prepared by solid-state irradiation.

Solid state polymerization is interesting because of the possibility of the formation of a crystalline polymer by a topochemical reaction. In such a reaction the reactivity of the monomer, the manner of growth of the polymer chain and its stereochemical and other properties are determined by the geometry of the crystal lattice of the monomer. Okamura et al.[202] were able to show that in the radiation-induced solid state polymerization of trioxane, β-propiolactone, diketene, and other heterocyclic monomers, there is a close identity between the lattices of the monomer and the polymer. This allows the crystalline monomer to transform easily to the crystalline polymer.

Morawetz and his group[203] demonstrated a chain growth controlled by the monomer lattice for vinyl compounds such as acylated p-amino-styrene and salts of acrylic acid. However it does not naturally follow that solid-state polymerization always results in the formation of a crystalline polymer if the monomer is crystalline at the temperature of the reaction. Even if the topochemical polymerization takes place in the case of 2,5-norbornadiene, warming the irradiated sample, containing the polymer with regular repeat units and the unreacted monomer, to room temperature causes the mixture to melt. There is sufficient rotation about the single bond connecting two adjacent nortricyclene units so that the regular structure could undergo a flipping of some of its units as shown below



This flipping probably causes disruption of the chain regularity.

4. Other Properties

The solubility characteristics of the polymers ties in closely

with the nature of the repeat units in the polymer, the crosslinking possibility, and morphological considerations which have been dealt with earlier in this discussion.

The thermal properties indicate the formation of aromatic or at least conjugated double bonds, giving rise to a colored appearance even in the absence of oxygen. The mechanisms for these reactions are not known. One can speculate that the strained cyclopropane ring opens at high temperature and then the cyclohexene, cyclohexadiene, and finally phenylic groups are formed.

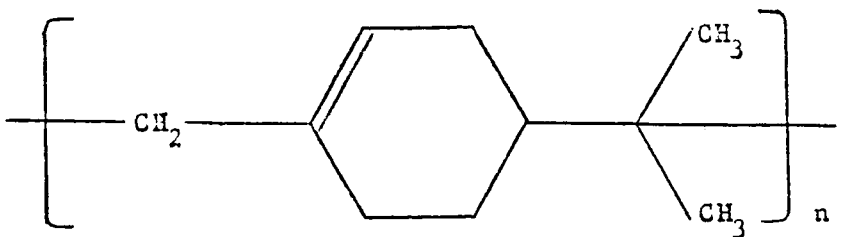
The auto-oxidized samples showed infra-red absorptions due to peroxide and ketone groups which were not further identified.

CHAPTER VII

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

A. CONCLUSIONS

The results of this work support the contention of previous workers[52,53,126] that the radiation-induced polymerization of β-pinene under super-dry conditions is cationic in nature. The homopolymer was formed with G-values of ca. 1000. About half of this polymer was partly insoluble in the monomer and precipitated from the irradiated β-pinene. The chemical characterization showed that the repeat unit had the structure



(I)

The poly(β-pinene) is believed to be stereoregular. The polymer was found to be highly crystalline by X-ray diffraction and birefrigence techniques. Crystallinity indices were determined for several fractionated samples and it was concluded that the unit cell is probably monoclinic or triclinic. Further morphological characterization to define the unit cell was not feasible since the polymer samples could not be oriented by the several techniques tried. Thermal characterization techniques showed a crystalline melting point of 206-208°C. Solubility characteristics showed that the polymer was completely soluble only above 80°C in a few solvents. The insoluble fractions were found

to be sensitive to auto-oxidation in the presence of light in the region 230-280 nm. The formation in the auto-oxidized polymer of peroxy and ketonic groups, the latter conjugated to the double bond in the repeat unit, suggests a mechanism involving allylic radicals as intermediates.

The characteristics of the poly(β-pinene) prepared by radiation-induced polymerization were compared with those of the Polyterpene Resin prepared commercially by Lewis acid catalysis. The latter polymer showed the presence of some methyl groups causing infra-red absorption as a singlet at 1375 cm^{-1}. Some terminal methylene groups were also present in the commercial polymer. The presence of these groups in this polymer has been attributed to the presence of a small number of repeat units, isomeric to the β-pinene repeat unit shown above, in its macromolecular chain. The majority of the repeat units had the same repeat unit structure as those in the radiation-prepared poly(β-pinene). The presence of a sufficient number of isomeric units in the polymer chain of the commercial resin would cause disruption of its stereo-regularity, thus preventing crystallization. This would explain the fact that the polymer prepared by Lewis acid catalysis is amorphous. This polymer is soluble in several solvents, even at room temperature. It showed a glass transition at about 125°C and melted at ca. 170°C.

Crystalline poly(β-pinene) was also prepared by thermal polymerization at 160°C. This polymer had the same chemical repeat unit and crystal structure as that of the polymer prepared by gamma irradiation. However, the widths of the crystalline peaks in the diffractometer scans were different in the two cases, indicating that the polymer

formed by irradiation contained larger crystallites than those in the polymer formed by thermal initiation. The effect of additives on the thermal polymerization of β-pinene indicated free radical propagation. Free radicals in the form of biradicals are probably formed by pyrolysis of β-pinene with the opening of the cyclobutane ring.

The radiation-induced copolymerization of β-pinene with styrene and with α-methyl styrene results in the formation of copolymers which are probably random. The molecular weights were ca. 3000, very close to those obtained for poly(β-pinene). These copolymerizations are believed to occur by cationic propagation. The low molecular weights relative to those of polystyrene and of poly(α-methyl styrene) is attributed to chain transfer reactions, especially to the less reactive β-pinene monomer.

The radiation-induced polymerization of 2,5-norbornadiene occurs four to five times faster in the solid state at -78°C than in the liquid state at ca. 25°C. The increase in the rate is probably due to lower termination rates in the frozen state. In both cases the propagation is probably cationic and results in a nortricyclene repeat unit. At doses above 6 Mrads and conversions greater than 18 %, the solid-state polymerizations resulted in gelation. This is attributed to crosslinking reactions. The polymer is amorphous, even in the case of the samples prepared by the irradiation of the crystalline monomer of -78°C.

B. SUGGESTIONS FOR FURTHER WORK

Further work is needed to clarify the mechanism of auto-oxidation

of poly(β-pinene). Experiments could be carried out to study hydrogenation, ozonolysis, and other reactions of this polymer, especially of the crystalline poly(β-pinene) prepared by irradiation. Since the poly(β-pinene) prepared by Lewis acid catalysis exhibits excellent adhesive properties,[111] it would be interesting to determine the adhesive characteristics of the radiation-prepared polymer in view of its crystallinity.

Chemical characterization of the poly(2,5-norbornadiene) prepared by gamma irradiation showed that it contained the same repeat unit as that in polymers obtained by cationic initiators such as Lewis acids. This, along with higher polymerization rates obtained using super-dry techniques than those obtained without special drying,[195] indicated the possibility of cationic propagation. Experiments using additives might help to establish the mechanism of the radiation-induced polymerization of 2,5-norbornadiene in the liquid state.

The molecular-weight distributions of all the polymers described in this dissertation could be carried out by gel-permeation chromagraphy. Thermo-gravimetric analysis would provide information about the thermal and oxidative degradation of these polymers.

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VITA

Ashok Mohan Adur was born in Bombay, India on January 3, 1950. He attended elementary and high schools in Bombay, Bhubaneshwar, and Pasighat. He was graduated from St. Andrew's High School, Bandra, Bombay in June 1964 with First Class. He attended Jai Hind College for the following year and then transferred to Parle College, both affiliated to the University of Bombay. He was the recipient of College Merit Scholarships for the years 1965-68. He was also awarded the V. G. Sathaye Prize in 1966-67. In November 1968 he graduated with First Class Honors at the top of his class with Chemistry and Physics as principal and subsidiary subjects.

He was selected as a Officer Trainee of the Bhabha Atomic Research Center and at its training school he took courses in Advanced Chemistry and Nuclear Science. After completion of training, he joined the Isotope Division of the Bhabha Atomic Research Center as a Scientific Officer on September 1, 1969. He carried out research and development in the areas of polymer science and applied radiation chemistry and was involved in the preparation, testing, and market development of polymer composites of wood, concrete, bamboo, and other materials. For three of the five years, he also acted as the group leader of the Radiation Processing Group. Simultaneously he worked towards an academic degree. For his thesis entitled "Physico-chemical Investigations on the Radiation Processing of Some Polymeric Composites," he was awarded the Master of Science (by Research) degree by the University of Bombay, Bombay in November 1974. Based on his work at the research

center, he has several publications to his credit. He is also listed as a co-inventor of a patent.

In September 1974, he began graduate work in chemistry, with a polymer science option, at the University of Tennessee and accepted a teaching assistantship from the Department of Chemistry. As a graduate student, he served as President of the India Association at UTK, Vice-President of the International Club, Vice-chairperson of the International Student Council, the representative of the Chemistry Department to the Graduate Student Council, and Secretary of the Graduate Student Council. He was also a member of the Circle K and the Gamma Beta Phi Society. He has presented a paper based on part of his doctoral research at the 12th Mid-Atlantic Regional Meeting of the American Chemical Society held in April 1978. He has also attended the 176th National Meeting of the American Chemical Society held in September 1978.

He will receive his Ph.D. degree in polymer chemistry in June, 1979. He will join the Research and Development Department of Chemplex Co., Rolling Meadows, Illinois as a Research Scientist. He is a member of the American Chemical Society, the Polymer Chemistry Division, and the Society of Plastic Engineers.