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I am submitting herewith a thesis written by James A. Aikins entitled "Preparation and Characterization of Polymers Formed by Gamma Irradiation of (+)-Limonene Oxide, α -Pinene Oxide and β -Pinene Oxide." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemistry.

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PREPARATION AND CHARACTERIZATION OF POLYMERS FORMED BY
GAMMA IRRADIATION OF (+)-LIMONENE OXIDE,
 α -PINENE OXIDE AND β -PINENE OXIDE

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Degree
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ABSTRACT

Using cobalt-60 gamma rays, the radiation-induced cationic polymerization (in bulk) of α -pinene oxide, β -pinene oxide and (+)-limonene oxide has been studied at room temperature. Typical conversions of monomer to polymer of the order of 40.0%, 5.3% and 7.8% per Mrad were recorded for (+)-limonene oxide, α -pinene oxide and β -pinene oxide respectively for the polymers obtained at 25°C. The number average molecular weight ($\overline{M}_n$) determined by vapor pressure osmometry (for monomers irradiated at 25°C) indicated the average degree of polymerization ($\overline{DP}_n$) of (+)-limonene oxide, α -pinene oxide and β -pinene oxide to be 12.4, 5.8 and 4.0.

Structural analysis with nuclear magnetic resonance (proton and carbon-13) and infra-red (I.R.) spectroscopy showed that upon the opening of the epoxide ring, the bicyclic bridge structure (cyclobutane ring) in α -pinene and β -pinene oxides undergoes a rearrangement during the propagation sequence. There was little or no polymerization through the isopropenyl pendant group of (+)-limonene oxide. The polymerizations of (+)-limonene and β -pinene oxides were strongly retarded by tripropylamine (a known cationic scavenger). Evidence from end groups for proton transfer was found in all three polymerizations. In addition, kinetic evidence for the dependence of the molecular weights on chain transfer was also obtained. Thermal analysis using Differential Scanning Calorimetry (D.S.C.) showed that these polymers have a softening range between 65°C and 85°C.

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CHAPTER I

INTRODUCTION

A. POLYMERS AND RING-OPENING POLYMERIZATION

Polymers are large molecules made up of small basic units called monomers, which are covalently bonded together. The process by which these large molecules are formed is called polymerization. The latter is divided into two categories: step and chain polymerization.

Step polymerization involves the stepwise reaction between bifunctional groups (e.g., a diacid and a diol) with the production of dimers, trimers, tetramers, etc. as the reaction proceeds until full-sized polymer molecules are formed. Chain polymerization entails the formation of full-sized polymer molecules by successive addition of monomer units to a reactive propagating species (ionic or free radical). The two polymerization processes differ basically in terms of the distribution of mers present during polymerization. High polymer is produced in chain polymerization even for very low monomer conversions whereas polymer is only achieved in step polymerization when most of the monomer has reacted.¹ In this thesis, ring-opening polymerization is considered to occur by a chain mechanism.

There are four major steps involved in epoxide ring opening polymerization: initiation, propagation, transfer and termination. Initiation involves the attack of an active (cationic) species on a

monomer heteroatom, oxygen, to form an oxonium ion. Propagation involves an S_N2 type of attack by a monomer heteroatom on the alpha carbon of the active oxonium ion, which subsequently opens up with the formation of a new active oxonium ion species. This process is repeated over with the formation of high molecular weight species until the active species is quenched. In ring-opening polymerization, termination is by recombination with the counterion or impurities. All these reactions can be summarized as follows:

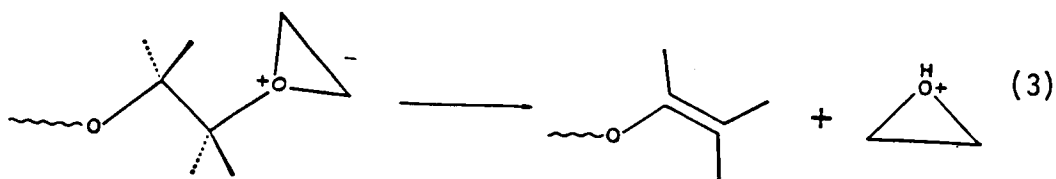
Initiation:



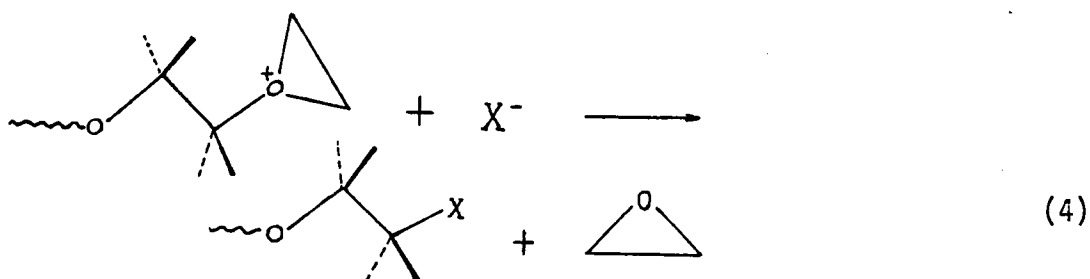
Propagation:



Transfer:



Termination:



One of the major problems associated with epoxide and other ring opening polymerization is backbiting. This comes about as a result of heteroatoms within the main polymer chain which are capable of attacking the alpha carbon of the active species. Thus, the possibility of cyclic products should not be ruled out, especially if a more stable cyclic product could be formed. This process of degradation of polymer structures leads to macrocyclic polymers or cyclic oligomers, and it is unique to three membered heterocyclics.

Epoxide ring-opening polymerization can only be achieved when the appropriate thermodynamic and kinetic conditions are favorable. Thermodynamically, a negative free energy (ΔG) of polymerization is a prerequisite if polymerization is to occur. Hence the unfavorable negative entropic ($T\Delta S$) phenomenon associated with polymerization must be overcome by a large negative enthalpy (ΔH) of polymerization. The negative enthalpy is guaranteed by the release of strain energy in the cyclic monomer, which involves the angle strain, conformational or torsional strain, and transannular strain.²

B. GAMMA RADIATION

The dual nature of nuclear radiation has been very well established. Radiation can be particulate or non-particulate; electrons, neutrons, deuterons, alpha particles and fission fragments are examples of particulate radiation while electromagnetic waves, from radio waves to cosmic rays, are non-particulate. Gamma rays fall under the heading of non-particulate (with typical energies between

a few KeV and 10 MeV). They originate as a result of spontaneous disintegration of the nucleus giving off excess excitation energy. In this thesis, irradiation was carried out with gamma rays from a cobalt-60 source. Slow neutron bombardment of cobalt-59, a stable isotope, in a nuclear reactor generates cobalt-60. It has a half life of 5.27 years and gives off two gamma photons with energies of 1.33 MeV and 1.17 MeV per decay. Figure 1 shows the radiation source used in this work.

One of the properties of gamma radiation is its penetrating power. As a result, it is able to cause electrons to be ejected from atoms and molecules to form ions, a phenomenon known as ionization. Most of the ions produced in this process occur by means of secondary ionization caused by the ejected high energy electrons. When a gamma ray passes through matter, some of its energy is lost either by scattering or absorption. Thus, the intensity of the radiation is reduced. The major processes operative in gamma energy dissipation are: photoelectric effect (a process where all the energy from the gamma ray is transferred to the ejected electron), Compton effect (where a gamma ray of medium energy undergoes elastic collisions with loosely bound orbital electrons, transferring part of its energy to the ejected electron), and pair production (gamma rays of energy greater than 1.02 MeV interact with the nuclear force field thereby producing an electron and a positron which travel in opposite directions).³ For the present study involving gamma rays of approximately 1 MeV and materials of low atomic number (Z), the

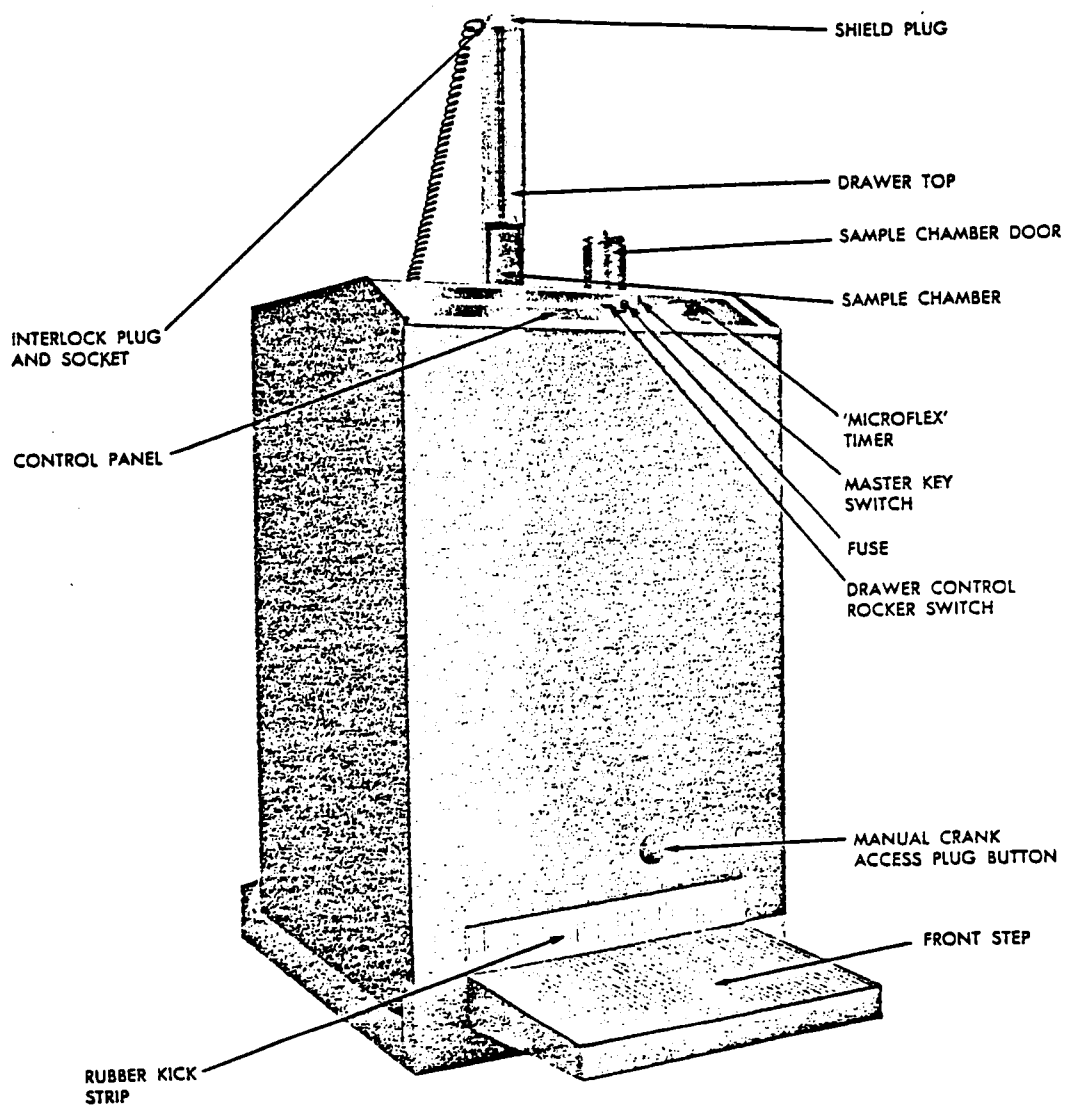


Figure 1. Overall view of Gammacell 200 cobalt-60 irradiator.

Compton effect predominates almost exclusively over the photoelectric effect and pair production.

The fast electrons produced as a result of the Compton effect bring about secondary ionization and excitation of the absorber molecules leading to the creation of spurs of excited molecules, radicals and ions along their tracks. These reactive species are responsible for all the chemical reactions in an irradiated sample. The spurs have a diameter of about $20 \text{ \AA}$ and on the average are about $10^4 \text{ \AA}$ apart in water and organic liquids.⁴ Due to the rapid diffusion of these species out of the spurs, a steady-state homogeneous distribution is attained in about a millisecond.

Since geminate charged pairs are produced in irradiated samples, a significant number of the ions undergo fast coulombic recombination without separating from each other. This is especially true when the distance r between the pair of ions is less than the distance, r_0 , between two ions at which the electrostatic and the thermal energies are equal.⁵ This parameter, r_0 , is defined by

$$r_0 = (e^2/\epsilon kT) \quad (5)$$

where e is the charge of electron, k is the Boltzmann constant, T is the absolute temperature and ϵ is the dielectric constant of the medium. In hydrocarbon liquids of low dielectric constant ($\epsilon = 2$), where r_0 is equal to $280 \text{ \AA}$, the probability (which is $\exp(-r_0/r)$, where r is the distance between a single pair of ions) of ions drifting apart against the inter-ionic force field is small and hence only

a small fraction of them become separated.⁶ These separated ions are called "free ions" and have a much longer lifetime than the geminate ions that do not escape.

Electrical conductivity measurements and both pulse radiolysis and steady state studies of ionic species generated during irradiation have shown that in hydrocarbon liquids of low dielectric constant, the yield of free ions is about 0.1-0.2 ions per 100 eV of energy input.⁷ This yield of free ions form the basis for the G_i in ionic polymerization which is defined as the number of initiating species produced per 100 eV of energy input in an irradiated sample. The relationships between G_i and other kinetic parameters used in radiation-induced polymerization will be introduced later in this chapter.

C. RADIATION-INDUCED POLYMERIZATION

The direct application of radiation to the synthesis of polymers is known as radiation-induced polymerization, the initiating species responsible for polymerization being generated by an ionizing radiation. In this thesis, the ionizing radiation is gamma radiation. As previously described in Section B, page 6, excited molecules, radicals and ion radicals are produced in an irradiated sample and hence are responsible for all the chemical reactions in the system. From a chronological point of view, the first use of radiation to induce polymerization was performed by Lind and Bardwell in 1925.⁸ Using an alpha particle as an irradiating source, they were able to

polymerize gaseous acetylene. To account for the initiating species responsible for polymerization, they proposed an "ion cluster" theory in which the positive ion formed after ionization by the alpha particle attracted neutral molecules to form a macroion. Thus upon neutralization, the macroion was thought to give rise to a polymer. This theory was challenged by Eyring et al.⁹ in an article in which they indicated that a macroion of that magnitude would probably not be stable enough to give rise to a polymer.

The polymerization of liquid vinyl monomers with high energy radiation has been studied since the 1930s. Some of the early researchers like Dainton et al.¹⁰ and Chapiro et al.¹¹ carried out extensive investigations on gamma radiation-induced polymerization of vinyl monomers in solution. Both groups indicated the mechanism of polymerization to be free radical in nature. Their conclusion was based on the fact that these polymerizations were inhibited by diphenyl picryl hydrazyl (DPPH), a known free radical scavenger.

Another method of distinguishing between radical and ionic polymerization is based on the copolymer composition of styrene-methyl methacrylate mixtures. Walling et al.¹² showed that a free radical mechanism led to a copolymer composition that approximated closely to the monomer composition. In contrast, ionic polymerizations were found to give only homopolymers of the individual monomers. Thus, in anionic polymerization, only the homopolymer of methyl methacrylate is formed and in cationic, the homopolymer of styrene is formed. Accordingly, the results of Seitzer and Tobolsky¹³ showing that the

copolymer composition was 50:50 for the radiation (fast electrons)-induced equimolar copolymerization of styrene and methyl methacrylate at room temperature strongly supported the free radical mechanism. Studies of the radiation-induced copolymerization of styrene-methyl methacrylate equimolar mixtures at lower temperatures (-78°C) also gave the same ratio of copolymer composition as that found in free radical copolymerization.¹⁴ As a result of these studies, radiation-induced polymerization was generally thought to be free radical in nature.

The successful polymerization of isobutylene in the liquid state at -78°C with high energy radiation demonstrated that ionic polymerization could be initiated in the liquid state, since this monomer is known only to undergo cationic polymerization.¹⁵ Di-isobutylene, a known conventional ionic inhibitor prevented polymerization of isobutylene from taking place. Further proof of ionic mechanism was established by the inability of DPPH to prevent the polymerization of isobutylene.¹⁶

For many years, it was believed that radiation-induced ionic polymerization occurred only at low temperatures. This idea was also promoted by the results obtained from the polymerization of styrene at -78°C in chlorinated solvents.^{14,17,18} Chapiro and Stannett¹⁴ determined the mechanism of polymerization of the styrene monomer to be cationic since neither oxygen nor benzoquinone affected the polymerization. The kinetics of this polymerization also indicated that the ionic contribution increased with the dose rate. In

free radical polymerization, the rate of polymerization is proportional to the half power of the dose rate whereas in ionic polymerization, the polymerization rate often shows a first order dependence. Ring-opening polymerization is generally diagnostic of ionic polymerization, and early studies (radiation-induced) on the polymerization of cyclic trimer hexamethylcyclotrisiloxane were also important in calling attention to the possibility of radiation-induced ionic polymerization.¹⁹

The investigations by Williams et al.^{20,21} and others²² in the early sixties clarified the conditions necessary for radiation-induced ionic polymerization. Essentially, they found out that radiation-induced cationic polymerization was greatly enhanced after the monomers were subjected to rigorous drying. Thus, the notion that ionic polymerization can occur only at low temperature was modified. Further work along these lines on isobutylene²³ and β -pinene²⁴ monomer confirmed the importance of drying in these systems, since these monomers do not respond to free radical polymerization. As explained in Section B, page 7, investigations in the sixties have shown that free ions ($G_i \sim 0.1-0.2$) that escape geminate recombination have long lifetimes (10^{-2} seconds at a dose rate of 1 Mrad hr.^{-1}). These free ions can bring about ionic polymerization. Depending on the susceptibility of the monomer to polymerization and the conditions of the reaction medium, either a free radical or an ionic polymerization will take place in radiation-induced polymerization. For example, in a dry system, the cationic species dominates the radiation-induced

polymerization of styrene which is known to polymerize by radical, anionic or cationic in conventional polymerization. Hayashi et al.²⁵ have shown that very low ($<10^{-5}$ M) concentrations of water in styrene are enough to stop the ionic contribution to the polymerization.

Once polymerization is initiated, the kinetics that govern the process follow conventional equations. Quantitatively, it can be shown that the high rates of propagation for free ion polymerization cannot be achieved if the system is not extremely dry and pure from other contaminants. In the absence of impurities such as water and other ionic scavengers the equation below:

$$R_p = \frac{k_p[M] R_i}{k_{tx}[X] + (R_i k_t)^{1/2}} \quad (6)$$

reduces to

$$R_p = k_p[M] (R_i/k_t)^{1/2} \quad (7)$$

where R_i represents the rate of initiation; k_{tx} is the termination rate constant of the reaction between the propagating ion and an impurity of added scavenger X , and k_t represents the mutual bimolecular termination rate constant between ions of opposite sign. In radiation-induced ionic polymerization, the propagating species is generally believed to be an ion pair. Also, it should be noted that much higher propagation rate constants (10^4 - 10^9 M⁻¹ sec⁻¹) are achieved for free ions than for free radicals. For example, k_p values of the order of 3.5×10^6 M⁻¹ sec⁻¹ and 35 M⁻¹ sec⁻¹ have been recorded for free ions (cationic at 15°C)²⁶ and free radicals²⁷ (at 20°C), respectively, in the polymerization of styrene.

D. EVOLUTION OF THE PROBLEM

In the past, most of the attention in radiation-induced polymerization studies has been focused on vinyl monomers. Except for the early work on the ring-opening polymerization of cyclic trimer hexamethylcyclotrisiloxane¹⁹ which drew attention to the possibility of radiation-induced ionic polymerization, few studies of ring-opening polymerization had previously been undertaken. A careful review of the literature pertaining to the liquid phase showed that only the radiation-induced polymerization of 1,2 epoxides had been studied. The best documented example is the polymerization of 1,2 cyclohexene oxide^{28,29,30} in which several of the characteristic features associated with the radiation-induced ionic polymerization of vinyl monomers, including the retarding effect of ammonia^{30,31} and the sensitivity to water²⁰ were found.

The successful catalytic cationic polymerization of (+)-limonene oxide, α - and β -pinene oxide monomers by Ruckel and co-workers³² also encouraged this work to be done. Basically, these authors found out that the opening of the epoxide ring in α - and β -pinene oxides was followed by the concomitant opening of the bicyclic bridge structure (cyclobutane ring) in the propagating step. Such a rearrangement process is also known to occur in the cationic polymerization of β -pinene.^{32,33,34,35,36}

E. TERMINOLOGY IN RADIATION-INDUCED POLYMERIZATION

Table I lists some of the terminologies used in radiation-induced polymerization and polymer chemistry.

The term "G value" which was introduced by Burton,³⁷ has found wide acceptance in radiation chemistry to denote the yield of individual chemical events occurring in a sample per 100 eV of energy absorbed. This is analagous to quantum yield in photochemistry. For example, G(-m) is used in radiation polymerization to define the number of monomer molecules that have been converted to polymer per 100 eV of energy input and is calculated as follows:

$$G(-m) = \frac{\text{Number of monomer molecules converted to polymer}}{\text{eV of energy absorbed}} \times 100 \quad (8)$$

$$G(-m) = \frac{\text{Wt. of polymer (g)}}{\text{Wt. of monomer (g)}} \times \frac{N_A \text{ (molecules/mole)}}{\text{M. Wt. of monomer (g mole}^{-1}\text{)}} \times \frac{1}{\text{Absorbed dose (Mrad)}} \times 1.602 \times 10^{-20} \frac{(\text{Mrad})}{(\text{eVg}^{-1})} \times 100 \quad (9)$$

combining all the constants in equation (9) yields:

$$G(-m) = \frac{964,885}{\text{M. Wt. of monomer}} \times \frac{\text{Wt. of polymer (g)}}{\text{Wt. of monomer (g)}} \times \frac{1}{\text{Dose (Mrad)}} \quad (10)$$

The stationary state assumption (R_p being independent of time) used in conventional polymerization to develop kinetic equations that govern polymerizations can be used in radiation-induced polymerization. The statement above allows the following expressions to be made:

TABLE I
TERMINOLOGIES IN RADIATION AND POLYMER CHEMISTRY

Symbol	Definition	Units
$G(-m)$	The number of monomer molecules converted to polymer per 100 eV of energy input.	Molecules/100 eV
G_i	The number of initiating species produced per 100 eV of energy input.	Molecules/100 eV
I	Dose rate.	$\text{eV g}^{-1} \text{sec}^{-1}$ or (rad hr^{-1})
$\bar{M}_n$	Number-average molecular weight $(\sum N_i M_i^2 / \sum N_i)$	
$\overline{DP}_n$	Degree of polymerization $(\bar{M}_n / \text{M. Wt. of monomer})$	
ν	Kinetic chain length $(G(-m)/G_i)$	Monomer molecules that have reacted per initiating species
R_p	Rate of propagation	M sec^{-1}
R_i	Rate of initiation	M sec^{-1}
k_p	Propagation rate constant	$(\text{M}^{-1} \text{sec}^{-1})$
k_t	Termination rate constant	$(\text{M}^{-1} \text{sec}^{-1})$
k_{tr}	Chain transfer rate constant	$(\text{M}^{-1} \text{sec}^{-1})$

$$R_i = \frac{G_i \text{ (molecules) (I) eV g}^{-1} \text{ hr}^{-1}}{100 \text{ eV } N_A \text{ (molecules/mole)}} \quad (11)$$

where R_i is the rate of initiation; I is the dose rate in $\text{eV g}^{-1} \text{ hr}^{-1}$; N_A is the Avogadro number (6.023×10^{23} molecules/mole); G_i (briefly discussed in Section B, page 7 of this thesis) is the number of molecules of initiating species produced per 100 eV of energy input.

Likewise,

$$R_p = \frac{G(-m) \text{ (molecules) (I) eV g}^{-1} \text{ hr}^{-1}}{100 \text{ eV } N_A \text{ (molecules/mole)}} \quad (12)$$

where R_p is the rate of propagation; I is the dose rate and N_A is Avogadro's number (6.023×10^{23} molecules/mole $^{-1}$). The equivalent form of equation (12) is:

$$R_p = \frac{k_p [M] R_i}{k_{tx} [X] + (R_i k_t)^{1/2}} \quad (13)$$

where k_p is propagation constant; $[M]$ is the monomer concentration; R_i is the rate of initiation; k_{tx} , the termination constant of impurities; $[X]$, the impurity concentration and (k_t) is the bimolecular termination between ions. With the knowledge of the $G(-m)$ and G_i , the kinetic chain length can be determined as follows:

$$\nu = \frac{G(-m)}{G_i} = \frac{R_p}{R_i} \quad (14)$$

In polymerizations where chain transfer processes are absent, the $\overline{DP}_n$ (obtained from the number average molecular weight divided by the molecular weight of the monomer) is related to $G(-m)$ and G_i according to equation (15).

$$G(-m) = \overline{DP}_n \times G_i \quad (15)$$

Molecular weight distribution is of paramount importance in polymer chemistry. As such, the following statistical relations for $\overline{M}_n$ and $\overline{M}_w$ have been developed to account for the differences in polymer sizes that occur during polymerization:

$$\overline{M}_n = \frac{\sum NiMi}{\sum Ni} \quad (16)$$

$$\begin{aligned} \overline{M}_w &= \frac{\sum NiMi^2}{\sum NiMi} \\ &= \frac{\sum wiMi}{\sum wi} \end{aligned} \quad (17)$$

where Ni refers to the number of molecules of species i with molecular weight Mi , and wi is the weight of species i which is the product of Ni and Mi . The numerical magnitude of the ratio $\overline{M}_w$ to $\overline{M}_n$ determines the polydispersity factor encountered. For the "most probable" distribution or what is generally known as the Poisson ratio, the polydispersity assumes a factor of 2.

CHAPTER II

EXPERIMENTAL: PREPARATION OF POLYMERS

A. MONOMERS AND MATERIALS USED

Table II shows a tabulation of all the chemicals used in this thesis. With the exception of the monomers which were purified, the chemicals were used as received.

B. MONOMER DRYING, PURIFICATION AND PREPARATION OF SAMPLES

The need to dry monomers in cationic radiation polymerization has been very well established.^{20,21,24,28,38} The presence of a small amount of water is known to drastically affect the rate of polymerization. Thus, stringent drying techniques are required to avoid the loss of ionic carriers by reaction with water if respectable $G(-m)$ values and hence high molecular weight polymers are to be obtained.

Cordischi et al.²⁸ dried a series of alicyclic epoxides with molecular sieves (type 3A) in order to obtain a high molecular weight polymer on gamma irradiation. Stannett et al.³⁸ studied alkyl vinyl ethers under super dry conditions by drying the monomers over potassium hydroxide (KOH) pellets and refluxing them over sodium metal to achieve a high molecular weight polymer.

In order to ensure a respectable $G(-m)$ value, a combination of Adur's³³ and Cordischi et al.²⁸ drying procedures was used. The

TABLE II
LIST OF MONOMERS AND CHEMICALS USED

List of Manufacturer/Supplier	Chemicals ^a
(a) Monomers	
Aldrich Chemical Company, Inc.	α -pinene oxide β -pinene oxide (+)-limonene oxide
(b) Drying Agents	
Fisher Scientific	silica gel, indicator tell-tale type, 6-16 mesh
(c) Solvents and Other Chemicals	
Aldrich Chemical Company, Inc.	benzil
Eastman Organic Chemicals	tripropylamine
Fisher Chemical Company	carbon tetrachloride
Fisher Chemical Company	chloroform dichloromethane pyridine methanol
Norrell Chemical Company	tetramethyl silane

^aAll chemicals are A. C. S. reagent grade or better unless otherwise stated.

latter procedure involved drying the monomers for 3 days on molecular sieves (type 3A). Figure 2 shows the glass manifold used in preparing the samples. Essentially, the glass manifold was baked-out in an oven at 350°C for 2-3 days under high vacuum. The sections A and B of the apparatus contained indicator-grade silica gel as drying agent. The baked-out glass manifold was then attached to a conventional vacuum line.

The monomers which had been sitting on molecular sieves for 3 days were then distilled under low pressure with a Nester-Faust spinning band column. This distillation set-up was necessary since these monomers ((+)-limonene oxide, α -pinene oxide and β -pinene oxide) were known to undergo rearrangement above 150°C.³² The distilled monomers were then introduced by way of a side arm (filled with silica gel and zeolite) into a flask on the conventional vacuum line.

A number of freeze-pump-thaw cycles were performed to degas the system. The degassing was followed by transferring the monomer into vessel C with a liquid nitrogen trap. The break seal in the tube connecting vessels C and B together was broken open. The monomer from vessel C was then condensed successively into the traps B and A and allowed to sit on molecular sieves for a day in each of these traps. The ampoules next to vessel A were then filled with the monomer and sealed off. The sealed sample tubes were then irradiated in a Gammacell-200 (Atomic Energy of Canada Ltd.) cobalt-60 source with varying doses. A few low-temperature irradiations were carried out in a Dewar flask containing ice (0°C), solid carbon dioxide (-78°C)

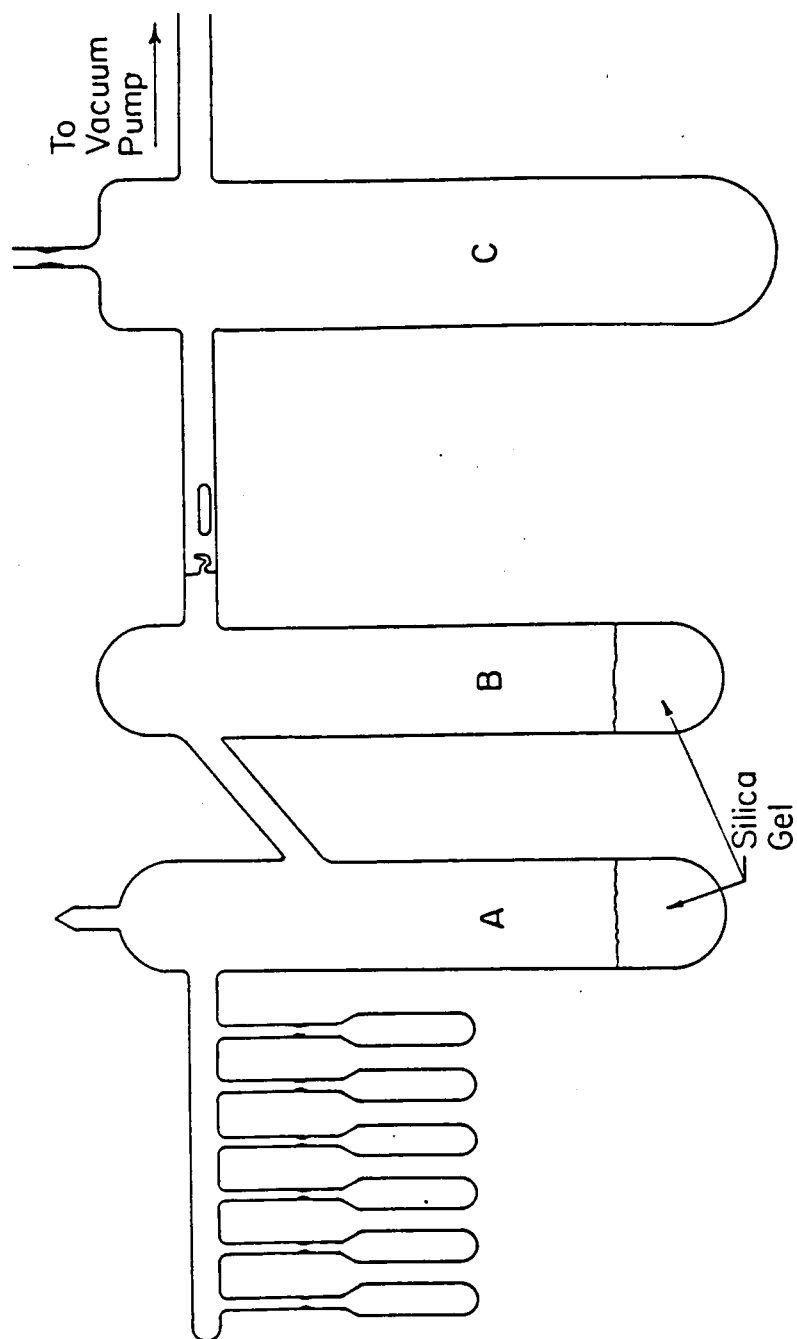


Figure 2. Glassware for the preparation of monomer samples.

and liquid nitrogen (-196°C). The rest of the samples were irradiated at room temperature.

The polymerization mechanism was determined by doping the last of the sample ampoules within each batch with tripropylamine. Periodic checks during irradiation of these monomer samples showed that an increase in viscosity had occurred except for the sample doped with tripropylamine (a known cation scavenger).

C. RECOVERY, PURIFICATION, AND ESTIMATION OF POLYMERS

The recovery of these polymers required a special set-up. Allylic and double bond sites within the polymer were found to be susceptible to oxidation and hence it was necessary to do all the recovery work in a glove bag flushed with dry nitrogen.

The viscous monomer-polymer sample obtained from the opened ampoule was dissolved with methylene chloride which had been dried on molecular sieves. The dissolved sample was then poured into a beaker (500 ml capacity), containing dried methanol (150 ml) and a magnetic stirrer. The polymer precipitated out as a white powder on contact with the methanol. The precipitated polymer was then filtered with a medium porosity fritted disc. Further dissolution and precipitation was performed to ensure a monomer-free polymer. Proton nuclear magnetic resonance showed no monomer peaks. The recovered polymer was evacuated to dryness (constant weight) in a vacuum dessicator. The percent conversions of monomer to polymer were calculated as follows:

$$\text{Percent conversion} = \frac{\text{Weight of polymer (g)}}{\text{Weight of monomer (g)}} \times 100 \quad (18)$$

D. RADIATION DOSIMETRY

Dosimetry in radiation chemistry involves the measurement of energy absorbed by a sample exposed to radiation. In this thesis, emphasis is on the absorbed dose. A common unit is the rad, which is defined as 100 ergs of energy absorbed by 1 gram of material exposed to ionizing radiation.³⁹ Absorbed dose measurements are determined chemically by what is known as Fricke dosimetry.⁴⁰ Briefly, the Fricke dosimetry is based on the amount of ferrous ions that have been converted to ferric ions in a gamma source after some known time of irradiation. Since the ferric ion gives an ultraviolet absorption peak at 304 mμ, an optical density (O.D.) can be obtained. Thus using Beer-Lambert Law, the concentration of the ferric ion can be determined as follows:

$$\Delta(\text{O.D.}) = \epsilon cl \quad (19)$$

where c is the concentration of ferric ions (in moles liter⁻¹), ϵ is the extinction coefficient in (liter mole⁻¹ cm⁻¹), and l is the path length (in cm). Solving for c in equation (19) yields

$$c = \frac{\Delta(\text{O.D.})}{\epsilon l} \quad (20)$$

which can then be converted to molecules per gram as shown below:

$$c = \frac{\Delta(\text{O.D.})}{\epsilon l} \times \frac{6.023 \times 10^{23}}{\rho 1000} \quad (21)$$

where ρ is the density of the Fricke solution, 1.025 g cm⁻³.

From the G value definition, the $G(\text{Fe}^{+3})$ is calculated as

$$G(\text{Fe}^{+3}) = \frac{c \text{ molecules g}^{-1}}{\text{Absorbed dose eV g}^{-1}} \times 100 \quad (22)$$

Since 100 eV g^{-1} is equivalent to $1.602 \times 10^{-18} \text{ Mrad}$, the above equation in conjunction with equations (20) and (21) can be converted to the dose rate in Mrad hr^{-1} (with the knowledge of the Fricke solution irradiation time). Thus,

$$\text{Absorbed dose rate} = \frac{\Delta \text{O.D.}}{\epsilon l} \times \frac{6.023 \times 10^{23}}{G(\text{Fe}^{+3})} \times \frac{1.602 \times 10^{-18}}{\rho \times 1000 \times t} \text{ Mrad hr}^{-1} \quad (23)$$

The absorbed dose rate (units in Mrad per hour) depends on the electron density of the compound under study. As such, the value obtained from Fricke dosimetry had to be adjusted for compounds of different electron densities:

$$Q = \frac{(\Sigma Z/\Sigma A)_{\text{monomer}}}{(\Sigma Z/\Sigma A)_{\text{Fricke solution}}} \quad (24)$$

hence,

$$\begin{aligned} \text{monomer dose rate} &= \frac{(\Sigma Z/\Sigma A)_{\text{monomer}}}{(\Sigma Z/\Sigma A)_{\text{Fricke solution}}} \times \\ &\quad \times (\text{dose rate})_{\text{Fricke solution}} \\ &= Q \times (\text{dose rate})_{\text{Fricke solution}} \end{aligned} \quad (25)$$

where Z and A are the atomic number and atomic weights. The Fricke solution $\Sigma Z/\Sigma A$ value has been determined experimentally to be 0.553.⁴¹ Table III shows the correction factor Q calculated for each monomer.

TABLE III
DOSE RATE CORRECTION FACTORS (Q)

Monomer	Mol. Formula	ΣZ	ΣA	$\Sigma Z/\Sigma A$	Q
(+)-limonene oxide	$C_{10}H_{16}O$	84	152	0.5526	0.999
α -pinene oxide	$C_{10}H_{16}O$	84	152	0.5526	0.999
β -pinene oxide	$C_{10}H_{16}O$	84	152	0.5526	0.999

The G(-m) value derived in Chapter I, Section E, of this thesis was multiplied by a correction factor Q to get the actual G(-m) value, since the dose rate is known to be dependent on the electron density of the monomers:

$$G(-m) = \frac{964,885}{\text{M. Wt. of monomer}} \times \frac{\text{Wt. of polymer (g)}}{\text{Wt. of monomer (g)}} \times \frac{1}{\text{Dose (Mrad)}} \times \frac{1}{Q} \quad (26)$$

The dose rate and the dose in the equations above refer to the measurements made with the Fricke dosimeter.

Since the dose rate of cobalt-60 is time dependent, it was necessary, periodically, to calculate the correct dose rate. This was accomplished using the dose rate determined by Adur⁴² and the first order rate law as follows:

$$\ln D_0/D_t = k_t \quad (27)$$

where k (the rate constant) is calculated from the half life; D_0 represents the initial dose rate (0.151 Mrad hr⁻¹ in 1979, January); D_t is the dose rate after some time t (3.66 years). Substitution of k, D_0 and time (t) in equation (27) yields a dose rate of 0.0941 Mrad hr⁻¹ (August 1982) to 0.078 Mrad hr⁻¹ (January 1984) as a result of cobalt-60 decay with a half life of 5.27 years.

CHAPTER III

EXPERIMENTAL: CHARACTERIZATION OF POLYMERS

A. STRUCTURAL CHARACTERIZATION

Structural analysis studies were performed with proton and carbon-13 nuclear magnetic resonance (nmr) and infrared (I.R.) spectroscopy. Nuclear magnetic resonance spectroscopy has been used quite extensively as an analytical tool to determine the polymer structure, tacticity, and percent composition (in copolymers).^{43,44} Polymer solutions (20%) were prepared in deuterated chloroform (CDCl_3) as a solvent and tetramethyl silane (TMS) was used as the reference for the proton and carbon-13 nmr spectra. The spectra were obtained with a Nicolet N.T. 200 nmr instrument.

Functional groups within the polymer structures were elucidated with infrared spectroscopy. The use of such a tool is very well documented.^{45,46} To obtain infrared spectrum of each polymer, the polymers were dissolved in methylene chloride (a volatile solvent), after which a few drops of the polymer solution were placed on a sodium chloride (NaCl) cell plate. The solvent was then allowed to evaporate with subsequent formation of a polymer film on the cell plate. The infrared spectra were obtained with a Perkin Elmer 727 instrument from 4000 cm^{-1} to 625 cm^{-1} .

B. MOLECULAR WEIGHT DETERMINATION

Molecular weight determinations were carried out with Knauer vapor pressure osmometer (v.p.o.) at 60°C with pyridine as solvent. The v.p.o. was calibrated using known concentrations of benzil $[(C_6H_5)CO]_2$ in pyridine. The results of the osmometer readings corresponding to benzil concentrations are compiled in Table IV. The calibration constant (K_{cal}) was determined by plotting the ratio of the osmometer readings to benzil concentrations (y-axis) against benzil concentrations (x-axis) as shown in Figure 3. By means of linear regression analysis, the intercept value, K_{cal} , on the y-axis was determined. Using the same procedure with serially diluted polymer solutions, the intercept value, K , for the polymers was obtained. The ratio K_{cal} to K yielded the number-average molecular weight ($\bar{M}_n$). Additional molecular weight determinations were performed by Galbraith Laboratories Inc., with chloroform as the solvent at 45°C and phenacetin as the calibration factor.

C. THERMAL ANALYSIS OF POLYMERS

Thermal investigations were performed with a Perkin Elmer Differential Scanning Calorimetry (D.S.C.-2) equipped with a model 3600 Thermal Analysis Data Station. Substances have different specific heats and therefore respond differently to thermal effects. This phenomenon is the principle behind Differential Scanning Calorimetry.

TABLE IV
CALIBRATION OF V. P. O. WITH BENZIL

No.	Concentration mg/ml ^a	Concentration moles/litre	Average Reading	Reading per Molarity ^b	K _{cal}
1	4.2	.02	63.5	3165.5	
2	8.4	.04	117.5	2937.5	
3	12.6	.06	174.9	2916.6	3350 ^c
4	16.8	.08	221.2	2765.0	
5	21.0	.10	274.0	2740.0	

^aSolution in pyridine.

^bMolecular weight of benzil = 210.23 grams per mole.

^cAn independent check of this value by a linear regression analysis gave 3212.

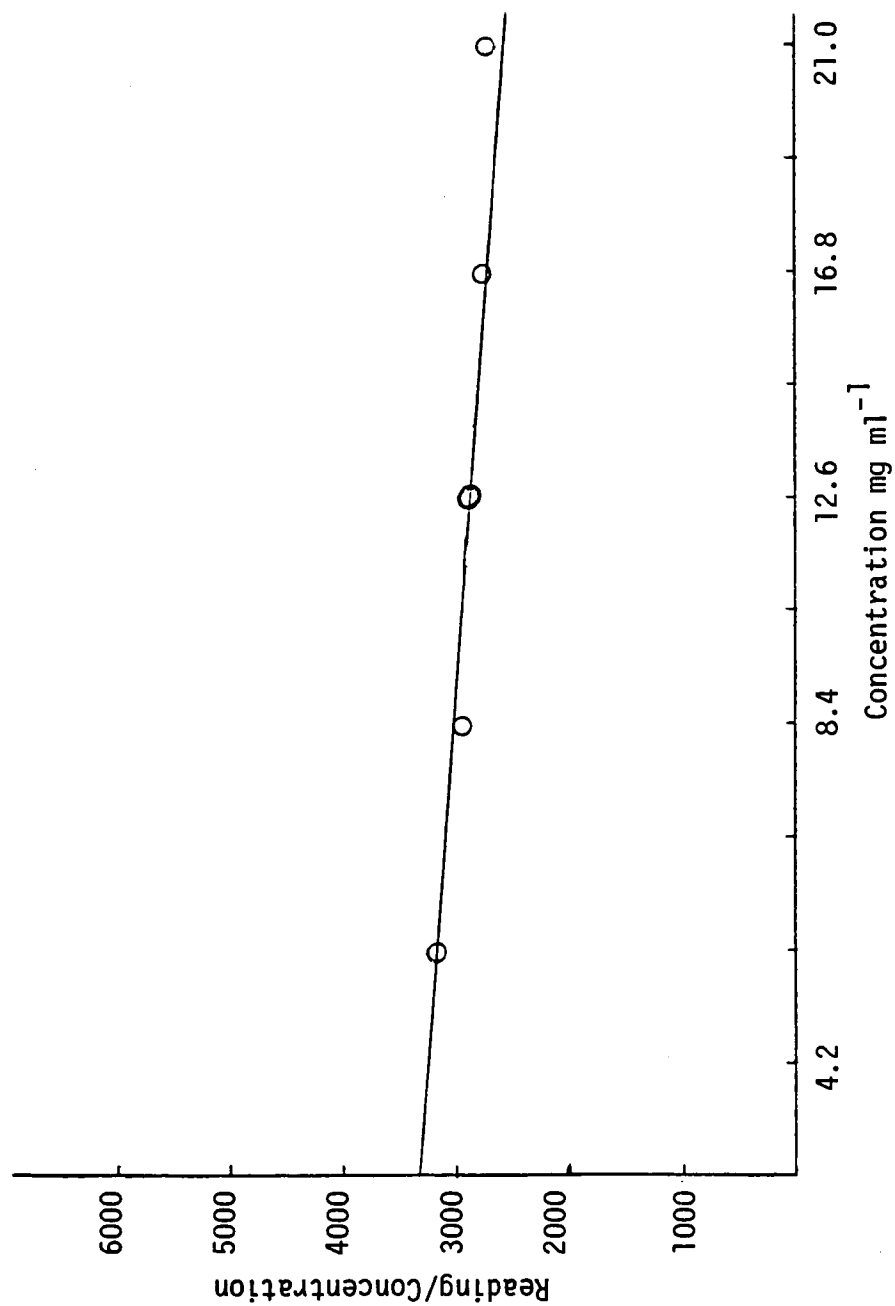


Figure 3. Calibration curve for vapor pressure osmometry with benzil in pyridine.

In D.S.C., a reference material (usually an empty aluminum pan) and the sample to be tested are subjected to the same programmed rate of heating. Since both the reference and the sample have different responses to thermal effects, a change in the normal heat flow pattern is observed. This change (either endothermic or exothermic) is related to the physical and/or chemical change.

Thermographs of the polymers were obtained by weighing between 2.0 to 5.0 milligrams of polymer samples into aluminum pans which were then sealed with a crimper. The empty reference pan and the sample pan were placed in their respective heating chambers on the instrument. A heating rate of 20°C per minute was applied. A thermograph of the differential power (i.e., differences in rate of energy supply) against temperature was recorded as shown in Figure 4 in the case of indium, the calibration standard.

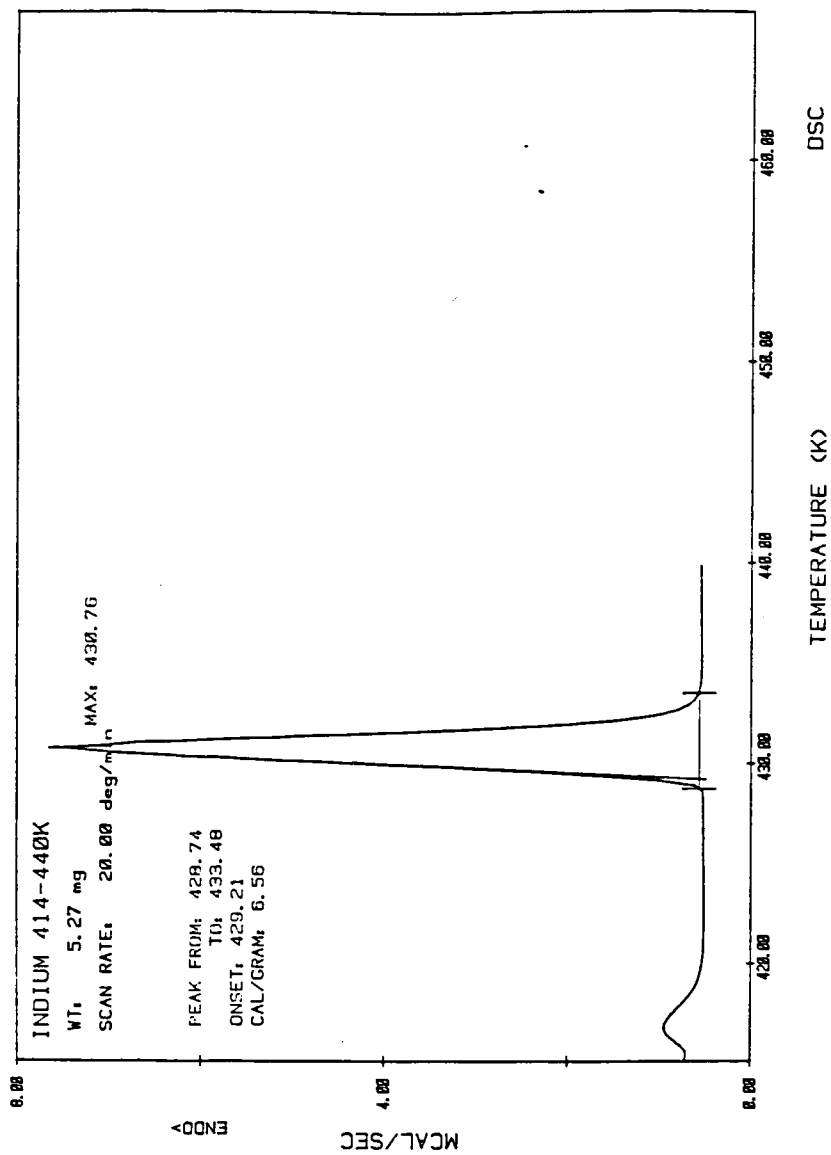


Figure 4. A D.S.C. graph of indium calibration standard.

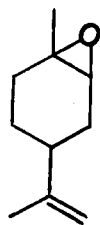
CHAPTER IV

RESULTS AND DISCUSSION

A. POLY((+)-LIMONENE OXIDE)

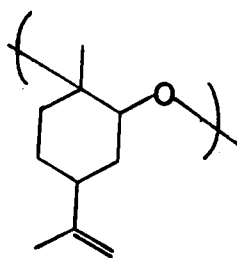
1. Introduction

The optically active (+)-limonene oxide monomer (Structure I) has been shown to polymerize cationically with PF_5 to yield a 1,2 trans



Structure I

polyether repeat unit as shown in Structure II.³² No evidence was found pertaining to polymerization through the double bond. Encouraged



Structure II

by the successful conventional cationic polymerization of this monomer, the present investigation was undertaken with emphasis on characterization.

2. Poly((+)-Limonene Oxide) Prepared by Irradiation

a. Results of irradiation of (+)-limonene oxide. Table V represents a compilation of the results obtained from the irradiation studies of (+)-limonene oxide. A survey of the data illustrates the degree of reproducibility attained in this work. The level of scatter in the results is indicative of the difficulties encountered in radiation-induced polymerization even when extreme precautions are taken to minimize impurities, e.g., water. High conversions of monomer to polymer per unit dose of the order of 40% Mrad⁻¹ were achieved for monomers irradiated at 25°C whereas much lower rates were obtained for the same dose rate at low temperatures. The average G(-m) values obtained at 25°C from eight determinations (Batch I-1 to II-4) was 2472. The G(-m) values obtained from batch III at 25°C were found to be much lower than the mean by a factor of 4. This deviation from the mean with respect to batch III is probably attributable to a bad batch. Assuming a G_i value of 0.1 to 0.2 (briefly discussed in Chapter I, Section B, page 7), the kinetic chain length (G(-m)/G_i) is estimated to be between 12,360 to 24,720 (using a G(-m) value of 2472).

Although the data available is not sufficient for any rigorous analysis of temperature dependency to be made, it is interesting to note that the G(-m) values obtained at -78°C and -196°C are significantly lower than at 0°C and 25°C. While further temperature studies would be needed for any firm conclusions to be drawn, the observed

TABLE V
RESULTS OF IRRADIATION OF (+)-LIMONENE OXIDE

Code No.	Temp. (°C)	Monomer (grams)	Dose (Mrad)	Polymer (grams)	Percent Conversion	G(-m)
I-1	25	2.069	1.355	1.641	79.3	3710
I-2	25	2.236	0.930	0.733	32.7	2239
I-3	25	2.236	1.820	1.733	77.5	2695
I-4	25	2.023	0.460	0.263	13.0	1776
II-1	25	5.740	1.840	2.932	51.0	1757
II-2	25	6.588	1.590	4.411	67.0	2668
II-3	25	6.294	0.850	1.810	28.7	2136
II-4	25	6.868	1.230	3.710	54.0	2793
II-5	-196	2.744	1.990	0.044	1.6	5151
III-1	25	5.044	3.715	2.397	47.5	819
III-2	-78	3.191	25.500	0.382	12.0	30
III-3	0	3.587	3.680	0.764	21.3	368
III-4	25	5.314	9.000	1.558	29.0	204
IV-1	25	3.668	8.060	1.766	48.1	379
IV-2	25	3.821	1.781	1.883	49.2	1756
IV-4 ^a	25	1.890	8.065	0.000		

^aSample was doped with 1.5% by volume of tripropylamine.

effect could be due simply to the change into the solid phase at the lower temperatures.

Evidence for the cationic nature of the propagating species was established by doping a monomer sample with 1.5% by volume of tripropylamine, a known cationic scavenger. As can be seen from Table V (code number IV-4), no polymer was recovered in this experiment after a dose of about 8.065 Mrad.

b. Molecular weight studies. The number-average molecular weight of the polymers were determined with a Knauer vapor pressure osmometer as described in Chapter III, Section B of this thesis. Typical osmometer readings of a sample are shown in Table VI. The ratios of the readings to concentrations were plotted against the concentrations. Extrapolation of the graph to zero concentration by means of a linear regression analysis in Figure 5 yielded the intercept value (K) of 2.125 divisions ml mg^{-1} . Using the value of K_{cal} (3350) from the calibration curve in Figure 3 (page 29), the number average molecular weight of this sample was calculated to be 1576.

A summary of the molecular weight studies are presented in Table VII. The degree of polymerization ($\overline{DP}_n$) values obtained ranged from 7.6 to 18.6. Polymers obtained from samples irradiated at 25°C gave an average $\overline{DP}_n$ of 12.8. Since the kinetic chain length ($\nu = 12,360$) is much higher than the $\overline{DP}_n$, a high frequency of chain (proton) transfer is implicated, a factor which is consistent with the cationic mechanism of polymerization.

TABLE VI
VAPOR PRESSURE OSMOMETRIC DETERMINATION OF MOLECULAR WEIGHTS
OF A TYPICAL SAMPLE OF POLY((+)-LIMONENE OXIDE)

No.	Concentration (mg ml ⁻¹)	Average Reading	Reading ml mg ⁻¹	K ^a	$\bar{M}_n = \frac{K_{cal}}{K}$
1	10.0	21.5	2.15		
2	20.0	37.0	1.85		
3	30.0	52.4	1.75	2.12	1576
4	40.0	60.2	1.51		

^aIntercept value in divisions ml mg⁻¹ from Figure 5.

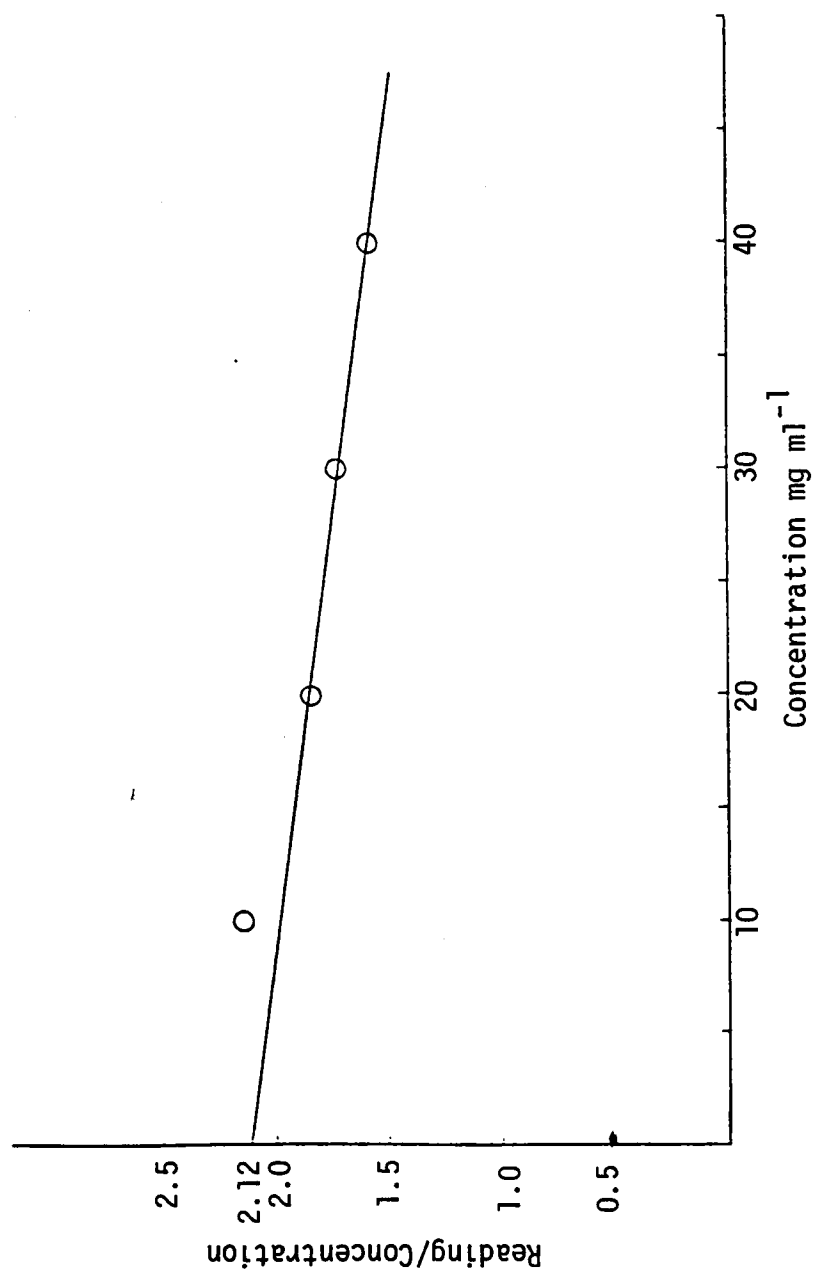


Figure 5. V.P.O. plot of a typical poly((+)-limonene oxide).

TABLE VII
NUMBER-AVERAGE MOLECULAR WEIGHTS OF
POLY((+)-LIMONENE OXIDE)

Sample No.	Temp. (°C)	Percent Conversion	Dose (Mrad)	G(-m)	$\bar{M}_n$	$\bar{DP}_n$
II-2	25	67.0	1.59	2668	2303	15.1
II-3	25	28.7	0.85	2136	1443	9.5
II-4	25	54.0	1.23	2793	2838	18.7
III-1	25	47.5	3.72	819	1201	7.9
III-2	-78	12.0	25.50	30	1618	10.6
III-3	0	21.3	3.68	368	2333	15.3

c. Structural characterization of poly((+)-limonene oxide).

Analyses were performed with proton and carbon-13 nmr spectroscopy and infrared spectroscopy. Figures 6 and 7 show the monomer and polymer spectra of (+)-limonene oxide obtained with a Nicolet N.T. 200 nmr instrument.

The monomer spectrum (Figure 6) shows two doublet peaks at 1.27δ - 1.29δ , and additional resonances at 4.64δ and between 2.9δ - 3.0δ . The strong peaks at 1.6δ and 4.64δ are assigned to the methyl and vinylidene protons of the isopropenyl ($\text{CH}_3-\overset{\text{I}}{\text{C}}=\text{CH}_2$) pendant group. The resonances at 1.27δ - 1.29δ and 2.9δ - 3.0δ are assigned respectively to the protons of the methyl group and the hydrogen atom directly linked to the epoxide ring.

The polymer spectrum (Figure 7) exhibits strong resonances at 1.18δ , 1.7δ , 4.68δ , and a broad peak at 3.5δ . Retention of the peaks at 1.7δ and 4.64δ in the polymer spectrum suggest little or no polymerization through the isopropenyl pendant group. The remaining peaks at 1.18δ and 3.5δ are assigned to the $\text{CH}_3-\text{C}-\text{O}$ and $\text{H}-\text{C}-\text{O}$ protons of the repeat unit shown in Structure II, page 32.

The proton-decoupled carbon-13 nmr spectrum of the polymer is shown in Figure 8. The major peaks of interest are located at 149.9δ , 108.4δ , and 20.7δ . These peaks are characteristic of the isopropenyl group found in limonene, the structure of which is shown on page 43, and their presence confirms that no polymerization occurred through the isopropenyl pendant group.

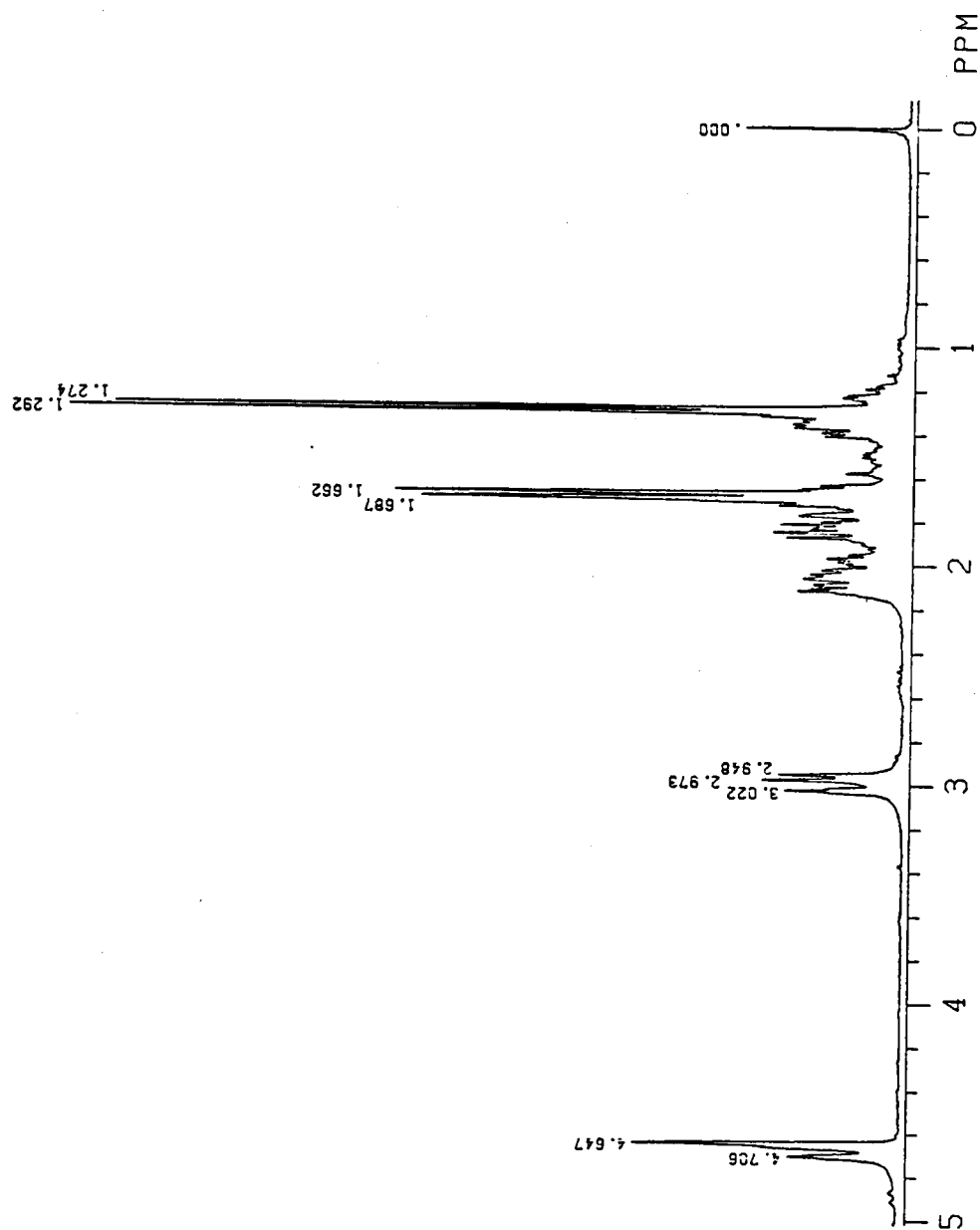


Figure 6. Proton nmr spectrum of (+)-limonene oxide monomer.

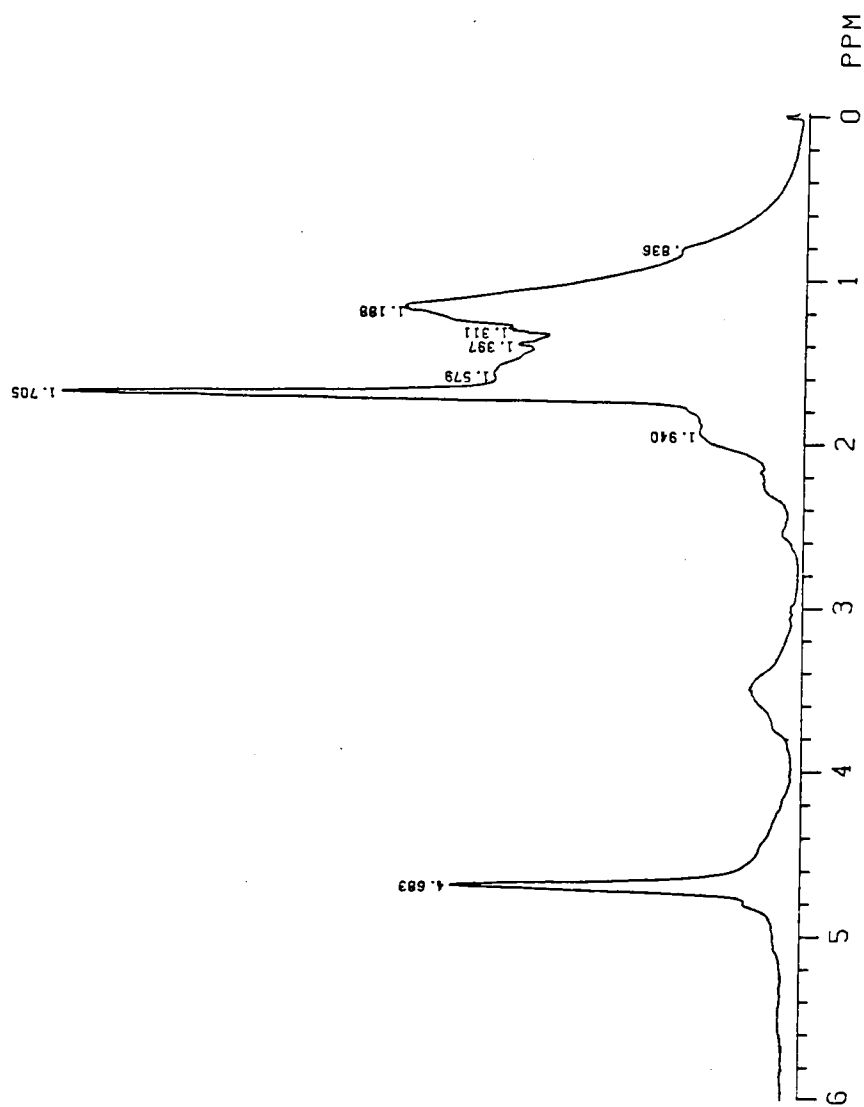


Figure 7. Proton nmr spectrum of poly((+)-limonene oxide).

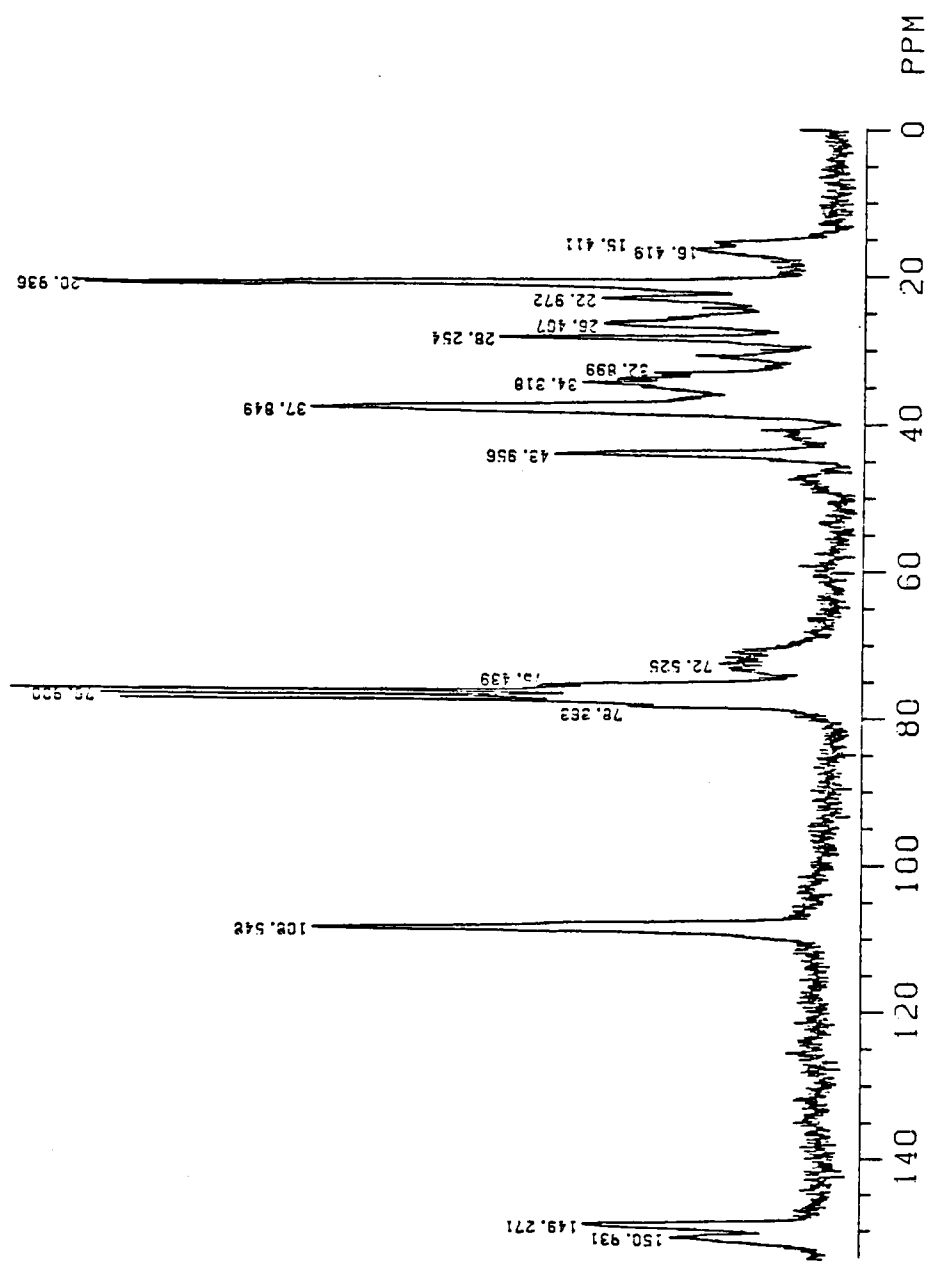
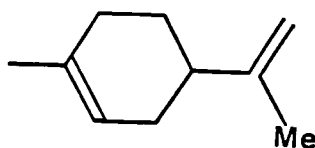


Figure 8. Carbon-13 nmr spectrum of poly((+)-limonene oxide).



The infrared spectrum of the polymer is shown in Figure 9. Essentially, the characteristic absorption frequencies of interest are 1638 cm^{-1} , 1000 cm^{-1} to 1300 cm^{-1} and 890 cm^{-1} which are respectively assigned to C=C stretch, C-O-C stretch, and C=C-H bending. A summary of the peak assignments is shown in Table VIII. The strong absorption at 1638 cm^{-1} is attributed to the exocyclic carbon-carbon double bond of the isopropenyl group.

d. Thermal analysis of poly((+)-limonene oxide). A thermograph of the polymer is shown in Figure 10. The transition observed between 65.2°C and 84.5°C represents the softening range of the polymer. The enthalpy change associated with this transition (endothermic) was found to be approximately 0.3 cal gram^{-1} .

3. Discussion

This work essentially demonstrates that, under dry conditions, (+)-limonene oxide undergoes radiation-induced polymerization in the liquid state through the ring opening of the epoxide group, and that the mechanism is cationic. High conversions of monomer to polymer were obtained (at least up to 80%) with increase in the time of irradiation. This strongly suggests that side reactions to non-polymerizable products were minimal. Since the $\overline{\text{DP}}_n$ values are much

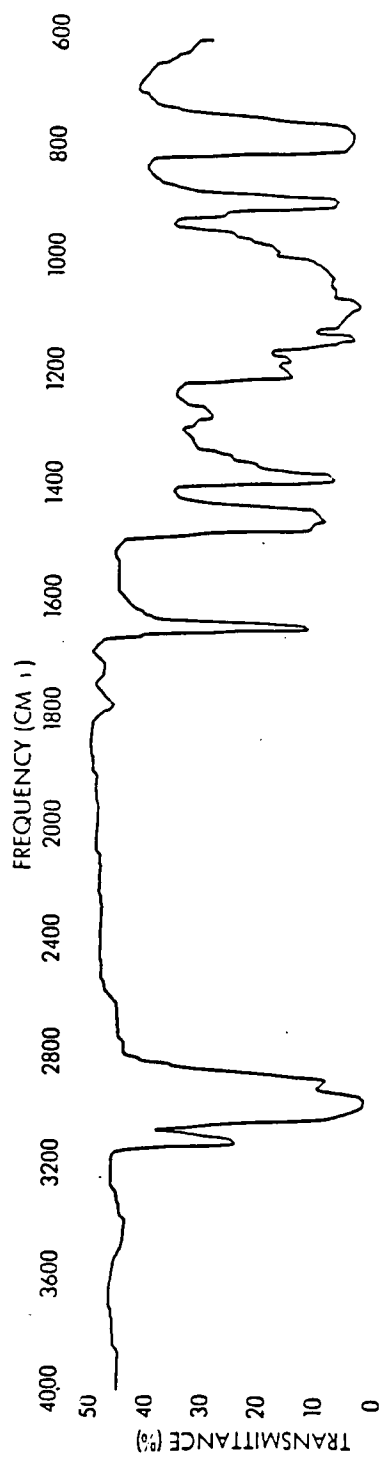


Figure 9. Infra-red absorption spectrum of poly((+)-limonene oxide.

TABLE VIII
ASSIGNMENTS OF INFRA-RED SPECTRAL ABSORPTIONS OF
POLY((+)-LIMONENE OXIDE)

Absorptions (cm^{-1})	Intensity	Assignment
3100	medium	C=C-H asymmetric stretching
2820-3000	strong	C-H stretching
1655	strong	C=C
1450-1475	strong	CH_3 asymmetric bending
1375	strong	CH_3 symmetric bending
1050-1150	broad	C-O-C stretch
890	strong	$\text{CH}_2=\text{C}<$ non-cyclic

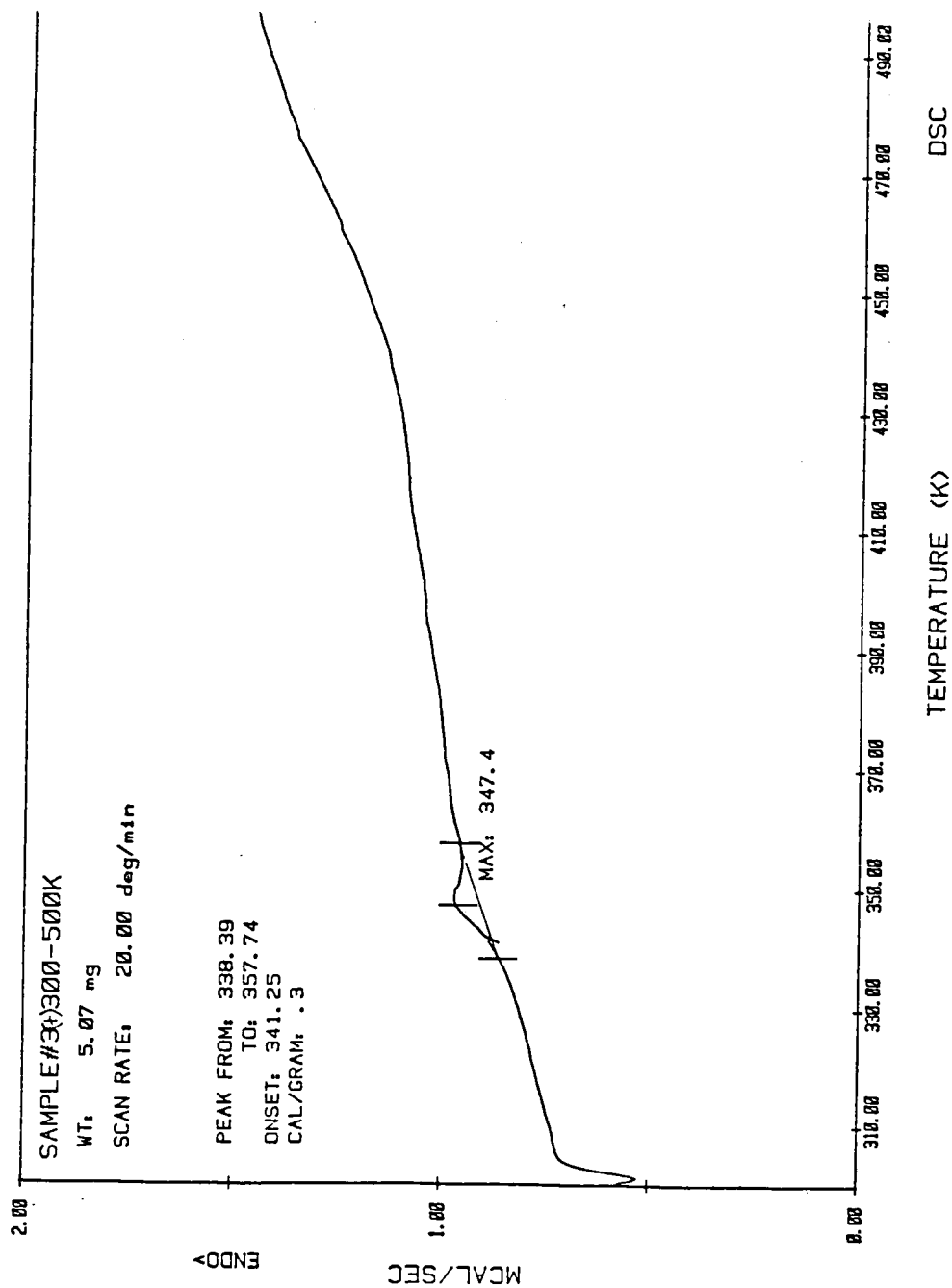
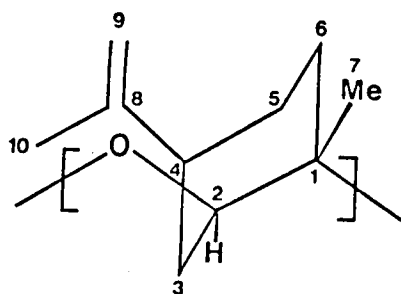


Figure 10. A D.S.C. thermograph of poly((+)-limonene oxide).

lower than the kinetic chain length, these results indicate the importance of chain (proton) transfer. Evidence from the proton nmr analysis suggests (according to the structure below) that, following the opening of the epoxide ring with the subsequent formation of a tertiary carbenium ion at the C-1 position, a proton transfer probably occurs predominantly from the C-2 or C-7 rather than the C-6 position:

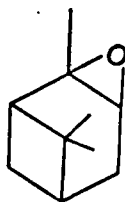


This is inferred from the lack of a peak at 5.22 δ in the proton nmr spectrum, which is indicative of endocyclic olefinic protons (i.e., cyclohexene). No evidence was found for polymerization through the isopropenyl pendant group.

B. POLY(α -PINENE OXIDE)

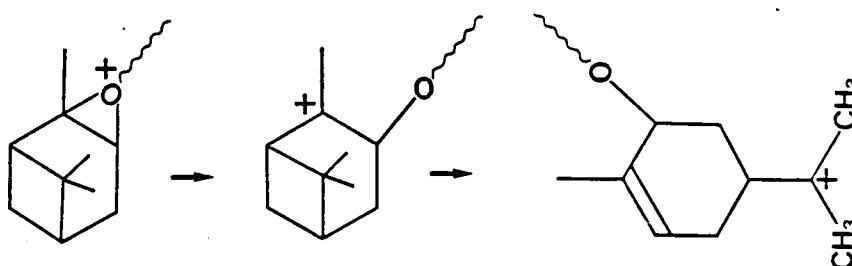
1. Introduction

The catalytic cationic polymerization of α -pinene oxide monomer (Structure III) has been studied by Ruckel and coworkers³² using BF_3 or PF_5 as co-initiators and tert-butyl chloride or adventitious amount of water as initiators.



Structure III

According to their results, the repeat unit suggests some form of rearrangement of the cyclobutane ring beta to the epoxide during the propagation step as shown below:



In view of the successful catalytic cationic polymerization of this monomer, the radiation-induced polymerization studies were carried out with the emphasis on characterization.

2. Results of Poly(α -Pinene Oxide) Prepared by Irradiation

a. Results of irradiation of α -pinene oxide. Data for the radiation-induced polymerization of α -pinene oxide monomer are presented in Table IX. As compared to (+)-limonene oxide, lower conversions per unit dose ($\sim 5.4\% \text{ Mrad}^{-1}$) of monomer to precipitable polymer were obtained both at ambient temperatures (25°C) and at 0°C temperatures (0°C). The average $G(-m)$ value obtained for 16 runs was 350.

TABLE IX
RESULTS OF IRRADIATION OF POLY(α -PINENE OXIDE)

Code No.	Temp.	Monomer (grams)	Dose (Mrad)	Polymer (grams)	Percent Conversion	G(-m)
I-1	25	0.910	3.26	0.248	27.2	530
I-2	25	0.847	3.27	0.064	7.6	148
I-3	25	1.292	4.21	0.072	5.6	85
I-4	25	1.580	4.36	0.173	10.9	159
II-1	25	3.400	3.09	0.655	19.3	395
II-2	25	3.090	1.48	0.789	10.0	428
II-3	25	3.386	3.00	0.488	14.4	304
II-4	25	4.168	5.11	0.906	21.7	270
III-1	25	5.146	5.83	1.777	34.5	375
III-2	25	5.345	3.91	1.310	24.5	396
III-3	25	4.873	3.91	1.638	33.6	544
III-4	25	4.750	5.83	1.423	30.0	326
IV-2	25	5.413	3.16	1.205	22.3	462
IV-3	0	5.664	3.71	1.105	19.5	345
IV-4	0	5.382	4.05	1.069	19.9	322
IV-5	25	2.143	3.28	0.549	25.6	495

Using a conservative G_i value of 0.2,⁷ the kinetic chain length was estimated to be 1750. Lack of reproducibility in the $G(-m)$ values and percent conversions indicate the difficulties associated with radiation-induced polymerization even when extreme drying procedures are used to minimize impurities such as water.

b. Molecular weight studies. The results of the molecular weight determinations are presented in Table X. The polymers from α -pinene oxide are of lower molecular weight than those from (+)-limonene oxide. The average $\overline{DP}_n$ for α -pinene oxide samples irradiated at 25°C was 5.5 whereas polymerizations carried out at 0°C had an average $\overline{DP}_n$ of 13.4.

In the absence of chain transfer, the kinetic chain length ν is expected to be equal to the $\overline{DP}_n$. However, the kinetic chain length ($\nu = 1750$) was found to be about 320 times the average $\overline{DP}_n$ of 5.5 which is highly indicative of transfer (proton) processes.

c. Structural characterization of poly(α -pinene oxide). The proton nmr spectra of α -pinene oxide monomer and polymer are shown in Figures 11 and 12. A look at the monomer spectrum indicates three inequivalent methyl resonances (0.955 δ , 1.296 δ and 1.313 δ) in comparison to two resonances (0.95 δ and 1.30 δ) reported by Ruckel and co-workers.³² Apparently they were not able to resolve the peak at 1.30 δ , which was twice the intensity of the peak at 0.95 δ . The methyl group attached to the epoxide ring in (+)-limonene oxide (a model compound) shows up at 1.28 δ in the proton nmr. It follows by analogy

TABLE X
NUMBER-AVERAGE MOLECULAR WEIGHTS OF
POLY(α -PINENE OXIDE)

Sample No.	Temp. (°C)	Percent Conversion	Dose (Mrad)	G(-m)	$\bar{M}_n$	$\bar{DP}_n$
II-4	25	14.4	3.00	304	500	3.3
IV-2	25	22.3	3.16	462	632	4.2
IV-3	0	19.5	3.71	345	2457	16.1
IV-4	0	19.9	4.05	322	1628	10.7

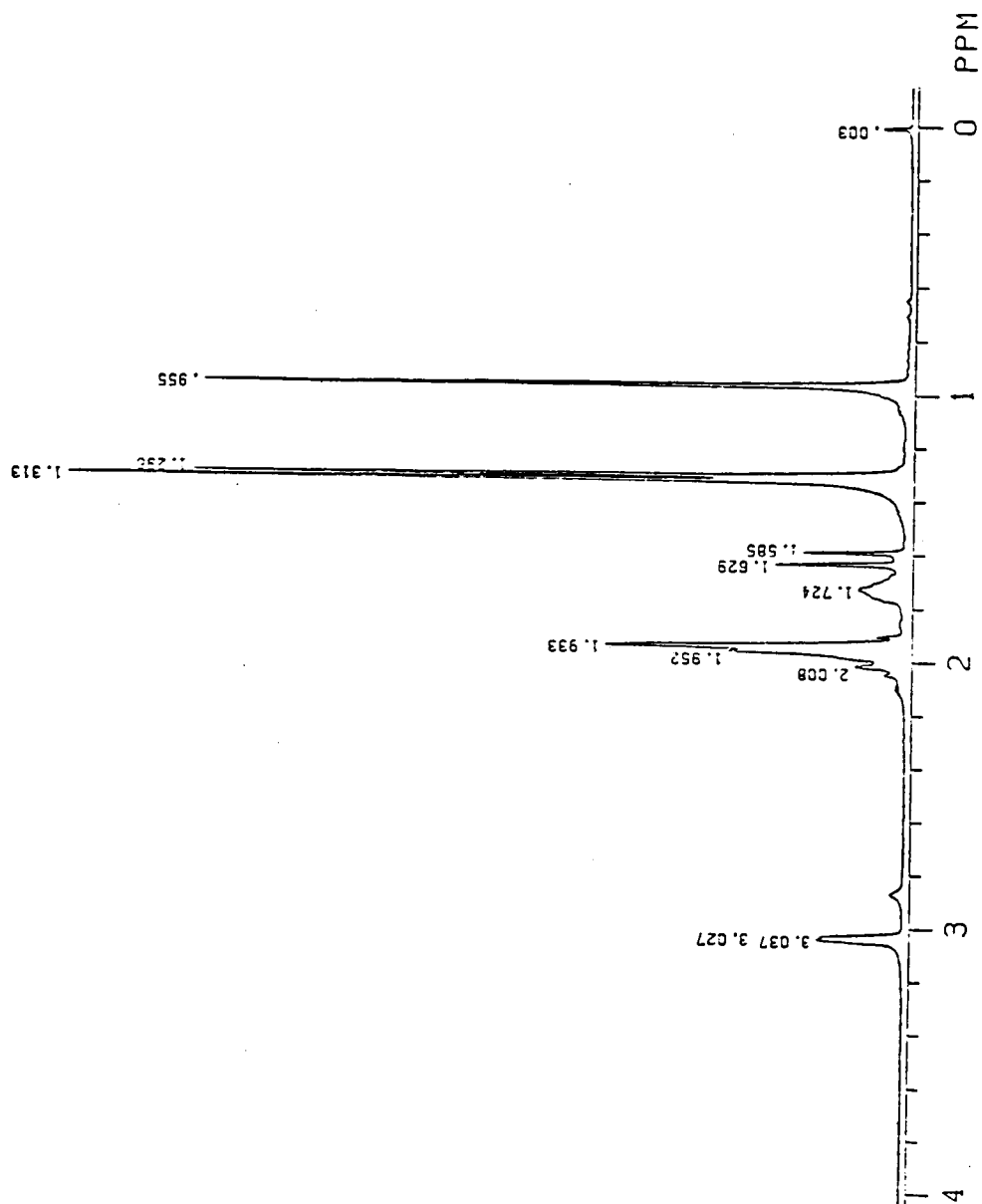
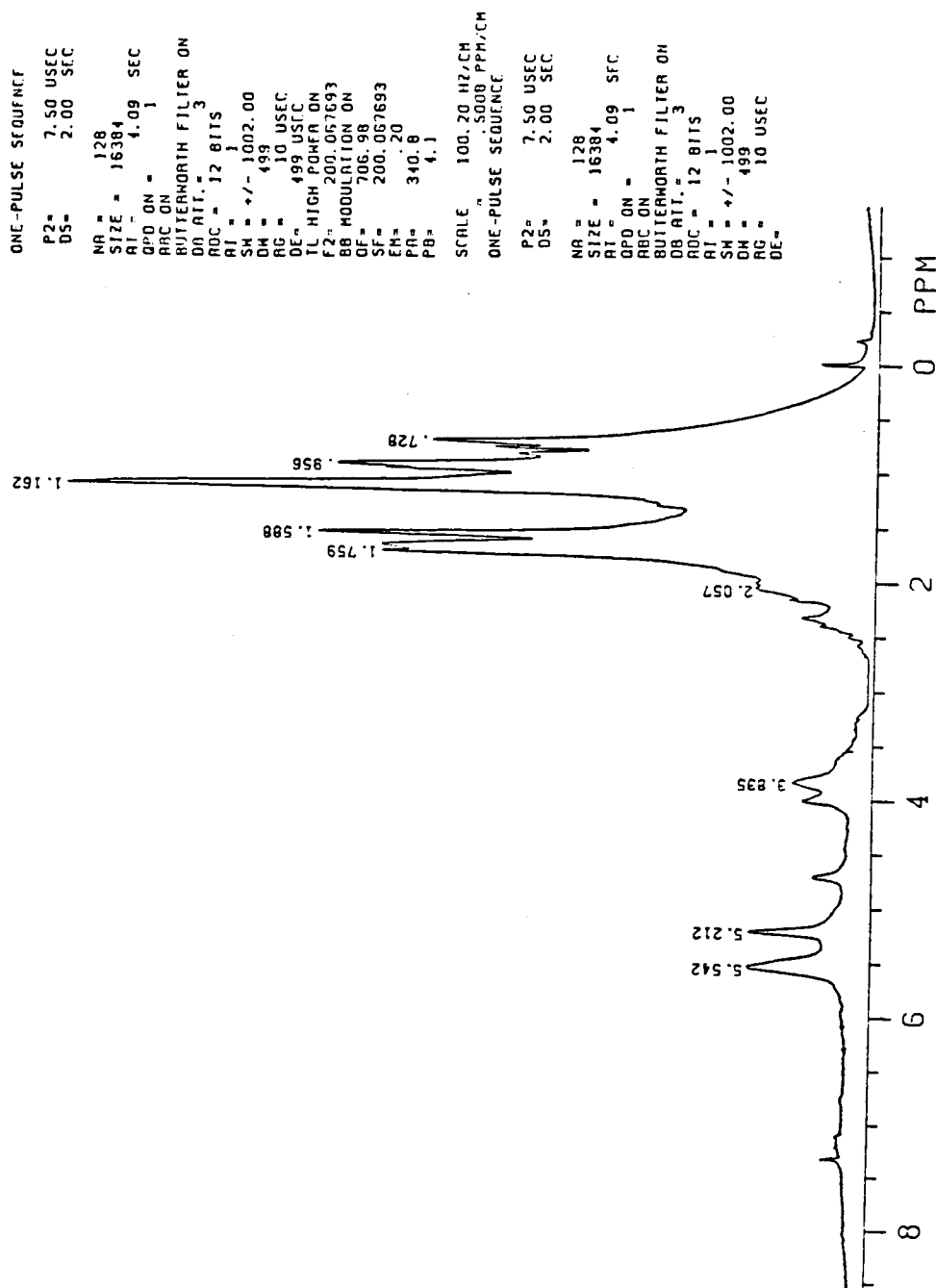


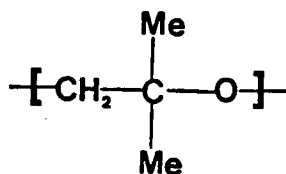
Figure 11. Proton nmr spectrum of α -pinene oxide monomer.

Figure 12. Proton nmr spectrum of poly(α -pinene oxide).

then that the peak at 1.296 δ of the α -pinene oxide monomer spectrum (Figure 11) be similarly assigned. The peaks at 0.955 δ and 1.30 δ must therefore be due to the gem-dimethyl absorption. The polymer spectrum (Figure 12) shows two types of allylic hydrogens (1.6 δ and 1.7 δ), three types of olefinic protons (4.64 δ , 5.15 δ and 3.95 δ), two H-C-O protons (3.83 δ and 3.95 δ), and three methyl hydrogen peaks (1.16 δ , 0.97 δ , and 0.74 δ).

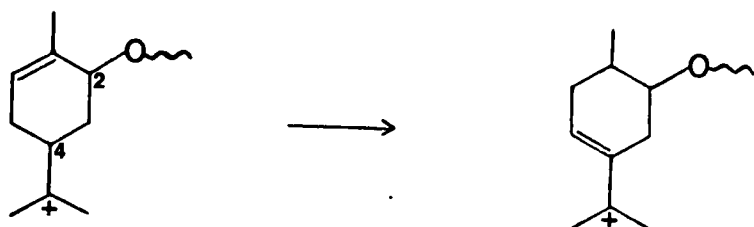
Assignments of these polymer peaks can be developed using the approach of Ruckel and coworkers.³² Essentially, they proposed an opened and closed bicyclic bridge structure (cyclobutane ring in the monomer as seen in Structure III) as contributing to the repeat unit.

Evidence for the opened cyclobutane ring is obtained from the proton nmr peak at 1.16 δ . This peak is attributed to the gem dimethyl moiety as shown below in the case of poly(isobutylene oxide) repeat unit:



Thus, following the opening of the epoxide ring in α -pinene oxide monomer, the bicyclic bridge structure rearranges to form a tertiary carbenium ion, which can then propagate or chain (proton) transfer. The proposed proton transfer process is accounted for by the peaks at 1.7 δ and 4.64 δ , which are similar to the isopropenyl pendant group resonances in (+)-limonene oxide, a model compound.

The dual nature of the endocyclic olefinic protons (5.44 δ and 5.45 δ) has been suggested independently to be due to occasional isomerization of the repeat unit Structure IV to Structure V:

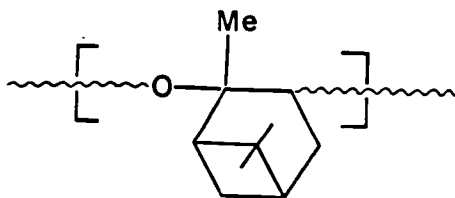


Structure IV

Structure V

According to Ruckel and coworkers,³² the driving force for such an isomerization could be due to the minimization of the steric interaction between positions 2 and 4 in Structure IV.

The peaks at 0.74 δ and 0.97 δ suggest occasional polymerization through the epoxide ring without participation from the bicyclic bridge structure. Hence, the nonequivalent gem-dimethyls could be assigned to these peaks. A possible contributing structure to poly(α -pinene oxide) would then be:



Two other extra peaks (0.95 δ and 1.3 δ) reported by Ruckel and coworkers³² were absent in the radiation-induced polymer. These peaks were assigned to the gem-dimethyl of the ring-closed mer (to use their terminology), thus assuming no change in the chemical shift between the monomer and the polymer.

The proton-decoupled carbon-13 nmr spectrum of poly(α -pinene oxide) is presented in Figure 13. Assignments of the peaks were carried out using model compounds such as sobrerol and limonene which are structurally related to the polymer.

Table XI represents a summary of the carbon-13 chemical shifts of both catalytic and radiation-induced polymerized poly(α -pinene oxide). Included in the table are chemical shifts for sobrerol (a model compound of the polymer repeat unit) for comparison. A survey of chemical shifts reveal the similarities between the radiation-induced polymer and the catalytically produced polymer.

The peaks at 148.3 δ , 108.2 δ -108.7 δ , and 21.5 δ are worth noting since they represent the carbon-13 resonances in the isopropenyl pendant group similar to those found in poly((+)-limonene oxide) (Figure 8, page 42). The presence of these peaks in the polymer spectrum support the proton transfer process proposed earlier in the analysis of the proton nmr of poly(α -pinene oxide).

The infrared spectrum of poly(α -pinene oxide) obtained with a Perkin Elmer 727 instrument is shown in Figure 14. Characteristic absorptions corresponding to C-O-C stretch, a gem-dimethyl doublet and vinylidene end groups are observed at 1100 cm^{-1} , 1375 cm^{-1} -1390 cm^{-1} , and 890 cm^{-1} (weak band) respectively. The rest of the absorption bands and assignments are compiled in Table XII.

d. Thermal analysis of poly(α -pinene oxide). The thermograph of poly(α -pinene oxide) is presented in Figure 15. Essentially, it

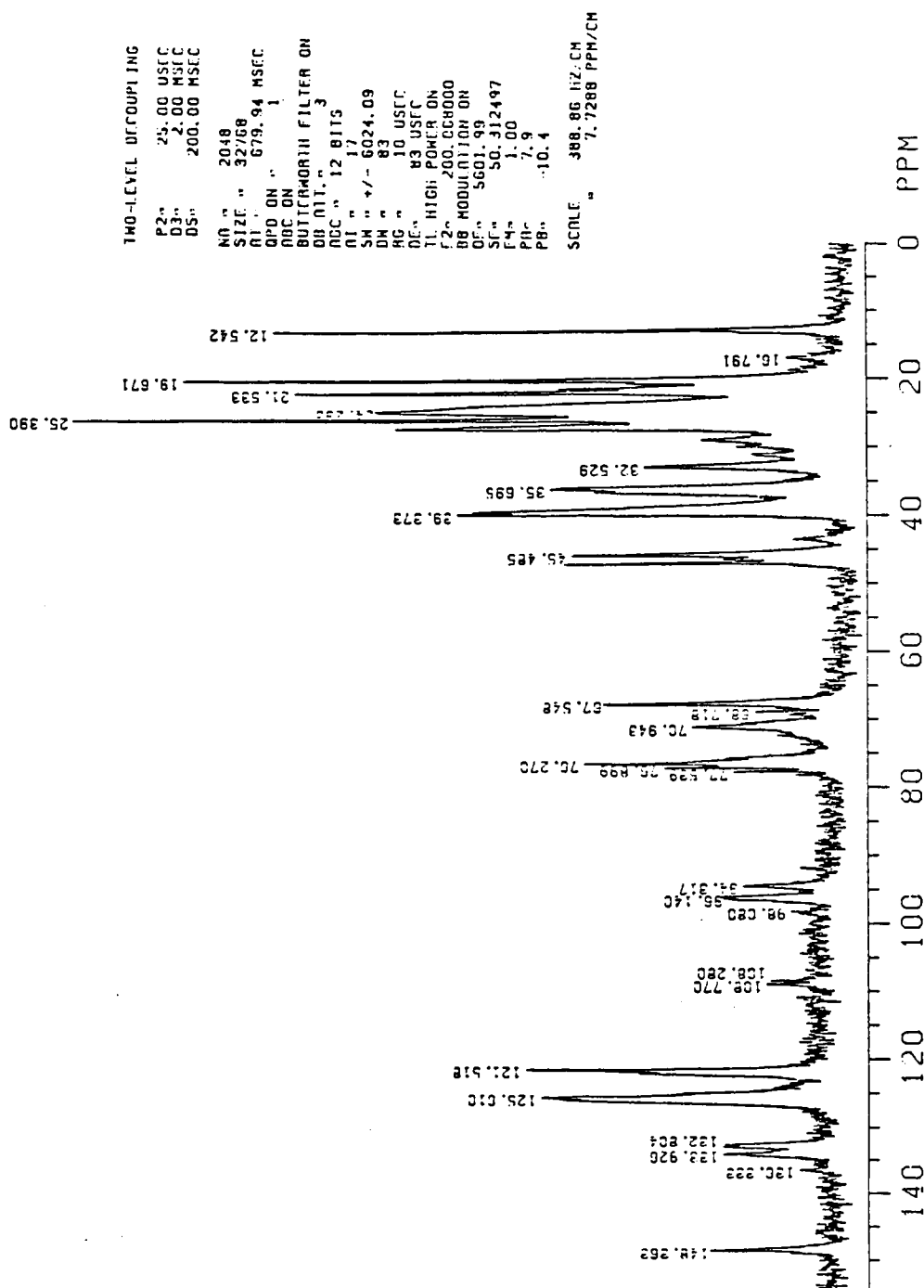
Figure 13. Carbon-13 nmr spectrum of poly(α -pinene oxide).

TABLE XI

CHEMICAL SHIFT (PPM) DATA OF POLY(α -PINENE OXIDE): COMPARISON
OF POLYMERS PREPARED BY IRRADIATION AND CATALYSIS

Sobrero ³²	Chemical shift in ppm (a)	
	Poly(α -pinene oxide) (conventionally polymerized) ³²	poly(α -pinene oxide) (radiation poly- merized)
CH ₃ 21.0 ^a	12.6 ^a	12.5 ^a
CH ₃ 26.0 ^a	19.8 ^a	19.6 ^a
CH ₃ 27.3 ^a	20.1	21.5 ^a
CH 27.7 ^a	20.8	24.2
CH 32.8 ^a	21.7 ^a	25.3 ^a
CH 38.7 ^a	25.7 ^a	26.2 ^a
CHOH 68.0 ^a	26.6 ^a	32.5 ^a
COH 71.5 ^a	27.1 ^a	35.7 ^a
=CH 124.6 ^a	27.6 ^a	38.7 ^a
=C< 134.8 ^a	32.8 ^a	39.4
	35.6 ^a	45.5 ^a
	38.9 ^a	47.0 ^a
	44.3	67.5 ^a
	45.2 ^a	70.9 ^a
	47.0 ^a	94.3
	68.7 ^a	96.1
	72.3	108.2
	121.6 ^a	108.7
	125.3 ^a	121.5 ^a
	133.1 ^a	125.6 ^a
		132.8 ^a
		133.9 ^a
		148.4
		CDCl ₃ (75.8,77.0,78.3)

^aRelates chemical shift similarities.

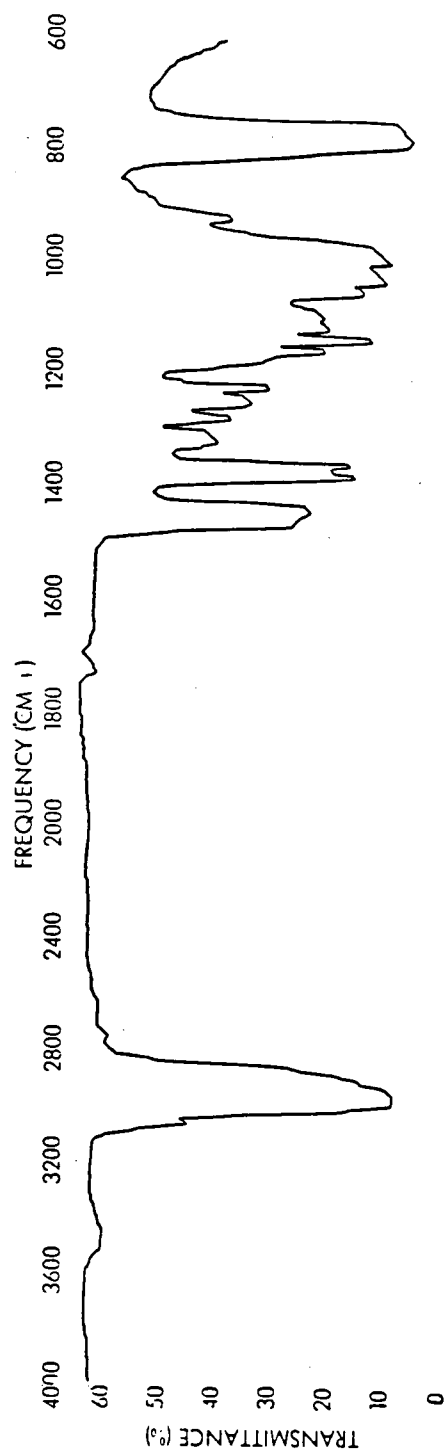


Figure 14. Infra-red absorption spectrum of poly(α -pinene oxide).

TABLE XII
ASSIGNMENTS OF INFRA-RED SPECTRAL ABSORPTIONS
OF POLY(α -PINENE OXIDE)

Absorptions (cm^{-1})	Intensity	Assignment
2800-3000	strong	C-H stretching
1650-1670	not prominent	C=C-H nonconjugated stretching
1430-1460	strong	$-\text{CH}_2$ deformation
1365-1383	strong	$-\text{C}(\text{CH}_3)_2$ sym. deformation
1000-1180	broad	C-O-C stretching
890	weak	$-\text{CH}_2=\text{C}<$ non-cyclic
850-870	absent	cyclobutane ring deformations and stretching

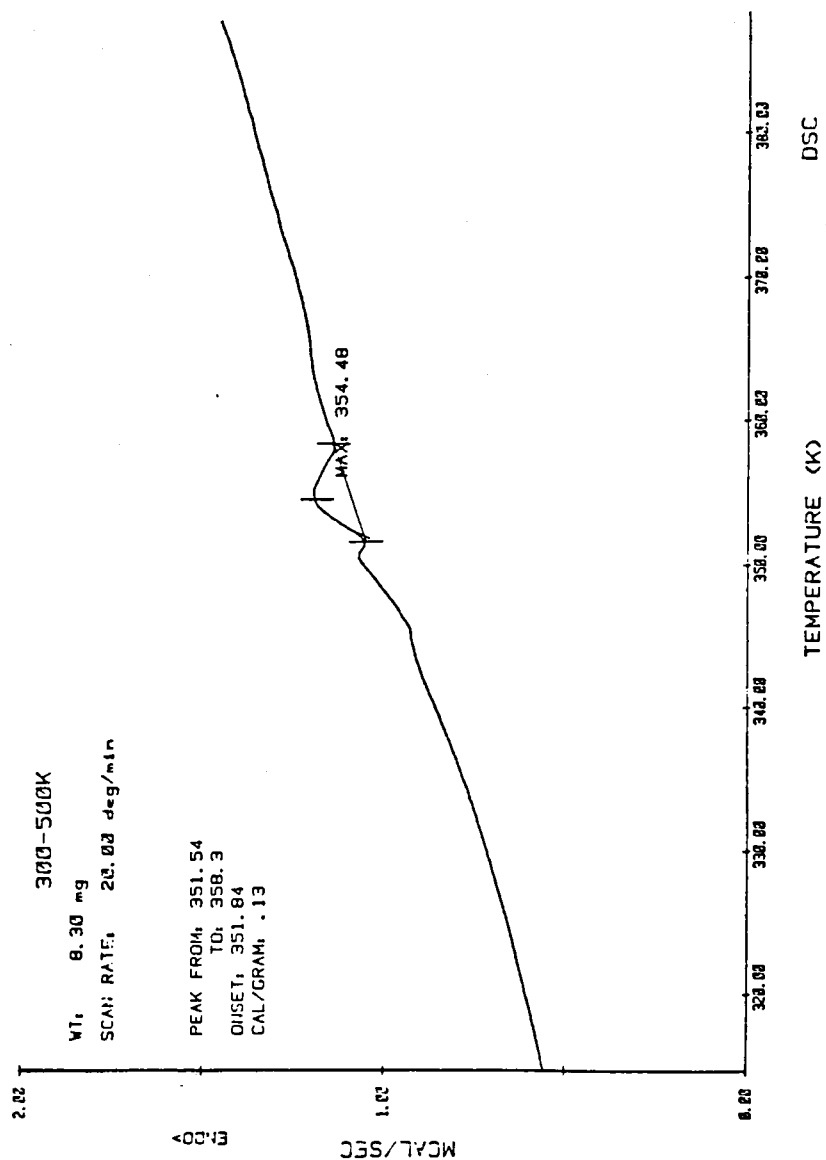


Figure 15. A D.S.C. thermograph of poly(α -pinene oxide).

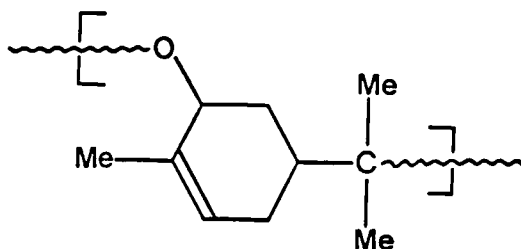
reveals the softening range of the polymer to be 65.2°C to 84.5°C which corresponds well with the values reported for the catalytically-prepared polymers. Furthermore, the graph shows an endothermic transition and the enthalpy change ($\Delta H = 0.3$ cal per gram) associated with it.

3. Discussion

This work demonstrates that under dry conditions, α -pinene oxide can undergo radiation-induced cationic polymerization. The average $G(-m)$ value obtained was 350. The $\overline{DP}_n$ for seven molecular weight determinations averaged 5.6. Although only two determinations were carried out, the molecular weights of the polymers prepared at 0°C appear to be higher than those prepared at 25°C. The estimated kinetic chain length was much greater than the average $\overline{DP}_n$, thus indicating proton transfer to monomer.

Apart from the proton nmr peaks at 0.95 δ and 1.30 δ which were absent in the radiation-induced polymer but present in the catalytically produced mer, the remaining proton nmr peaks were found to be identical in both systems. This suggests the same repeat unit for the polymers obtained from gamma radiation and catalytically produced mers. At this point, it is worthwhile to note that the monomer spectrum of α -pinene oxide has similar resonances at 0.95 δ and 1.30 δ ; hence it is possible that the polymers recovered by Ruckel and coworkers³² were not free of monomer. However, a personal communication with Ruckel and coworkers⁴⁷ indicated that they had gone through a lot of trouble to ensure a monomer-free polymer. As such, the only statement that

can be made to this effect is that these peaks do not exist in the polymers prepared by gamma radiation. On the basis of the structural analysis, the structure below is considered to be the major contributor to the repeat unit:



Another difference found in this work pertains to the proton nmr interpretation of the peaks at 1.7δ and 4.7δ in which Ruckel and coworkers³² assigned to $\text{CH}_3\text{C}=\text{C}$ - proton resonance in the branched mer and H-C-O protons in the polymer spectrum. These two resonances produced as a result of proton transfer correspond very well with the methyl and olefinic protons in an isopropenyl pendant group found in poly((+)-limonene oxide) which has similar resonances (Figure 7, p. 41). The carbon-13 nmr spectrum was also supportive of the proton transfer proposed since chemical shifts 148.3δ , 108.2δ - 108.7δ and 21.5δ corresponded very well with carbons of the isopropenyl pendant group.

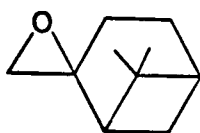
In comparison to catalytic polymerizations³² which were carried out at -78°C and -130°C in order to minimize rearrangement of the monomers to nonpolymerizable products and dimers, gamma radiation-induced polymerization gave much higher conversions of monomer to precipitable polymer at ambient temperatures (25°C).

One of the aspects in this work that corresponded well with the report by Ruckel and coworkers³² was the concomitant rearrangement of the cyclobutane ring following the opening of the epoxide ring during the propagation step.

C. POLY(β -PINENE OXIDE)

1. Introduction

The cationic polymerization of β -pinene oxide monomer (Structure VI) with Lewis acid co-initiators has been studied by Ruckel and coworkers.³² They proposed a propagating species in which the opening of the epoxide ring was followed by rearrangement of the cyclobutane ring similar to α -pinene oxide.



Structure VI

Molecular weights of the polymers obtained in the above work translated to a degree of polymerization of 6.0. Furthermore, rearrangement of this monomer during polymerization accounted for the low yield in their precipitable polymer. In view of the successful catalytic polymerization of this monomer, the radiation-induced polymerization was carried out with emphasis on characterization.

2. Poly(β -Pinene Oxide) Prepared by Irradiation

a. Results of irradiation of β -pinene oxide. Table XIII represents a compilation of the data obtained from the irradiation of β -pinene oxide monomer. An overview of the results illustrates the problem of reproducibility associated with radiation-induced polymerization. Conversions of monomer to polymer as high as 80% were obtained by suitably increasing the total dose. The average conversion per Mrad was 6.88%. This corresponds to an average $G(-m)$ value of 460 which is comparable to that obtained in α -pinene oxide. Assuming a G_i value of 0.2,⁷ the kinetic chain length is conservatively estimated to be 2300. The last sample (Table XIII, IV-5) doped with tripropylamine, a known cationic scavenger, yielded only 1.4% of polymer as compared to a "control" sample (IV-4) which gave 35% of polymer for the same total dose.

b. Molecular weight studies. The results of the molecular weight studies carried out with a Knauer vapor pressure osmometer are compiled in Table XIV. The average $\overline{M}_n$ corresponded to a $\overline{DP}_n$ of 4.0. Since this value is much lower than the kinetic chain length, a facile chain (proton) transfer process, is suggested by these results.

c. Structural characterization of poly(β -pinene oxide). The proton nmr spectra of β -pinene oxide monomer and polymer are shown in Figures 16 and 17. Analysis of the monomer spectrum indicate strong resonances at 0.922 δ and 1.24 δ which are easily assigned to

TABLE XIII
RESULTS OF IRRADIATION OF POLY(β -PINENE OXIDE)

Code No.	Temp. (°C)	Monomer (grams)	Dose (Mrad)	Polymer (grams)	Percent Conversion	G(-m)
I-1 ^a	25	1.469	5.91	--	--	--
I-2	25	2.164	5.14	0.503	24.6	304
I-3	25	1.586	4.18	0.405	25.6	388.
I-4	25	2.164	3.39	0.437	19.9	373
II-1	25	4.163	0.88	0.133	2.7	195
II-2	25	4.137	1.76	0.338	8.2	294
II-3	25	4.205	2.65	0.375	8.9	213
II-4	25	4.220	3.53	0.346	8.2	147
III-2	25	4.222	3.80	3.396	80.4	1342
III-3	25	4.335	4.44	2.034	46.9	670
III-4	25	3.821	4.46	1.538	40.2	572
IV-1	25	5.047	4.97	1.873	37.1	474
IV-4	25	5.230	3.98	1.873	35.0	557
IV-5 ^b	25	5.074	3.98	0.072	1.4	23

^aSample was spilled.

^bSample was doped with 1% by volume of tripropylamine.

TABLE XIV
NUMBER-AVERAGE MOLECULAR WEIGHTS
OF POLY(β -PINENE OXIDE)

Sample No.	Temp. (°C)	Percent Conversion	Dose (Mrad)	G(-m)	$\bar{M}_n$	$\bar{DP}_n$
III-2	25	46.9	4.44	670	750	5.0
III-3	25	40.2	4.46	572	460	3.0

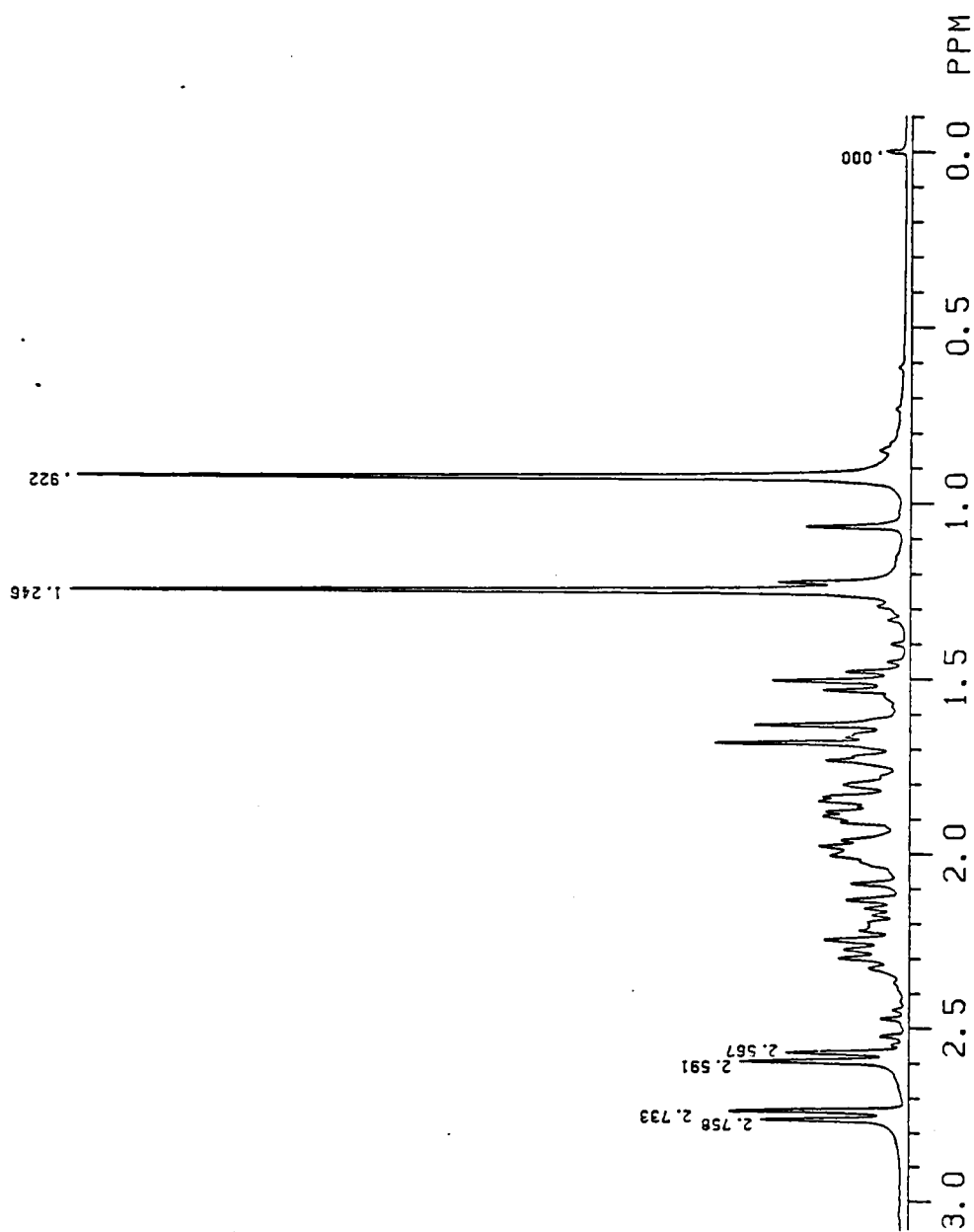
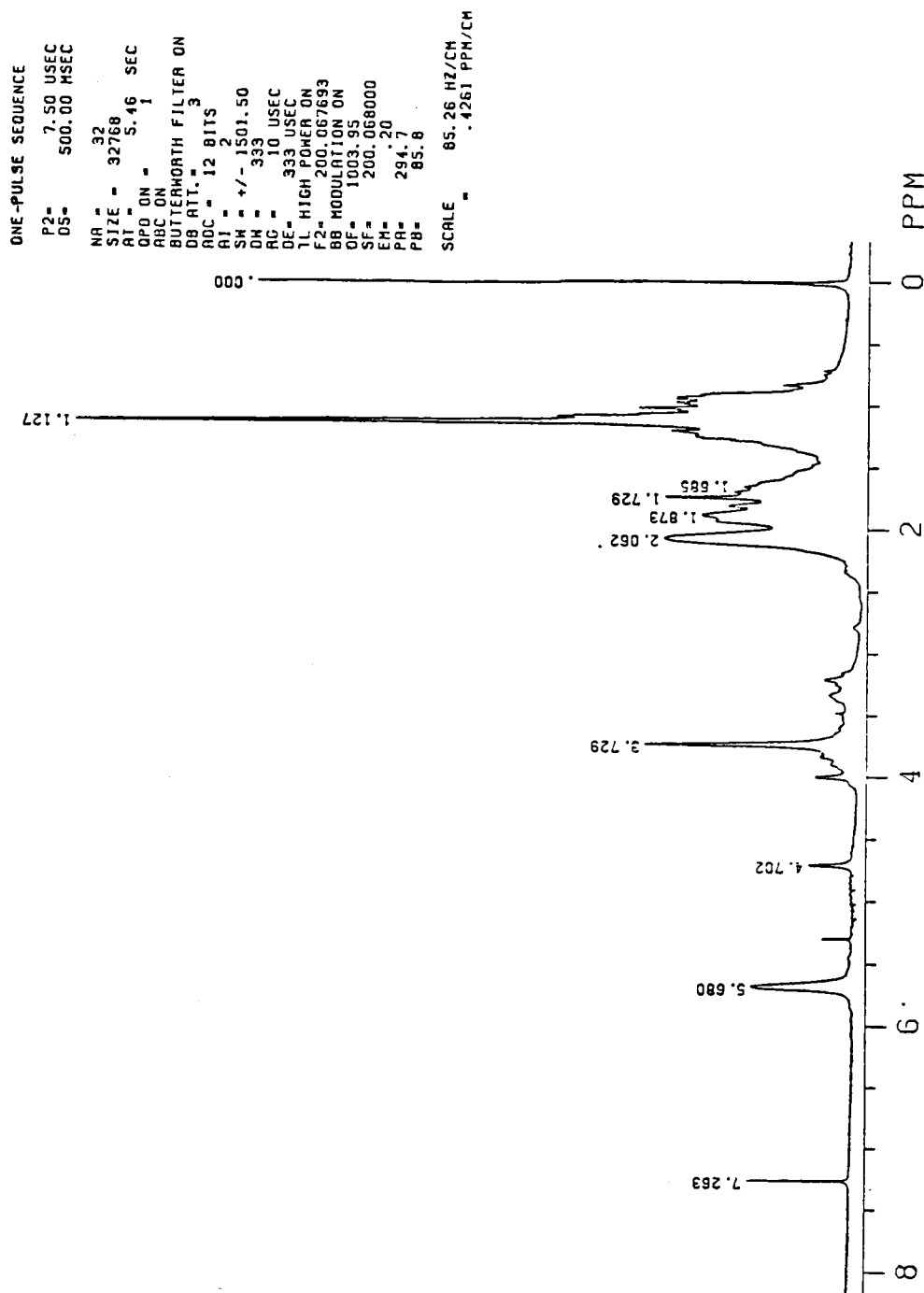


Figure 16. Proton nmr spectrum of β -pinene oxide monomer.

Figure 17. Proton nmr spectrum of poly(β -pinene oxide).

the gem-dimethyl moiety of the bicyclic bridge structure. The remaining peaks from 1.4 δ to 2.8 δ are assigned to the methylene, methine and O-C-H protons.

The proton nmr spectrum of the polymer shows a distinct sharp peak at 1.127 δ similar to the gem-dimethyl group found in poly(isobutylene oxide) repeat unit. Hence, by analogy, such an assignment is made. Other peaks seen in the polymer spectrum are two olefinic protons (4.7 δ and 5.68 δ), a broad O-C-H proton (3.0 δ to 4.0 δ), and a methyl hydrogen peak at 1.729 δ .

The resonance peaks at 1.729 δ and 4.70 δ are similar to the chemical shift assignments of the pendant isopropenyl group found in both poly((+)-limonene oxide) and poly(α -pinene oxide). The olefinic endocyclic peak at 5.68 δ comes from the opening of the bicyclic bridge structure.

The carbon-13 nmr spectrum of poly(β -pinene oxide) shown in Figure 18 exhibits peaks at 20.8 δ , 108.0 δ and 149.0 δ which are attributed to the isopropenyl pendant group chemical shifts found in both (+)-limonene oxide (Figure 8, page 42) and α -pinene oxide (Figure 13, page 57) polymer spectrum.

Further characterization work was carried out with a Perkin Elmer infrared spectrophotometer. The spectrum of the polymer is shown in Figure 19. Characteristic absorption frequencies corresponding to the gem-dimethyls were observed at 1370 cm^{-1} and 1390 cm^{-1} . Table XV lists the remaining frequencies and their assignments.

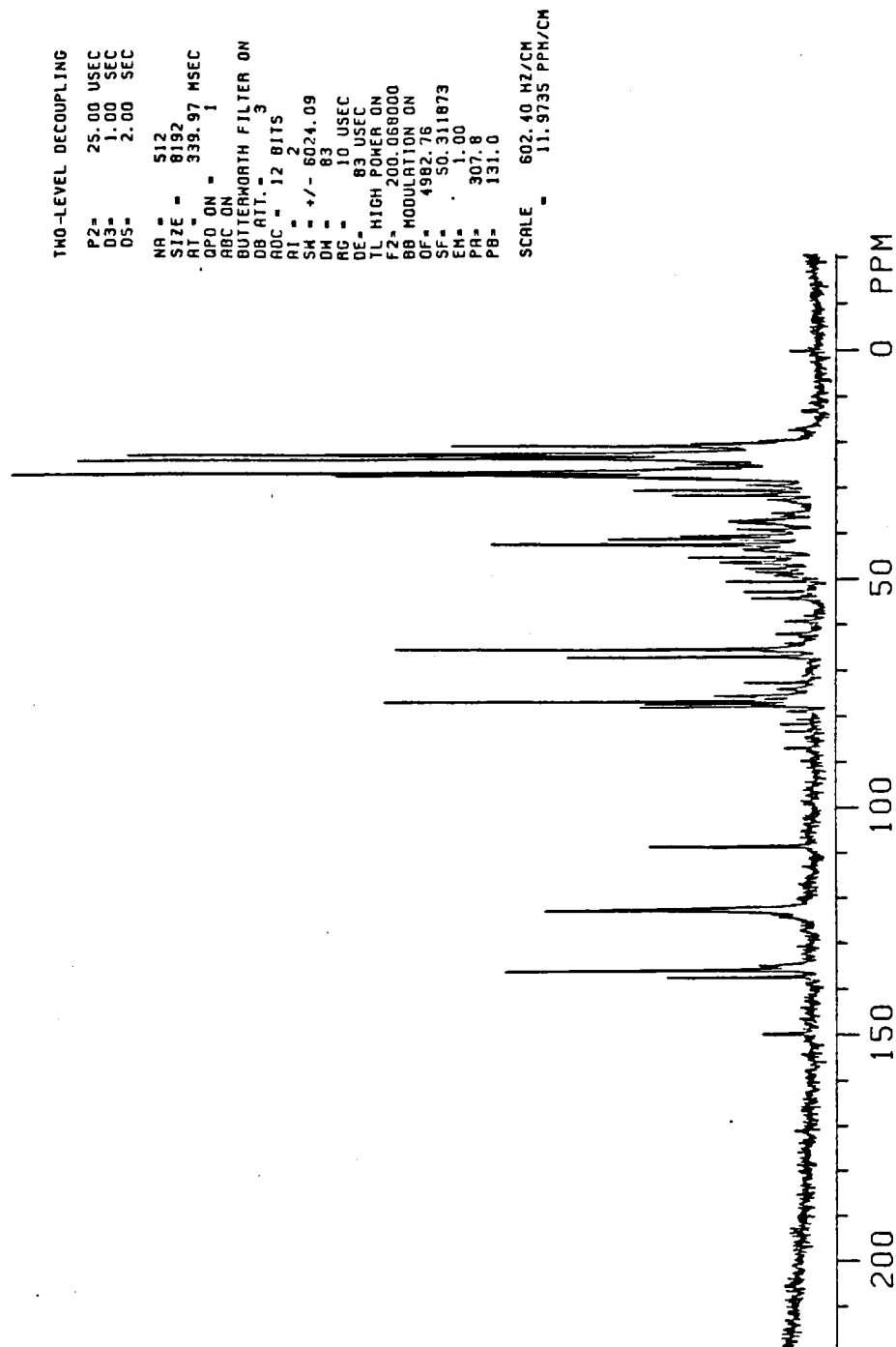


Figure 18. Carbon-13 nmr spectrum of poly(β -pinene oxide).

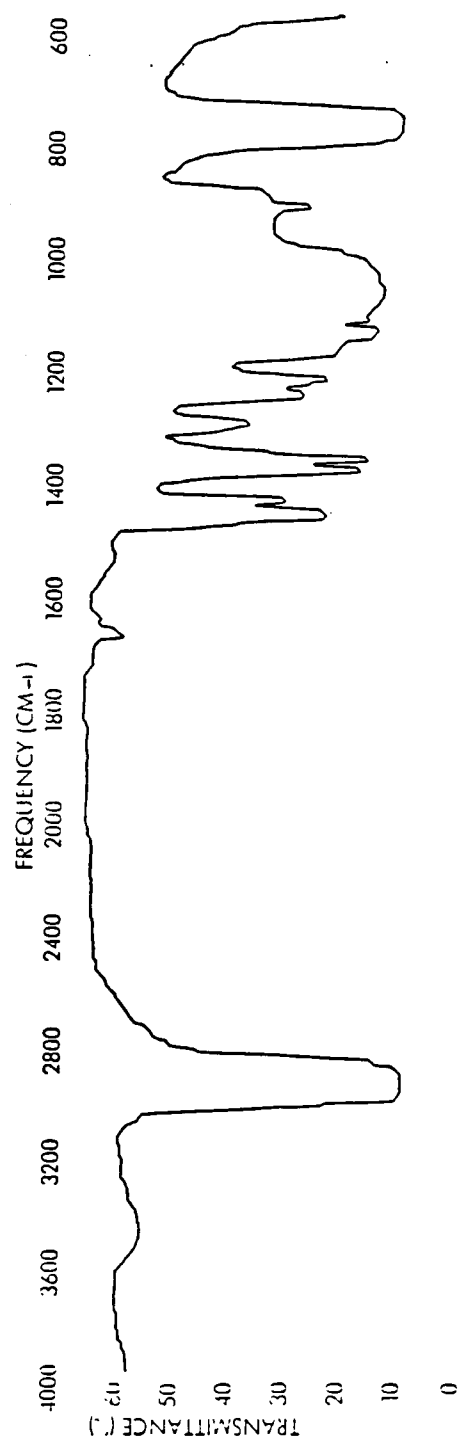


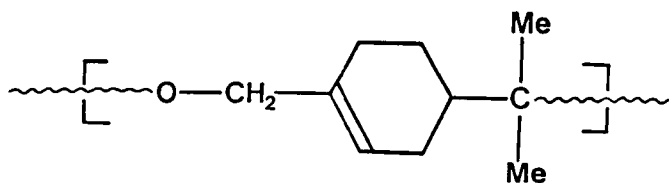
Figure 19. Infra-red absorption spectrum of poly(β -pinene oxide).

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

Absorptions (cm^{-1})	Intensity	Assignments
3020	weak	C=C-H stretch
2800-3000	strong	C-H stretch
1665-1670	weak	C=C
1430-1469	strong	-CH ₂ deformation
1365-1383	strong	-C(CH ₃) ₂ sym. deformation
1000-1180	broad	C-O-C stretch
890	weak	-CH ₂ =C< non-cyclic
850-870	absent	cyclobutane ring deformations and stretching

3. Discussion

Under dry conditions, β -pinene oxide monomer undergoes radiation-induced cationic polymerization. High conversions of monomer to polymer were obtained at high doses. In contrast to catalytic polymerization where side reactions accounted for a large percentage of the yield, the amount of precipitable polymer obtained from radiation-induced polymerization was much higher. $G(-m)$ values obtained on the average were 460. Since the $G(-m)$ value calculated for the amine-doped sample was only 22.6 as compared to the "control" value of 557, it is clear that the kinetic chain length is affected by the amine. The $\overline{M}_n$ corresponded to a $\overline{DP}_n$ of 4.0. Since the estimated kinetic chain length ($v = 2300$) is much larger than the $\overline{DP}_n$, a chain (proton) transfer process is implicated. Evidence for the proposed proton transfer was also found in the proton and carbon-13 nmr analysis of the polymer spectrum. Structural analysis indicates that the structure given below is the main repeat unit of poly(β -pinene oxide):



CHAPTER V

CONCLUSION

This work clearly indicates that radiation-induced cationic polymerization of terpene epoxides ((+)-limonene oxide, α -pinene oxide and β -pinene oxide) can proceed in dry systems. Spectroscopic analysis of the α -pinene oxide and β -pinene oxide polymers showed unsaturated end groups consistent with a proton transfer mechanism of chain transfer. Further indication of proton transfer came from the rather large kinetic chain length in comparison with the $\overline{DP}_n$ ($v \gg \overline{DP}_n$). According to the $G(-m)$ values obtained in all three systems, (+)-limonene oxide monomer had the highest rate of polymerization. The rates of α -pinene oxide and β -pinene oxide polymerization were lower by a factor of 5. The strongly retarding effect of tripropylamine, a known cationic scavenger, confirmed the cationic nature of the propagating species. By irradiation, conversions of monomer to precipitable polymer of at least 80% were obtained for (+)-limonene oxide and β -pinene oxide. In contrast, rearrangement of the monomers in the catalytic polymerization often accounted for 90-95% of the products obtained.³²

Thermal characterization and structural nmr studies revealed that the polymers produced by irradiation have comparable properties and molecular structures to those of the polymers prepared catalytically. The nature of the propagating species is therefore likely to be similar in the two cases, and in particular, the opening of the epoxide ring for α -pinene oxide and β -pinene oxide polymerization

is accompanied by the concomitant opening of the cyclobutane ring structure. Similar rearrangement process has also been found to occur in the cationic polymerization of β -pinene.^{32,33,34,35,36}

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APPENDIX

APPENDIX

RESULTS OF PRELIMINARY STUDIES WITH CYCLOHEXENE OXIDE

TABLE XVI

RESULTS OF IRRADIATION OF CYCLOHEXENE OXIDE

Code No.	Temp. (°C)	Monomer (grams)	Dose (Mrad)	Polymer (grams)	Percent Conversion	G(-m) x 10 ⁻³
I-1	25	1.25	0.275	0.553	44.0	15.730
I-2	25	2.47	0.275	1.163	47.0	16.797
I-3	25	2.31	0.275	0.743	32.1	11.472
I-4	25	3.65	0.275	0.916	25.1	8.9701

VITA

James A. Aikins was born in Cape-Coast, Ghana, West Africa on the 20th of June 1952. He graduated from St. Augustine's Secondary School in June 1971. He attended Workers College in Accra, Ghana for two years before coming to the United States to go to college at Huntington, Indiana in the Fall of 1974. He graduated from Huntington College in the Spring of 1980 with a B. S. degree in chemistry.

In the Fall of 1980 he accepted a teaching assistantship from The University of Tennessee, Knoxville to study chemistry. He attended the 187th National Meeting of the American Chemical Society held in April 1984 at which his major professor presented a paper based on his thesis. He will receive his M. S. degree in chemistry, with emphasis in polymer chemistry in August 1984.

83°32'30"

GEOLOGY OF THE WINDING STAIR GAP AREA



35°07'30"

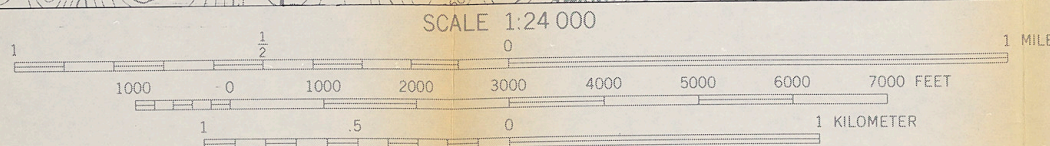
map symbols

- quartzo-feldspathic gneiss
- ▼ Bt-Hbl granulite
- ◆ Sil schist
- Bt-Grt granulite
- ✦ calc-silicate gneiss
- ★ orthopyroxenite
- 67 strike and dip of S_2 foliation and outcrop location

Wayah
Bald
Quadrangle

Rainbow
Springs
Quadrangle

geology by
Steve Absher



CONTOUR INTERVAL 40 FEET
NATIONAL GEODETIC VERTICAL DATUM OF 1929