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To the Graduate Council:

I am submitting herewith a thesis written by Bennie F. Kee entitled "Yielding and Crazing Properties of Modified Polystyrenes." I recommend that it be accepted for fifteen quarter hours of credit in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemical Engineering.

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YIELDING AND CRAZING PROPERTIES OF MODIFIED POLYSTYRENES

A Thesis

Presented to

the Graduate Council of

The University of Tennessee

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

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by

Bennie F. Kee

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ABSTRACT

The purpose of this investigation was to study the crazing and yielding properties of modified polystyrenes. An attempt was made to make a block copolymer of polystyrene and another molecule but the attempt was futile. Polystyrenes with modified end groups were made and tested.

Much time and effort were spent trying to synthesize a block copolymer from difunctional polystyrene molecules and small linking compounds. No samples were made that could be tested.

Higher molecular weight polystyrenes were synthesized with two different initiators. One initiator was used to place small nonreactive end groups on the polymer. The other places an organic acid group on the chain ends. Various alcohols were esterfied with the organic acid end groups. A range of molecular weights from 67,000 to 147,000 were prepared. The molecular weights were determined by gel permeation chromatography. The alcohols used were cyclohexanol and eicosanol. Rubidium hydroxide was also used. Tensile bars were made from the polystyrene using an injection molding machine. The tensile bars were then tested with an Instron tensile testing machine which was equipped with a craze detection mechanism that marked the onset of crazing on the Instron chart. Yield stress, crazing stress, fracture strain, and an apparent modulus were calculated for each sample. Glass transition temperatures were determined by a differential scanning calorimeter.

The end groups attached to the polymers had no effect on the crazing, yielding, or other properties of polystyrene tested. The molecular weights of the polystyrenes had an interesting effect. The higher molecular weight polystyrene had higher yield stresses, but the crazing stress remained almost constant. All the other parameters calculated increased proportionally with molecular weight except the modulus which remained constant.

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CHAPTER I

INTRODUCTION

Polystyrene is an amorphous, glassy polymer. It has many excellent properties including transparency and low density which make it desirable for many applications. However, a serious drawback in some uses is its low impact strength. Changes have been made in the basic material but one property is usually improved at the expense of another property. Rubber is generally added to increase the impact strength and produce what is called high impact polystyrene, but the tensile strength is reduced.

This experiment is conducted to determine the effects of small chemical modifications on the yielding properties of polystyrene. Bulky end groups are added to various size polystyrene chains and these results are compared with polystyrene chains of similar molecular weights with small end groups. An attempt was made to form a block copolymer of polystyrene and short chain molecules but no testable samples were made.

In order to understand the fracture process in polystyrene, careful attention must be given to the crazing process. Fracture generally initiates in the crazed material. Chapter II deals with the general properties of polystyrene. Emphasis is placed on crazing characteristics, molecular weight properties, and a few modifications to the basic polymer are discussed.

The other parts of the thesis discuss the experimental parts of the tests and compare the results to other experimenter's results.

CHAPTER II

PROPERTIES OF POLYSTYRENE

A. Crazing Properties

When polystyrene, poly(methyl methacrylate), polycarbonate, or other glassy thermoplastics are placed under a stress for a period of time, something appearing to be fine hair like cracks are formed in the specimen. Actually these cracks are not true cracks at all. They are filled with load bearing craze material which gives the polymer a white appearance and destroys the transparency of the material.[1-3] Cracks can propagate from the coalescence of voids within a craze and cause catastropic failure of the material.[1,4-9] Bearing this out, Roger Kambour[10] found eight of nine glassy thermoplastics tested tended to break in the craze material and amorphous polymers showed crazing response ahead of crack tips and on fracture surfaces.[3,10-15] In brittle thermoplastics like polystyrene, low impact strength is an undesirable characteristic. An improvement in performance characteristics of the thermoplastic material would seem to depend on modifying the crazing patterns of the plastic. In order to see how to modify crazing, one must first learn how crazing occurs and the properties of the craze material.

Much work has been done in determining the nature of the craze material and the mechanisms by which crazing occurs. Crazed material is much different from the bulk polymer which surrounds it. The craze

material is highly oriented in the direction of the applied stress. It has a lower density than the bulk polymer and has void volumes associated with it. These void volumes are interconnected as shown by Nielson[16] in his liquid crazing experiments. Generally polystyrene crazes have a void volume of about 40 percent as estimated by Kambour.[17] The elastic modulus of the craze is lower than that of the bulk polymer. Some controversy has developed over whether or not a craze is a region of impaired strength. Bird, Rooney, and Mann[18] took samples which were internally crazed, removed the outer uncrazed skin and tested them to failure. The mean fracture stress of the original samples was 41.8 MN/m^2. The crazed specimens broke at 43.5 MN/m^2. Hence they concluded that the formation of craze material is certainly not accompanied by a reduction of strength.

O. K. Spurr, Jr., and W. D. Niegisch[19] have proposed the following mechanism for the formation of stress induced crazes. It is divided into three parts: initiation, propagation, and termination. The initiation mechanism determines the location of the craze. It usually occurs at some discontinuity in the polymer which acts as a stress concentrator under tension. The discontinuity may be anything from submicroscopic monomer to dust, void, etc., to microscopic flaws, or it may be an orientation effect that lends itself to crazing.[16,20,21] Anything which acts as a stress concentrator is a discontinuity since it causes a mechanical weakness. Before crazing can occur a critical value of stress for craze initiation must be reached.[2,18,20,22-26]

This critical value is dependent on temperature, strain rate, strain history, and the orientation of the sample stressed. Even after the critical stress is reached crazing may not begin immediately. Often a time lag is observed, and if the strain rate is high enough, fracture may occur with little or no crazing. Temperature plays an important role in determining the critical stress. S. Sternstien, L. Ongchin, and A. Silverman[22] have plotted the critical stress versus temperature for a given load time of ten minutes for PMMA. R. N. Haward, B. M. Murphy, and E. F. T. White[2] have plotted critical crazing stress versus log strain rate at various temperatures for polystyrene. If the temperature exceeds the glass transition temperature, crazing does not occur at all and the material draws down as it yields.

The propagation step is the creation of craze material. A craze is formed by the plastic work of rearranging molecules surrounding a discontinuity. The craze generally opens in a direction perpendicular to the applied stress. Orientation of the craze material is thought to occur by chains slipping past one another on an intermolecular level with the ease of crazing depending on the difficulty of the chains slidding past one another. The process is anisotropic and nonhomogeneous throughout the sample. The nature of the rearrangement process seems to be a viscous flow with most of the energy needed to propagate the craze absorbed as heat.[2,20,22,23] The high degree of orientation in crazes is confirmed by X-ray diffraction, direction of craze growth, uniaxial strength, elongation patterns and healing of crazes with heat or solvents.

In some creep tests at high stresses, Spurr and Niegisch[19] observed that a specimen would support a stress for a period of time with little elongation then suddenly elongate rapidly. The elongated section was found to be stable over additional long periods of stress application. The crazes seem to grow rapidly at first, then when stress is dissipated over a larger area, grow at a much slower rate. The slowing of craze propagation also indicates that the craze material tends to strain harden as it is elongated.

Termination occurs after long stressing time when the craze no longer grows. The stress may be diluted to a value less than what would propagate a craze, or a distortion may occur at the craze tip which limits the craze. An indication that the latter mechanism occurs is observed in that crazes produced at lower stresses tend to be larger in both depth and width. Another way a craze may terminate is fracture of the craze material itself due to excessive stress or through a notch effect caused by a flaw in the craze material. The notch is caused by a coalescence of voids to form a large cavity which propagates slowly until a critical stress is reached at which fast crack propagation occurs. In the low fracture rate the craze material breaks in the center of the craze. As the fracture rate increases the cracks tend to jump between the interfaces of the craze material and the bulk material. This region is called the mirror region.[11,27] Proceeding the crack there appears to be dehesion of the craze material and bulk material, but the exact occurrences are not entirely explained. The third region is one of irregular crack propagation. It is rough with few details.[15,28]

In addition to tensile stress crazing, other types of crazing have been observed by flexing samples and by the action of solvents and nonsolvents on the samples. Nielson[16] exposed polystyrene to a nonsolvent, methanol, for a day, then to a solvent, S. Kelly solve B, and produced crazing in a few seconds. The liquid's effect is explained by pressures produced in the samples by the liquids. This is equivalent to saying that liquid crazing is produced in about the same manner that tensile crazing originates.

The surrounding environment of the test sample plays an important role in tensile crazing.[21,24,25,29] The critical stress may either be increased or reduced depending on whether the environment is crazing or noncrazing. For example, Kambour and Kopp[30] used ethyl alcohol as a crazing environment for polycarbonate to lower the crazing stress. Carbon tetrachloride and wet nitrogen are crazing inhibitors, and water vapor shows healing effects on crazes.

B. Modifications to the Base Polymer

Another phenomenon which occurs when some thermoplastics are contacted with certain liquids. It is called plasticizing. The plasticizing agent is absorbed into the surface and lowers the glass transition temperature of the surface below the environmental temperature. The effect eliminates crazing on the surface. Internal crazes tend to be more stable under stress than surface crazes. The major difficulties in plasticizing are finding agents which will both stay in the surface and lower the glass transition temperature enough. Many plasticizing

agents tend to plate out on the surface or disperse throughout the polymer. Still all pasticizing can do is stop surface crazing and permit more elongation by sacrificing some yield strength.[31]

Others have tried various methods to improve impact strength in polystyrene and other thermoplastics. R. N. Haward and J. Mann[32] discuss some of these ways. Aside from the limited increases achieved by higher molecular weight or changes in molecular weight distribution, people have tried crosslinking through copolymerization, a tempering process, and the introduction of crack stopping mechanisms. The tempering process showed no change in tensile strength. Thus, it demonstrates crazing occurs throughout the material. In a polystyrene and rubber heterophase system used by Holliday[33] some improvement in impact strength is achieved. The rubber particles succeed in checking crack growth, however the rubber lowers the yielding strength. The yield stress of the polystyrene-rubber material is improved by copolymerizing the rubber and styrene instead of blending it together. Additional increases in yield strength result when acrylonitrile is added to the styrene-butadiene copolymer. R. S. Moore and C. Gieniewski[34] conducted experiments with acrylonitrile-butadiene-styrene (ABS) and styrene acrylonitrile (SAN) copolymers and polystyrene, and they determined the relative ease of crazing is opposite to the order listed. The copolymers must have a local mobility or a ductility which allows yielding before failure. The ABS copolymer seems to allow more yielding than the SAN copolymer, perhaps an extreme amount. The styrene acrylonitrile copolymer is prepared in a suspension or an emulsion polymerization similarly

to the way polystyrene is made. ABS is prepared commercially by two methods. First it may be blended in an alloying process. This is called type A. Another way is to prepare it by copolymerization of the monomers. In both types of ABS, the rubber is thought to exist as discrete particles as it does in high impact strength polystyrene. However, the presence of acrylonitrile increases the compatability some. As the amount of rubber is increased in the impact styrenes, the impact strength is increased, but the moldability, softening point, and surface finish is decreased. Five to 20 percent rubber is the normal amount of rubber used in this application. SAN has better chemical resistance, surface hardness, and mar resistance than normal polystyrene. But, a yellowish tinge must be overcome by adding a blueing agent. The ABS copolymer has high impact strength, good chemical resistance, and is extremely tough, but it is an opaque material and has a much lower tensile strength than polystyrene.[35-38] The copolymerized materials seem to have characteristics between the materials copolymerized. Thus to achieve yielding before fracture in polystyrene, a large sacrifice in yielding strength has been made, and changes in other physical properties result.

C. Molecular Weight Classifications

Three general classifications of polystyrene are used to denote distinctive properties for each type. Quick processing, general purpose, heat resistant grades differ in molecular weight average and distribution and have varying amounts of lubrication such as esters, organic acids, and mineral oils which in addition to improving flow reduce brittleness,

lower softening point, and increase setup time. Quick processing grades either reduce setup time or improve the flow characteristics. Fast setting resins have little lubrication and are often slightly lower in molecular weight than general purpose grades. The lower molecular weight improves flow slightly and aids in quick setting. Easy flow grades on the other hand have fairly large amounts of lubricant and a large portion of low molecular weight polystyrene. The brittleness of the low molecular material is offset slightly by the lubricant. Heat resistant grades are made from high molecular weight polystyrene with no lubricants. The flow is reduced and parts are more difficult to mold, and molded parts must be annealed to relieve stress. Typical viscosity determined molecular weights are: easy flow--60,000, general purpose--80,000, heat resistant--100,000, difficult to mold--120,000.[36,37]

D. Summary

In summary, crazes are associated with plastic deformation. They originate around a defect which acts as a stress concentrator and grow until the stress is diminished or until the material fractures. Once a material crazes it is much more subject to failure. The ease with which a sample crazes is dependent on such things as molecular weight, orientation, temperature, strain rate, and the history of the material.[32] There is a critical stress which must be reached before crazing will occur, but reaching this stress does not guarantee craze initiation. The craze material is a less dense, highly oriented polymer. Both the elastic modulus and the refractive index of the crazed material is less

than that of the bulk polymer. The refractive index change is the most often used method for detecting crazing. Overall, crazing is a process which initiates failure. Alterations to change the yielding properties of the thermoplastics have been tried on an intermolecular level with crack stopping mechanisms and on an intramolecular level with copolymerization, but these methods have undesirable properties associated with them.

CHAPTER III

EXPERIMENTAL PROCEDURE AND RESULTS

A. Block Copolymers

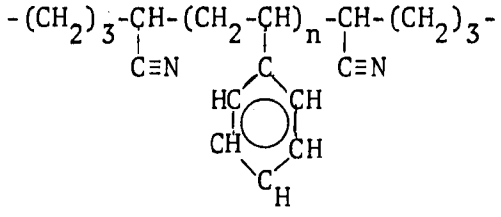
Synthesis 1: In the first experiment polystyrene with difunctional organic acid end groups[39] was prepared via solution polymerization. A calculated amount of 4,4' azobis (4-cyanovaleric acid) (ACVA) was used to achieve the desired molecular weight of 6000. (See Appendix A for calculations.) The ACVA initiator was dissolved in tetrahydrofuran (THF) and added dropwise to a one liter flask containing 230 ml. of styrene monomer and 355 ml. of reagent grade benzene. The contents were stirred while the mixture refluxed in an appropriate setup. The polymerization was conducted under a nitrogen atmosphere. After approximately three hours, the reaction mixture was cooled and precipitated in an excess of methanol. The precipitant was filtered and dried in a vacuum oven at 70°C overnight. The above procedure was essentially the same for all the preparations of the prepolymers. The amounts of materials varied, depending on the amount of prepolymer desired, but the ratio of the ingredients remained constant. The only exceptions occurred when the amount of initiator was changed in order to vary the molecular weight of the prepolymer. The molecular weights of the prepolymers were chiefly determined by gel permeation chromatography using a Water's Associate Chromatograph with calibration curves supplied by George Sadakne[40] and

Yoshika Ide. Other methods were used in later experiments to verify the results obtained by this method.

After the preparation of the prepolymer, it was redissolved in benzene and reacted with a fourfold excess of thionyl chloride (8.3 ml.)

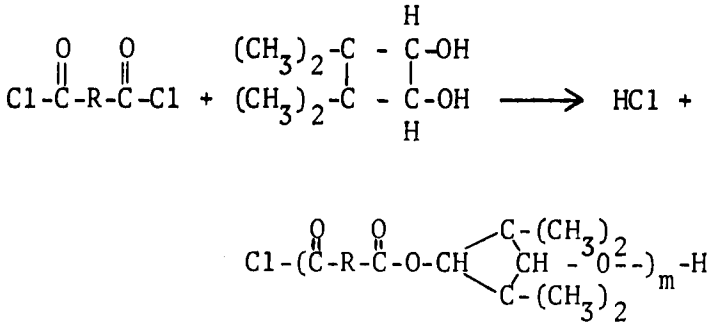
(3.1) $$HOOC\text{-}R\text{-}COOH + SOCl_2 \longrightarrow Cl\text{-}\overset{O}{\overset{\|}{C}}\text{-}R\text{-}\overset{O}{\overset{\|}{C}}\text{-}Cl + HCl$$

where R stands for:



The reaction ran for two hours while the mixture was stirred under a nitrogen atmosphere at room temperature in a liter flask. The contents of the flask were then put in a beaker, covered with perforated aluminum foil, and placed in a vacuum oven at 30°C to remove any excess thionyl chloride, benzene, and other low molecular weight products. The vacuum pump was carefully trapped with powdered sodium hydroxide and with a cold trap cooled by a dry ice and methanol mixture. Thionyl chloride is very corrosive and will quickly ruin the pump if it is not well trapped. The acid chloride prepolymer was redissolved in benzene and kept under a nitrogen atmosphere. A stoichiometric amount of 2,2,4,4, tetramethyl 1,3 cyclobutanediol was dissolved in THF and added dropwise to the acid chloride.

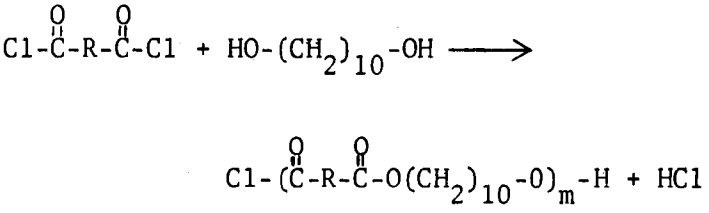
(3.2)



The product was precipitated in methanol and dried in a vacuum oven. All molecular weights for the copolymers were determined by gel permeation chromatography. The molecular weights for the copolymer and prepolymers are given in Table 3-1.

Synthesis 2: The procedure in synthesis 1 was repeated with the exception of pulling a vacuum on the reaction mixture while it was still inside the flask, rather than removing the mixture and placing the prepolymer acid chloride in a vacuum oven. The linking agent was 1,10 decanediol.

(3.3)



Synthesis 3. In this synthesis the reaction between the acid end groups and the thionyl chloride was run at an elevated temperature. The amount of thionyl chloride was increased to a twenty fold excess. In the early syntheses no thermometers were available, but the rheostate

TABLE 3-1

BLOCK COPOLYMER RESULTS

Synthesis	Prepolymer* $\bar{M}_n$	Prepolymer* $\bar{M}_w$	Copolymer* $\bar{M}_n$	Copolymer* $\bar{M}_w$	DP.	
1	6090	11,700	8800	12,800	1.44	
2	6090	11,700	8490	13,410	1.39	
3	7550	14,400	11,590	18,810	1.53	
4	8200	14,230	15,400	31,130	1.88	
5	----	------	------	------	----	
6	8680	16,800	17,160	35,400	1.98	
7	8490	16,230				
	8660**					
8	8490	16,230	8,930	20,500	1.03	(1 hr.)
			13,140	35,710	1.55	(2 hr.)
			16,110	50,930	1.90	(24 hr.)
9	8490	16,230	18,330	38,290	2.16	
10	polymer A					
	9460	15,700				
	9840**					
	polymer B					
	8640	14,170				
	8720**					
	8800[a]					
	10,640[b]					
11	8640	14,170	25,180	89,530	2.91	
12	----	------	------	------	----	
13	8640	14,170	15,760	43,150	1.83	
14	8640	14,170	------	------	1.0	
15	9460	15,700	------	------	1.0	
16	8640	14,170	12,500	38,150	1.45	(80%)
			13,220	39,290	1.53	(85%)
			13,110	42,310	1.52	(95%)
			12,990	40,710	1.50	(100%)
			12,470	40,690	1.45	(105%)
17	8640	14,170	------	------	1.0	
18	8640	14,170	------	------	1.0	
19	8640	14,170	------	------	1.0	
20	8640	14,170	------	------	1.0	
21	11,270	25,000				
	12,600[a]		30,400	113,000	2.70	(dried)
			25,400	96,770	2.25	(heptane)
			26,370	102,240	2.34	(d. hept.)
			15,100	57,130	1.34	(methanol)

TABLE 3-1 (continued)

Synthesis	Prepolymer* $\bar{M}_n$	Prepolymer* $\bar{M}_w$	Copolymer* $\bar{M}_n$	Copolymer* $\bar{M}_w$	DP.
22	7930 7320**	12,940	26,100	94,200	3.29
23	9460	15,700	18,900	49,700	2.00
24	8640	14,170	24,100	65,300	2.79
25	9460	15,700	------	------	1.0

*GPC determined molecular weight unless otherwise noted.

**Molecular weight determined by titrating the prepolymer to a phenolpthalien end point, and multiplying the equivalent weight by two.

[a]Molecular weight was determined by titrating the prepolymer to an end point determined using a pH meter and calculating it.

[b]Molecular weight was determined by using a vapor phase osmometer.

setting corresponded to approximately 30°C. The 1,10 decanediol was the linking agent.

Synthesis 4: The amount of material was reduced one half in this experiment. Excess thionyl chloride was removed by freezing the reaction mixture in the 500 ml. reaction flask. It was immersed into a mixture of dry ice and alcohol. Then a vacuum was applied and the benzene and excess thionyl chloride sublimated. This process ran overnight. The vacuum traps were changed several times during the procedure. The acid chloride prepolymer was then redissolved in benzene that had been dried with calcium hydride powder. The benzene and calcium hydride were stirred in a sealed flask at room temperature until a couple of hours before use. The mixture was allowed to settle, and the dry benzene pipetted from near the surface. The 1,10 decanediol was dried in a vacuum oven at 50°C prior to use.

Synthesis 5: This synthesis was identical to the previous one, but the temperature of the thionyl chloride reaction was too high (slightly less than 60°C) and a gel formed.[40]

Synthesis 6: Synthesis 5 was repeated at a slightly lower temperature (45°C) for the acyl chloride reaction. The linking agent was 1,10 decanediol.

Synthesis 7: A larger amount of prepolymer was made in this reaction. Three and a half times the amounts of ingredients used in the first synthesis were put in a three liter kettle reactor. Two less grams of initiator (ACVA) were used to increase the molecular weight slightly. About a gram of prepolymer was titrated with 0.00702 M sodium

hydroxide solution which was made from reagent grade methanol and a small amount of water plus sodium hydroxide pellets. The sodium hydroxide solution was standardized with potassium acid pthalate (KHP) dissolved in distilled water. Phenolpthalein was used to indicate the end point. The prepolymer was dissolved in about 200 ml. of reagent grade benzene and titrated until the first pink color was seen in the solution. Fresh sodium hydroxide was used, and the solution was protected against carbon dioxide while titrating by an Ascarite trap which consists of sodium hydroxide deposited on asbestos.

Synthesis 8: Prepolymer from synthesis 7 was used in this reaction. Dried 1,12 diaminododecane is the linking agent. All other details remain constant.

(3.4) $$Cl\text{-}\overset{O}{\overset{\|}{C}}\text{-}R\text{-}\overset{O}{\overset{\|}{C}}\text{-}Cl + H_2N\text{-}(CH_2)_{12}\text{-}NH_2 \longrightarrow$$

$$H(\text{-}NH(\text{-}CH_2)_{12}\text{-}NH\text{-}\overset{O}{\overset{\|}{C}}\text{-}R\text{-}\overset{O}{\overset{\|}{C}}\text{-})_m Cl + HCl$$

The copolymer molecular weight was checked at time intervals of one hour, two hours, and overnight.

Synthesis 9: The same prepolymer previously used was reacted, as above, except the step where the excess thionyl chloride is removed was omitted. The 1,12 dodecanediamine, linking agent, was added directly to the reaction mixture without dissolving it in a solvent.

Synthesis 10: Two more large prepolymer batches (A and B) were prepared in the same manner as in synthesis 7. The end groups were

titrated as before. Prepolymer B was titrated a second time using a pH meter to plot a curve which gave the end point of the titration. The titrations were repeated several times. The sodium hydroxide solution was also standardized using the pH meter. A Hitachi Perkin-Elmer Model 115 vapor phase osometer was used to give the number average molecular weight. The solvent for polystyrene was reagent grade methyl isobutyl ketone. A calibration curve using benzil as a standard was prepared (see Appendix B). The molecular weights were calculated corresponding to the concentrations at which they were obtained. This data was plotted, and the molecular weight at infinite dilution determined from the graph.

Synthesis 11: Prepolymer B from synthesis 10 was used. The reaction mixture was freeze dried to remove excess thionyl chloride. Some pyridine (5 percent) was added to the benzene as the acid chloride mixture was redissolved after freeze drying. After the 1,12 dodecane linking agent was added and mostly dissolved, the temperature of the mixture was slowly increased to its reflux point and refluxed for four hours. Other than these changes, the synthesis is done as in synthesis 9.

Synthesis 12: An attempt to make an unfreeze dried reaction as in synthesis 9 (the excess thionyl chloride not removed) failed when the mixture gelled.

Synthesis 13: Using prepolymer B synthesis 11 was repeated with a slightly higher temperature (50°C) for the thionyl chloride-acid end group reaction.

Synthesis 14: Instead of benzene as the solvent, methyl isobutyl ketone was used, and the previous procedure repeated.

Synthesis 15: Prepolymer A was used in this synthesis. The dried acid chloride prepolymer was redissolved in reagent grade xylene. The 1,8 octanediol was the linking agent. A small amount of concentrated sulfuric acid was used as a catalyst.

Synthesis 16: Prepolymer B was allowed 40 hours at 40°C to react with a twenty fold excess of thionyl chloride. The mixture was freeze dried and redissolved in benzene. A small amount of pyridine was added to aid in the removal of any hydrogen chloride product. The 1,8 diaminoctane was added incrementally from 80 percent to 105 percent of the stoichiometric amount. The molecular weights at each increment were checked.

Synthesis 17: The acid chloride prepolymer was made from prepolymer B at 40°C. The linking agent, 1,8 diamineoctane, was dissolved in methyl acetate and added to the redissolved acid chloride prepolymer.

Synthesis 18: In this synthesis 24.7 g. of prepolymer B was reacted with a five fold excess of thionyl chloride at 80°C. Otherwise the procedure remained constant. The 1,8 diamineoctane was the linking agent.

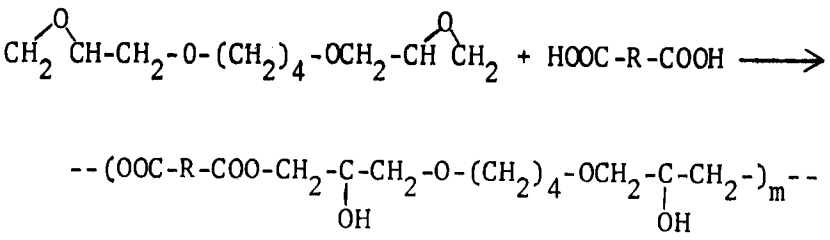
Synthesis 19: As in the previous experiment, the thionyl chloride reaction was changed. At a temperature of 54°C, 17.8 g. of prepolymer B were reacted with a ten fold excess of thionyl chloride. Other variables were held constant.

Synthesis 20: Prepolymer B was reacted with a twelve fold excess of thionyl chloride at 60°C. Otherwise this synthesis was identical to the one preceding it.

Synthesis 21: A new batch of prepolymer was made as in synthesis 7 in the three liter kettle reactor. It was precipitated twice from benzene solutions with methanol. The prepolymer was titrated as before using a pH meter to determine the end point. This prepolymer was reacted with a twenty fold excess of thionyl chloride for 20 hours at 40°C. Next the acid chloride prepolymer was separated from excess thionyl chloride by freeze drying. It was redissolved in a benzene-pyridine mixture which was dried with sodium metal and distilled just prior to use. An equivalent amount of 1,8 diamineoctane was added and the temperature gradually increased until the mixture was refluxing. A portion of the copolymer was taken from the reaction mixture and dried in a vacuum oven. Other portions were precipitated in undried heptane, in heptane dried with sodium metal and distilled, and in methanol. An attempt was made to fractionally remove the low molecular weight copolymer, but it did not succeed.

Synthesis 22: A difunctional prepolymer was prepared and titrated in the same manner as in synthesis 7. Sixty grams of it were dissolved in 150 ml. of benzene. An equivalent amount (2.2 g.) of RD-2 Ciba Products Company diepoxide and 0.54 grams of tri-n-butyl amine was added. The solution was stirred and refluxed, then freeze dried. The solid left was ground, put in a compression mold, and given one hour to react at 175°C.

(3.5)



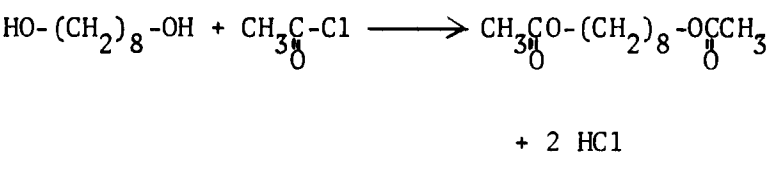
A sheet was formed, but it was extremely brittle and could not be cut without fracturing.

Synthesis 23: Eighty-eight grams of prepolymer B from synthesis 10 were dissolved in xylene. An equivalent amount of diepoxide (2.74 g.) was added along with 1.50 grams of tri-n-butyl amine. The mixture was refluxed for several hours.

Synthesis 24: Prepolymer A (100.6 g.) from synthesis 10 was mixed with 3.22 grams of diepoxide and 1.576 grams of tri-n-butyl amine. The mixture was dissolved in benzene then placed in a vacuum oven and allowed to react under a vacuum at 190-200°C.

Synthesis 25: In order to make 1,8 octyl methyl diacetate, five grams of 1,8 octanediol and 15 ml. of acetyl chloride were mixed in a 250 ml. reaction flask. After the diol reacted into solution, the temperature was slowly increased to about 100°C.

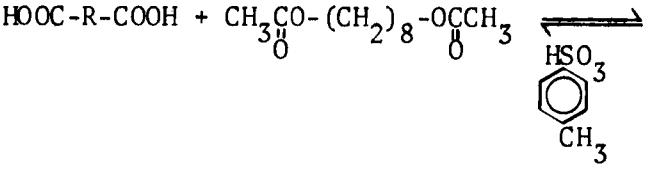
(3.6)



Prepolymer A (42.808 g.) was dissolved in xylene. The mixture was placed in a 250 ml. reaction flask and thoroughly dried by refluxing

over sodium metal in a Dean Stark trap. The 1,8 octyl methyl diacetate (1.13 ml.) was added to the flask along with a small amount of p-toluene sulfonic acid. The sodium metal was left in the Dean Stark trap to capture any acetic acid given off by the reaction. The reaction ran for 48 hours. A nitrogen atmosphere was used throughout the reaction.

(3.7)



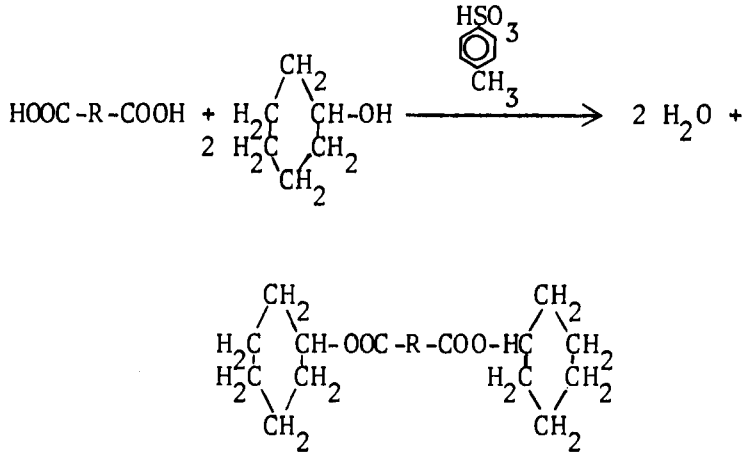
$$HOOC\text{-}R\text{-}COOH + CH_3CO\text{-}(CH_2)_8\text{-}OCCH_3 \rightleftharpoons CH_3\text{-}COO\text{-}((CH_2)_8\text{-}OOC\text{-}R\text{-}COO\text{-})_mH + CH_3COOH$$

B. End Group Modifications

Synthesis 1: A long chain diacidic polystyrene was prepared by solution polymerization. The procedure was similar to the polystyrene syntheses outlined in the Block Copolymer Section, only the amount of initiator was decreased to give a higher molecular weight. A liter of styrene monomer, 1500 ml. of benzene, and 0.378 g. 4,4' azobis (4-cyanovaleric acid) were added to a three liter kettle reactor. The reaction mixture was refluxed and stirred under a nitrogen atmosphere for six hours. The reaction mixture was then added slowly to a 4-1/2 gallon battery jar containing three or four gallons of methanol. The precipitating solution was stirred by a nonsparking stirrer. The excess alcohol was decanted, and the remaining solution filtered through a vacuum funnel. The polystyrene was air dried in the filter then further

dried in a vacuum oven at 80°C. The molecular weight of the polystyrene was determined by a Waters Associate's Gel Permeation Chromatograph. All the polymers synthesized in this section were characterized in this manner. In order to add bulky end groups to the polymer, seventy grams of the dried polymer were dissolved in xylene in a 1000 ml. reaction flask. An excess of cyclohexanol (10 ml.) was esterfied with the acid end groups on the polystyrene chains. A small amount of p-toluene sulfonic acid (0.1 g.) was added as a catalyst. The mixture was refluxed through a Dean Stark trap containing sodium metal to remove any water present. The reaction was run for 24 hours.

(3.8)



The reaction mixture was then precipitated as before, filtered, and dried in a vacuum oven. The reaction mixture was titrated to determine the conversion of the end groups. About two grams of the polymer were dissolved in 300 ml. of benzene. This solution was titrated with 0.045N sodium hydroxide-methanol solution. Phenolphthalein was used to indicate the end point.

Another portion of the polymer (60 g.) was dissolved in benzene. An excess of rubidium hydroxide was added to the solution. The solution was allowed several hours to react while stirring at room temperature.

(3.9) $$HOOC\text{-}R\text{-}COOH + RuOH \longrightarrow Ru\text{-}OOC\text{-}R\text{-}COO\text{-}RU + 2\ H_2O$$

This mixture was precipitated, filtered, and dried. This polymer was also titrated with the sodium hydroxide-methanol solution.

In order to make the polymer usable in the injection molder, the polystyrene was dried at a high enough temperature (120-140°C) in a vacuum oven to cause it to melt and flow into a slab. The slab was broken with diagonal pliers into smaller chunks. These chunks were put in a Waring Blender and made into small pellets and coarse powder.

Synthesis 2: In this polymerization 805 ml. of styrene monomer and 1400 ml. of benzene were reacted with 0.050 g. ACVA in the three liter kettle reactor as before. The reaction was allowed 12 hours for completion, then the polymer was precipitated, filtered, and dried. Sixty grams of the polymer were dissolved in xylene and reacted with cyclohexanol. The polymer was again precipitated, filtered, dried, and made into pellets. A titration was conducted, and the molecular weights were determined for the polymer.

Synthesis 3: A polymerization of 805 ml. styrene and 1400 ml. benzene with 0.077 g. ACVA was conducted as in the previous syntheses. The polymer end groups were reacted with cyclohexanol. Titrations and molecular weight determinations were made, and the polymer was pelletized.

Synthesis 4: A different initiator was used to initiate this polymerization (2,2' azobis (2-methyl propionitrile)). The same amounts of styrene (805 ml.) and benzene (1400 ml.) were added to 0.290 g. of the AIBN initiator. The different initiator was the only change in the polymerization. The molecular weight determination, precipitation, and pelletizing were done as before. This initiator puts a small nonreactive end group on the polymer. Therefore, no end group reactions or titrations were made.

Synthesis 5: Another polymer was made using 0.121 g. AIBN to initiate 805 ml. of styrene monomer dissolved in 1400 ml. of benzene. The polymer was prepared for use exactly as before.

Synthesis 6: AIBN (0.080 g.) was used to initiate 805 ml. of styrene monomer dissolved in 1400 ml. of benzene. The reaction and preparation of the polymer was done as before for AIBN initiated polystyrene.

Synthesis 7: One liter of styrene and 1.5 liters of benzene were reacted with ACVA as the initiator. The initiator was added in two increments of 0.167 g. and 0.155 g. waiting approximately three half lives (six hours) between additions. Two increments were added to increase the yield of the polymer without drastically changing the molecular weight. One hundred grams of the dried polymer was redissolved in benzene and reacted with an excess of 1-eicosanol (10 g.). P-toluene sulfonic acid was used as the catalyst. The reaction was refluxed through a Dean Stark trap containing sodium metal.

(3.10) $$HOOC\text{-}R\text{-}COOH + 2\ CH_3\text{-}(CH_2)_{19}\text{-}OH \longrightarrow 2\ H_2O +$$

$$CH_3\text{-}(CH_2)_{19}\text{-}OOC\text{-}R\text{-}COO\text{-}(CH_2)_{19}\text{-}CH_3$$

After 24 hours the polymer was precipitated in methanol, filtered, and pelletized as before. The remainder of the unreacted polymer made in this synthesis was redissolved in benzene and reacted with an excess of rubidium hydroxide. The reaction was maintained at room temperature for about 16 hours. The polymer was then precipitated in methanol, filtered, and pelletized. Both reacted polymers were titrated, and the molecular weights determined.

Synthesis 8: AIBN (0.164 g. and 0.157 g.) was used in increments six hours apart to initiate a liter of styrene dissolved in 1.50 liters of benzene. Standard procedure was used to get the polymer ready for use.

Synthesis 9: Synthesis 7 was exactly repeated using one liter of styrene monomer dissolved in 1.50 liters of benzene. Only the increments of ACVA (0.210 g. and 0.190 g.) were increased. The same end groups were added.

Synthesis 10: A liter of styrene dissolved in 1.50 liters of benzene was initiated by 0.140 g. AIBN. The polymer was precipitated, filtered, and prepared for use as before. (See Tables 3-2 and 3-3.)

TABLE 3-2

MOLECULAR WEIGHT DATA OF END GROUP MODIFIED POLYMERS

Synthesis	Polymer	End Group	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w \times 10^{-3}$	$\overline{M}_w / \overline{M}_n$
1	A1	C	67.5	161	2.39
1	A2	R	67.5	161	2.39
2	A3	C	147	347	2.36
3	A4	C	122	316	2.58
4	B1	-	68.0	180	2.64
5	B2	-	123	334	2.71
6	B3	-	146	410	2.81
7	A5	E	124	435	3.51
7	A6	R	124	435	3.51
8	B4	-	75.1	209	2.78
9	A7	E	92.5	288	3.11
9	A8	R	92.5	288	3.11
10	B5	-	111	355	3.20

C - Cyclohexanol esterfied polymer.

E - Eicosanol esterfied polymer.

R - Rubidium hydroxide reacted polymer.

A - ACVA polymer.

B - AIBN polymer.

TABLE 3-3

CONVERSION OF END GROUPS

Polymer	Percent Conversion
A1	97.6
A2	97.4
A3	100.
A4	92.8
A5	85.2
A6	98.8
A7	92.3
A8	94.5

C. Preparing Tensile Test Samples

A Hillard Model PM-20 injection molding machine was used to make tensile specimens from the polymers synthesized in the laboratory. The injection molding machine was modified to accept a mold with an ASTM D 638 type I tensile bar (see Appendix C) machined into it. The molded tensile specimens were very close to the configuration differing by only a few thousandths of an inch. The tensile bars had a gauge length of two inches and a cross section of 0.500 inches by 0.125 inches.

When the tensile bars were viewed through polarized lenses, some color was apparent which indicates residual stress or orientation. B. M. Murphy[41] showed that the residual stresses in his moldings of polystyrene to be less than 210 psi, and that most of the color came from orientation. The orientation in the samples at the surface was in the direction of flow (parallel to the gauge length) however a short distance from the surface, transverse areas of orientation were found. Stable crazes grew readily in these transverse areas rather than from the surface where craze growth can cause catastrophic failure. Most of the injection molded samples tested by Murphy showed "stable crazing". Nevertheless, he did produce some samples without the transverse area which failed catastropically. Annealing produced gross contractions in the tensile bars. This was also thought to be an orientation effect.

The laboratory polymer tensile bars were used exactly as they were made. Some of the high molecular weight materials proved to be very difficult to mold. Many short shots occurred due to inadequate pressure available to the molding machine. But in the lower ranges of molecular

weights, the tensile bars were easily made. Minimum molding conditions necessary to make a full tensile bar were used for most polymers. The temperature and pressures used for molding are given in Table 3-4.

Some other samples were made from a sheet of polystyrene manufactured by Commercial Plastics and Supply Corporation. Samples were cut from this sheet using a jewelers saw, then mounted on a router, and machined to a tensile bar pattern. The edges were sanded and polished until all the machine marks were gone.

D. Testing The Samples

Glass Transition Temperature

The glass transition temperatures were determined for each polymer using a Perkin Elmer Differential Scanning Calorimeter Model B-1. Most determinations were made at scanning speeds of five degrees centigrade per minute and ten degrees centigrade per minute. Several runs were made with each polymer at different speeds, and the results taken from the average of the values if much variation occurred. The maximum sensitivity of the instrument was used. The results are given in Table 3-5.

Tensile Testing

The polystyrene specimens were tested for tensile strength and crazing properties on a Instron Tensile Testing Machine. Craze initiation was detected using the reflective properties of crazes. A light was focused to a one inch circle on the specimen. Until crazing occurred the light shined through the specimen. At the onset of crazing, the

TABLE 3-4

MOLDING CONDITIONS

Polymer	Plasticating Temp. (°F)	Pressure (psi)	Rate*	Mold Temp. (°C)
A1	400	11,000	5.0	65
A2	400	11,000	5.0	65
A3	440	11,000	6.0	90
A4	420	11,000	6.0	68
A5	420	11,000	6.0	68
A6	415	11,000	6.0	68
A7	410	11,000	6.0	65
A8	410	11,000	6.0	65
B1	410	11,000	5.0	65
B2	430	11,000	6.0	68
B3	440	11,000	6.0	90
B4	400	11,000	5.0	65
B5	420	11,000	5.5	68
Shell	380	9,300	6.0	60
Dow	380	9,300	5.5	60

*Rate refers to the speed at which the plunger comes through the plasticating cylinder. Zero is the minimum and six is the maximum.

TABLE 3-5

GLASS TRANSITION TEMPERATURES

Polymer	T_g (°C)
A1	86
A2	87
A3	105
A4	102
A5	101
A6	102
A7	95
A8	93
B1	88
B2	100
B3	107
B4	89
B5	101
Shell	80
Dow	85
Commercial	97

light was reflected up to a photo resistor which was connected through an adjustable bridge circuit to a relay. (Circuit diagram Appendix D.) The relay activated a Pip Control event marker on the Instron chart. The craze detection equipment (Figure 3-1) was mounted on the Instron Frame with a bracket. The photo-resistor was shielded from the outside light by putting black paper around the opening and as a background. The relay was set to activate after about five units of deflection of the pointer. A potentiometer was used to adjust the circuit. A standard 1-1/2 volt hobby cell was used as the reference voltage. The craze detection mechanism used here was very similar to the ones used by Maxwell and Rahm[20] and Haward et al.[2]

The Instron Testing Machine was a floor model TT-D. It had wedge action jaws which tightened as the specimen was stressed. A DR load cell measured the load applied at a constant jaw separation rate of 0.02 in./min. The data from the Instron came in the form of a load (in pounds) versus time. The area of each specimen was measured and yield stress calculated. Since the craze detection mechanism was used, it was not possible to find the actual strain rate of the specimens using a strain gauge. Crazing was visible over approximately 3.6 inches in many of the samples. The elongation for the samples was calculated based on the time axis of the curves. It was not a true strain.

Only a few samples tested did not craze prior to failure. These were generally made from lower molecular weight polymer and were very brittle. A few of these samples even fractured in the jaws. The higher molecular weight polymers exhibited very good crazing properties. The crazes formed tended to be more stable and uniform than in low molecular

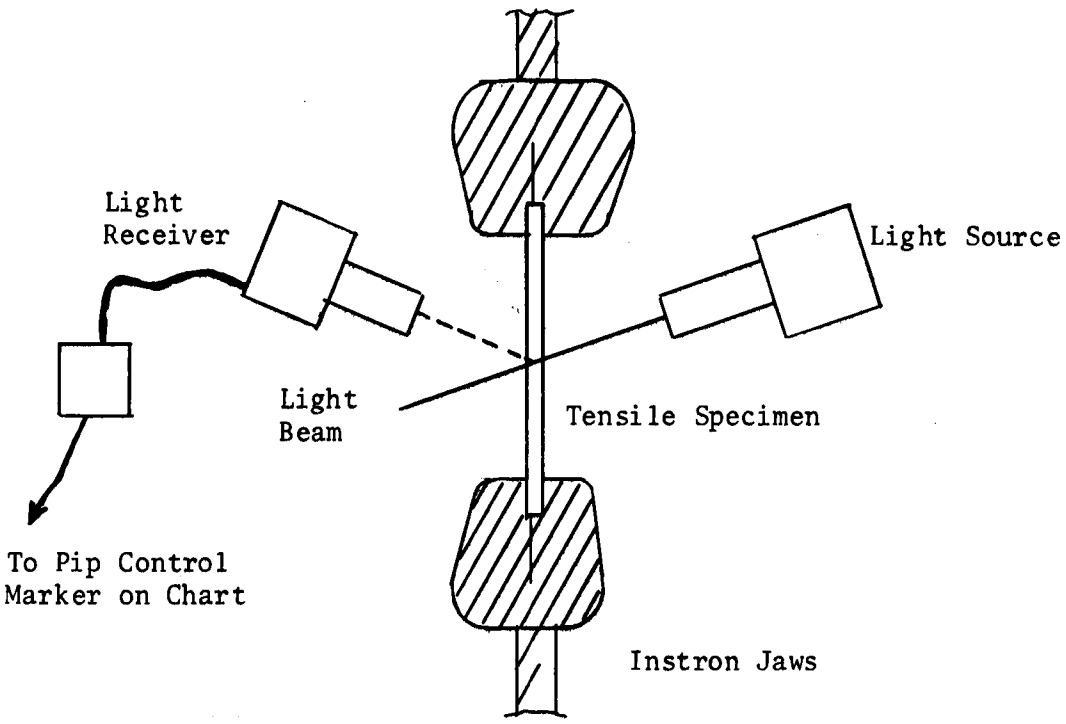


Figure 3-1. Craze detection mechanism.

weight material. Some of the high molecular weight specimens even had a breaking stress slightly less than the yield stress.

All samples made were tested even though some of these had visible flaws (bubbles, foreign material). The ones which obviously failed in these flaws were discounted. The remaining data is listed in Table 3-6.

Additional data not directly related to the molecular weight-end group data, was taken for commercial polymers, Dow Styron 678, Shell TC 3-30, and a commercial sheet of polystyrene. Samples were made from these materials and tested at various jaw separation rates to investigate the effect of strain rate on yield stress and craze initiation stress. The Shell and Dow polymers were general purpose pellets which were injection molded at the conditions shown in Table 3.4, page 32. The results of the tests are plotted in Figure 3-2.

TABLE 3-6

TENSILE MEASUREMENTS

Polymer	Yield Stress[b] (psi)	Crazing Stress[c] (psi)	Elongation (in)	Modulus[a] (psi) $\times 10^{-5}$
A1	4410 ± 320	3920 + 200*	0.0978	2.21
A2	3840 + 190	3710 + 200*	0.0941	2.07
A3	6960 + 700	4570 + 90	0.1644	2.11
A4	6560 + 230	4700 + 280	0.1490	2.14
A5	6580 + 140	4330 + 310	0.1491	2.11
A6	6300 + 390	4430 + 480	0.1453	2.08
A7	5900 + 140	4560 + 340	0.1230	2.11
A8	5860 + 70	4230 + 550	0.1200	2.12
B1	4330 + 210	3750 + 70*	0.0909	2.15
B2	6670 + 500	4270 + 400	0.1515	2.15
B3	7200 + 570	4610 + 250	0.1641	2.17
B4	5470 + 280	4290 + 240	0.1148	2.14
B5	6160 + 320	4400 + 430	0.1336	2.13
Shell	5860 + 650	3900 + 960	0.1240	2.28
Dow	5480 + 730	4380 + 600	0.1130	2.34

*All of these samples did not craze. The crazing stress is the average of the ones that did craze before failure.

[a]This is an apparent modulus.

[b]Yield stress is actually the ultimate tensile strength.

[c]Crazing stress is the stress where crazing is detected by the craze detection mechanism.

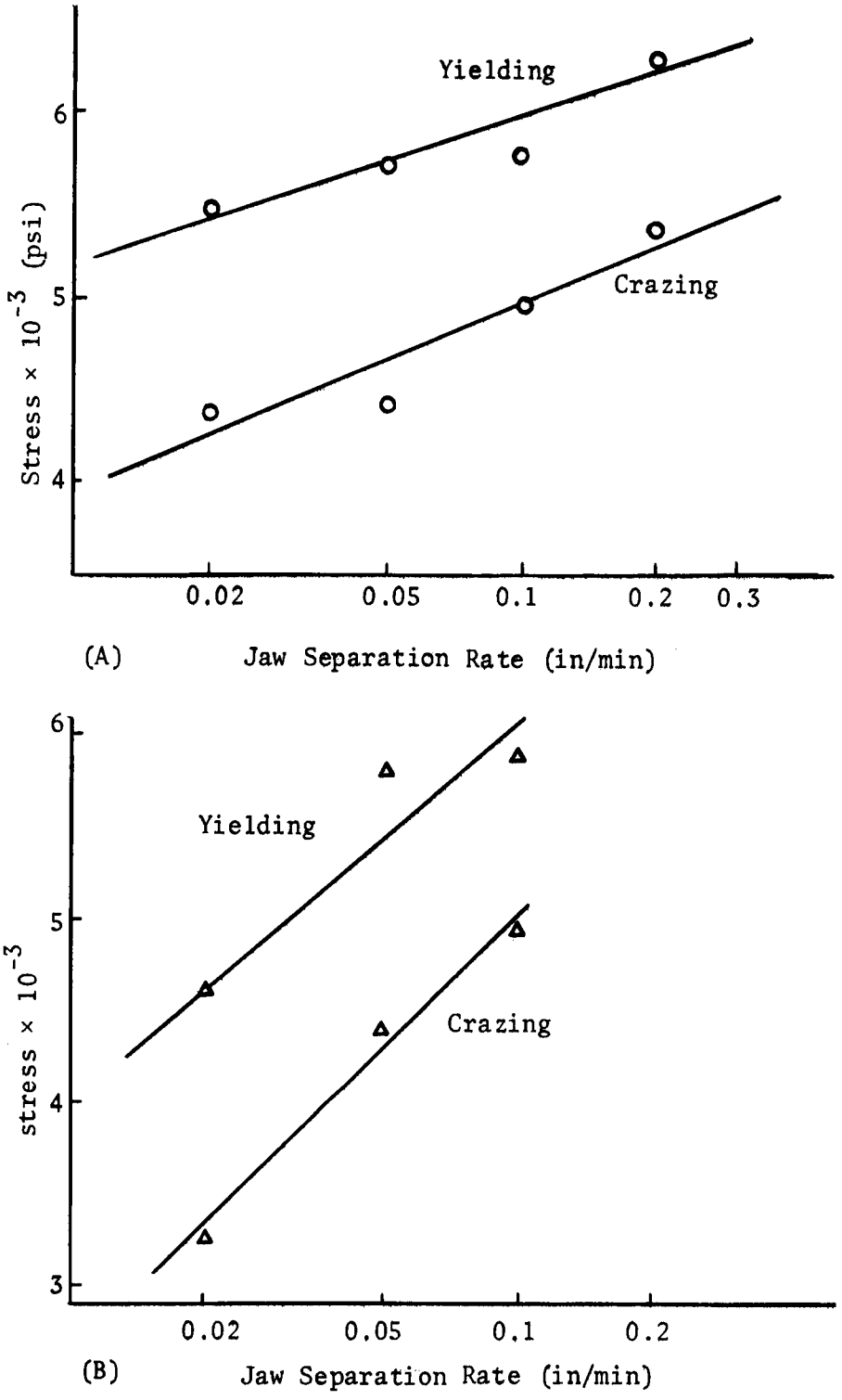


Figure 3-2. Yield stress versus jaw separation rate. (A) Dow Styron 678 and (b) Commercial Plastics sheet.

CHAPTER IV

DISCUSSION OF RESULTS

A. Block Copolymers

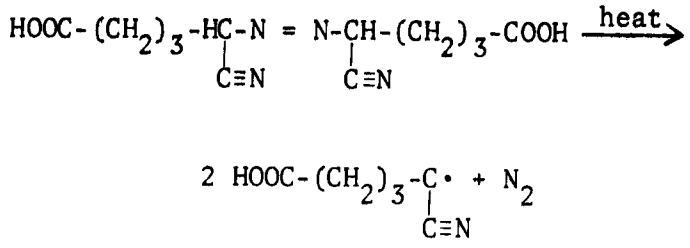
Introduction

Several methods were used in an attempt to synthesize a block copolymer which consists of a long polystyrene chain about 6000 to 10,000 number average molecular weight, linked with short molecules containing eight to twelve carbon atoms. In order to mold the copolymer and test its tensile properties, a molecular weight of 60,000 or greater is deemed necessary. The syntheses were not successful in achieving the desired molecular weight. However, the degree of polymerization (DP) was increased in the latter copolymerizations over the first copolymers synthesized.

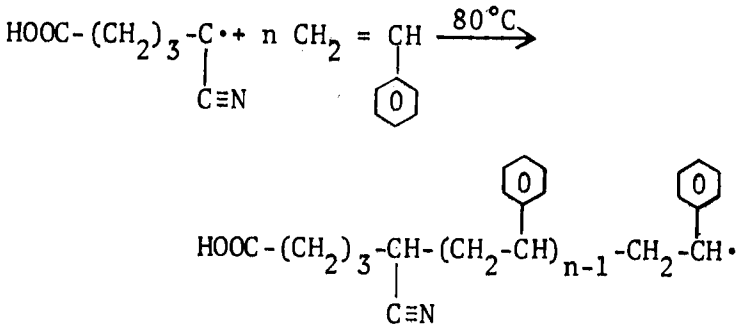
Prepolymer Preparation

The prepolymers for all the reactions were made in an identical manner. Slight changes in the amount of initiator were made to vary the molecular weights. (See calculations in Appendix A.) The initiator (4,4' azobis (4-cyanovaleric acid)) was decomposed by heat in refluxing benzenestyrene monomer solution. The initiator has a half life of approximately two hours,[42] and the reaction ran for several half lives. The initiation and propagation steps occur as follows:

(4.1)

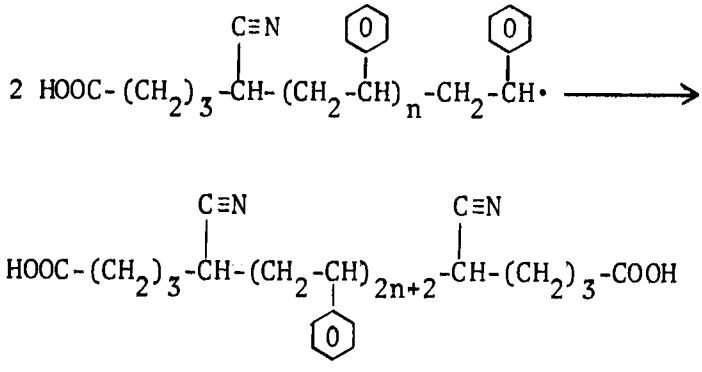


(4.2)



The termination step occurs by combination which produces a difunctional molecule.[43] The difunctionality of the prepolymers was verified by comparing titration, GPC, and vapor phase osmometry molecular weight data. Comparing the titration and GPC data of five determinations indicates the average prepolymer had 1.99 organic acid groups per prepolymer molecule. The titration and vapor phase osometer data show that the prepolymer had 2.42 organic acid groups per molecule.

(4.3)



Acyl Chloride Reaction

The conversion of the acid end groups to acyl chloride groups is a common reaction used by others[39,44] with the difunctional polystyrene.

(4.4) (where R = polystyrene $HOOC\text{-}R\text{-}COOH + SOCl_2 \longrightarrow$

$$Cl\text{-}\overset{O}{\overset{\|}{C}}\text{-}R\text{-}\overset{O}{\overset{\|}{C}}\text{-}Cl + HCl + S \text{ oxides}$$

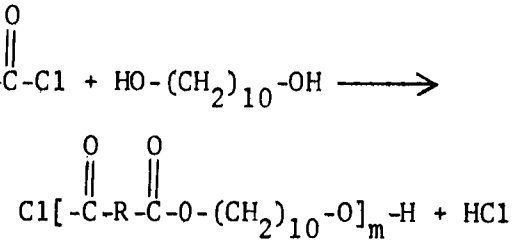
The temperatures of the reaction mixture and concentrations of thionyl chloride were varied in the ranges of the other experimenters. Great care was taken to guard against even trace amounts of moisture when working with the acyl chloride polymers. The solid reagents were generally dried in a vacuum oven below their melt point. The liquid reagents were dried with calcium hydride, barium oxide, or sodium metal, then distilled just prior to use. A nitrogen atmosphere was used for all reactions and to break the vacuum in the freeze drying process.

Linking Reaction

The linking reaction was the Schotten-Bauman reaction. A diol was esterfied with the acyl chloride. Hydrogen chloride was a by-product. This reaction is extremely rapid and requires no catalyst, but bases were used to remove the hydrogen chloride to influence the equilibrium. More reactive diamines were later substituted for the diols, but no large increases in molecular weights were seen. The linking reactions were run in several solvents at various temperatures. The best results

were obtained at 80°C in benzene with a small amount of pyridine added. (See Table 3-1, page 15.)

(4.5)



The copolymers were precipitated in methanol in most of the reactions. Some of the latter copolymers, which were linked with 1,8 octyl diamine, show a decrease in molecular weight during this precipitation. Dried heptane was used to precipitate these copolymers with slightly better results.

Comparable Results From Others

The degrees of polymerization achieved were not sufficient to make a moldable sample. The other papers cited for this work also did not produce high molecular weights. Inagaki and Miyamato[44] produced a copolymer consisting of two polymethyl methacrylate chains linked to a difuntional polystyrene molecule. Their molecular weights were around 33,000 using polystyrene chains of 10,000 to 15,000 molecular weight. The polystyrene chain was the center of the molecule with the PMMA chains being added on the ends. Three prepolymer molecules were connected in their experiments. Inagaki and Miyamato used reaction methods established by Bamford, Jenkins, and Wayne[39] in their work. However,

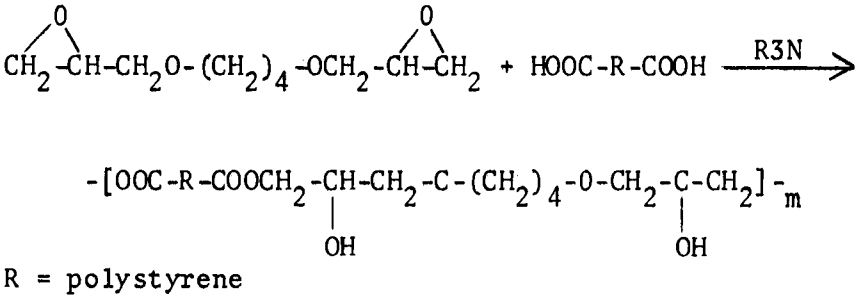
in conversations with Dr. Tadao Kotaka, who is noted for contributions in that article, two years were spent getting the reaction to run satisfactorily.

Bamford, Jenkins, and Wayne[39] reacted difunctional polystyrene with small difunctional molecules to produce a block copolymer. Their prepolymer molecular weights ranged from 1200 to 19,000. The degrees of polymerization varied from 1.0 to 8.7. Using a prepolymer with a molecular weight of 8600, a copolymer with a maximum degree of polymerization of 4.1 was produced. The molecular weight of this copolymer was 33,500. Other linking reactions produced degrees of polymerization as high as 8.7 and 7.5, but the molecular weights of the prepolymers were not given. Many of the prepolymers have molecular weights in the 3000 to 4000 range. When these prepolymers were used, the copolymer still had a molecular weight less than 40,000. There were many practical problems in this synthesis (noted by Bamford et al.) and achieving a high molecular weight by this method seems futile.

Diepoxide Reaction

Other methods were tried in a less extensive manner to get the polystyrene block copolymer. A diepoxide RD-2, made by Ciba Products was reacted with the diacid prepolymer.[45,46]

(4.6)



R = polystyrene

This reaction gives no by-products and may be reacted directly in a compression mold. A sheet was made this way, but it was too brittle to cut and machine into tensile bars. This reaction generally produced results as good as the acid chloride reaction but it lacked the flexibility of substituting linking groups as readily as the diols and diamines. The reaction was run in both solution and in the melt. Similar results were obtained in either manner.

Transesterfication Reaction

A transesterfication reaction[47] was also attempted.

(4.7) $$HOOC\text{-}R\text{-}COOH + CH_3COO\text{-}(CH_2)_8\text{-}OOC\text{-}CH_3 \xrightarrow{\substack{HSO_3 \\ \bigcirc \\ CH_3}}$$

$$CH_3\text{-}COO\text{-}[(CH_2)_8\text{-}OOC\text{-}R\text{-}COO]_m\text{-}H + CH_3COOH$$

The 1,8 octyl methyl diacetate was made from 1,8 octane diol and acetyl chloride. The reaction is quick and all the diol should be reacted as it goes into solution. The excess acetyl chloride was boiled away leaving only the acetate which has a much higher boiling point than either the diol or the acetyl chloride.

(4.8) $$HO\text{-}(CH_2)_8\text{-}OH + CH_3\overset{\overset{O}{\|}}{C}\text{-}Cl \longrightarrow CH_3\overset{\overset{O}{\|}}{C}\text{-}O\text{-}(CH_2)_8\text{-}O\overset{\overset{O}{\|}}{C}\text{-}CH_3 + 2\ HCl$$

The interchange reaction ran at the reflux temperature of xylene. A Dean Stark trap containing bits of sodium metal was used first to dry the system before the reaction and later during the reaction to remove the acetic acid which was refluxed into the trap. Para-toluene sulfonic acid[48] was the catalyst for the reaction. The results showed no increase in molecular weight. The copolymer GPC curve was identical to the prepolymer curve.

Reasons Behind Making Block Copolymers

The chief reason for attempting to make the block copolymer was to study the effect on crazing of small linking groups connecting polystyrene chains. The small linking molecules would be more flexible than the stiff polystyrene chains, thus providing yielding points within the copolymer chains for the molecule to yield in a homogenous manner without crazing. Some intramolecular motion would occur before the intermolecular motion, which causes crazing, begins. This would produce more uniform yielding and allow it to yield more than polystyrene before fracturing. Ideally the flexible segments would yield at a stress slightly less than the crazing stress and yield several percent. Since the area under the stress-strain curve is related to fracture energy, any increase in this area would improve the impact strength of polystyrene. Figure 4-1 shows a stress-strain curve for polystyrene and a stress-strain curve for an ideal block copolymer. The copolymer should have very similar properties to polystyrene since the amount of the linking agent would be less than five weight percent.

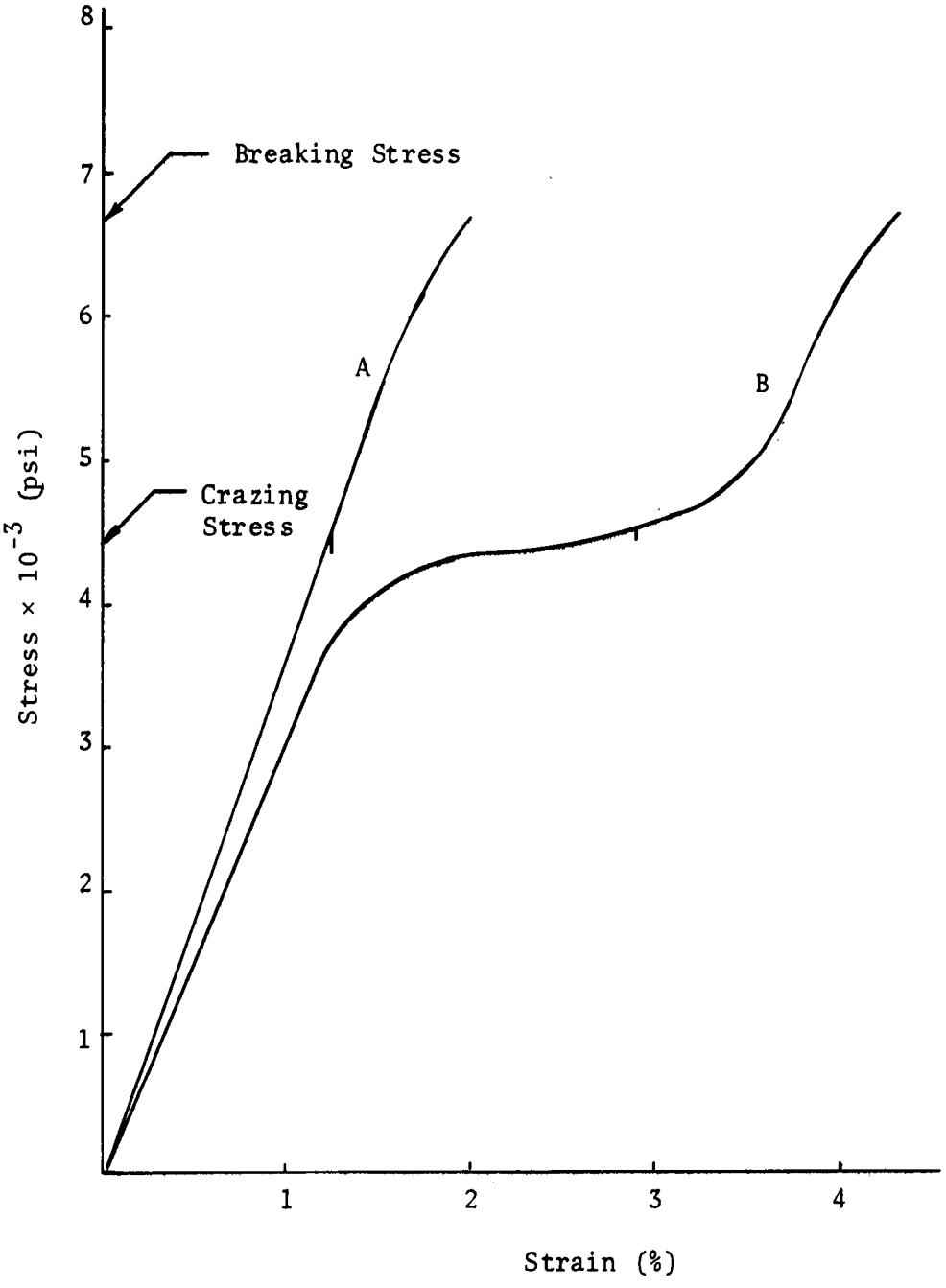


Figure 4-1. Stress-strain curves for polystyrene and an ideal copolymer. A: polystyrene. B: block copolymer.

B. End Group Modifications

Introduction

Long polystyrene chains were synthesized in this part of the experiment. The polymers prepared have number average molecular weights from 67,000 to 147,000. Two types of polymers were made. ACVA initiator, used in the previous Block Copolymer Section, gave a polymer with an organic acid group on each end. AIBN (2,2' azobis 2-methyl propionitrile) initiator gave a polymer with relatively small nonreactive end groups. Polymers of each type were prepared over the molecular weight range indicated.

End Group Reactions

The ACVA polymers were reacted with compounds to give them bulky end groups. Two ACVA polymers were reacted in an acid-base titration type reaction with rubidium hydroxide.

(4.9) (where R = polystyrene) $HOOC\text{-}R\text{-}COOH + RuOH \longrightarrow$

$$RuO\text{-}\overset{\overset{O}{\|}}{C}\text{-}R\text{-}\overset{\overset{O}{\|}}{C}\text{-}ORu + H_2O$$

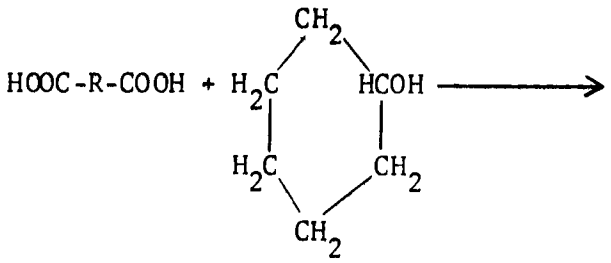
Two polymers were esterfied with 1-eicosanol.

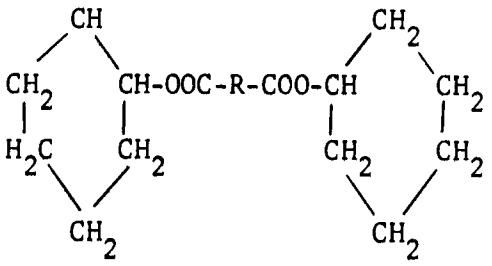
(4.10) $HOOC\text{-}R\text{-}COOH + CH_3\text{-}(CH_2)_{19}\text{-}OH \longrightarrow$

$$CH_3\text{-}(CH_2)_{19}\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}R\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}(CH_2)_{19}\text{-}CH_3 + 2\ H_2O$$

Three polymers were esterfied with cyclohexanol.

(4.11)





The esterfication reactions were done as indicated by Lenz[47] and his references.[48,49] Para-toluene sulfonic acid was the catalyst. Titrations for remaining acid groups (Table 3-2, page 28) indicated most of the acid groups did react.

Effect of End Groups on Polystyrene

Tensile tests. In tensile test experiments no detectable differences were found between molecules with or without the bulky end groups tested. A curve of yield stress and crazing stress versus molecular weight (Figure 4-2) is plotted from the data in Table 3-6, page 37, and all the polymers have stresses that lie close to the lines. Two sets of lines were plotted. One set represents the AIBN polymers, and the other set of lines represents the ACVA polymers with bulky end

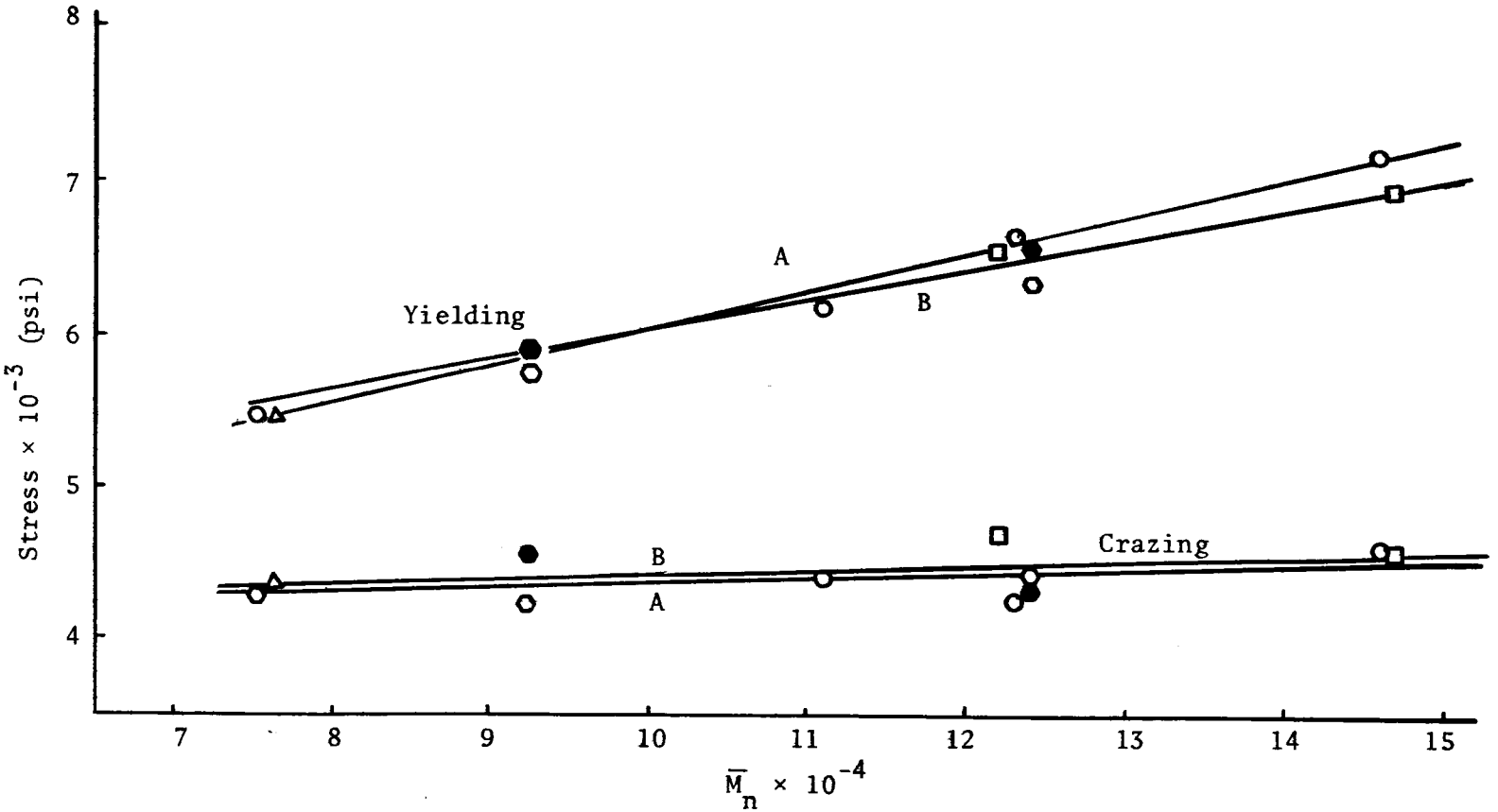


Figure 4-2. Stress versus molecular weight. A: AIBN lines. B: ACVA lines. (○) AIBN. (□) cyclohexanol end groups. (⬡) rubidium end groups. (⬢) eicosanol end groups. (△) Styron.

groups. None of the end group polymers vary greatly from the line plotted for them which indicates that none of these end groups have much influence on the polymer chains. The amount is not measurable within this test. The maximum difference between the two lines plotted for yield stress occurs in the region of high molecular weight, where the effects due to the end groups should be the smallest. Even in this region the differences are well within the 50 percent confidence range calculated. The craze initiation stress lines are extremely close together. The end groups certainly have no effect on crazing.

Some slipping occurred in the jaws of the Instron Tensile Testing machine as later tests confirmed. This was due to the jaws being insufficiently tight. Since they are the self tightening type, only the low region of stress was affected. To correct for this slipping, the straight region of the load-time graph was extrapolated to zero stress (see Appendix E). The time axis was measured from the extrapolated line and converted to a fracture elongation using the jaw separation rate of 0.02 in./min. Fracture elongation from Table 3-6, page 37, versus molecular weight is plotted in Figure 4.3. No apparent differences in polymers with or without bulky end groups was noted. All of the molecular weights tested more or less fall in line. There was not as drastic decrease in the 60,000 molecular weight range for elongation as for the yield stress data. However, this data does not fall in line quite as well as the stress versus molecular weight data. Perhaps this is due to inaccuracies incurred through slipping and extrapolating.

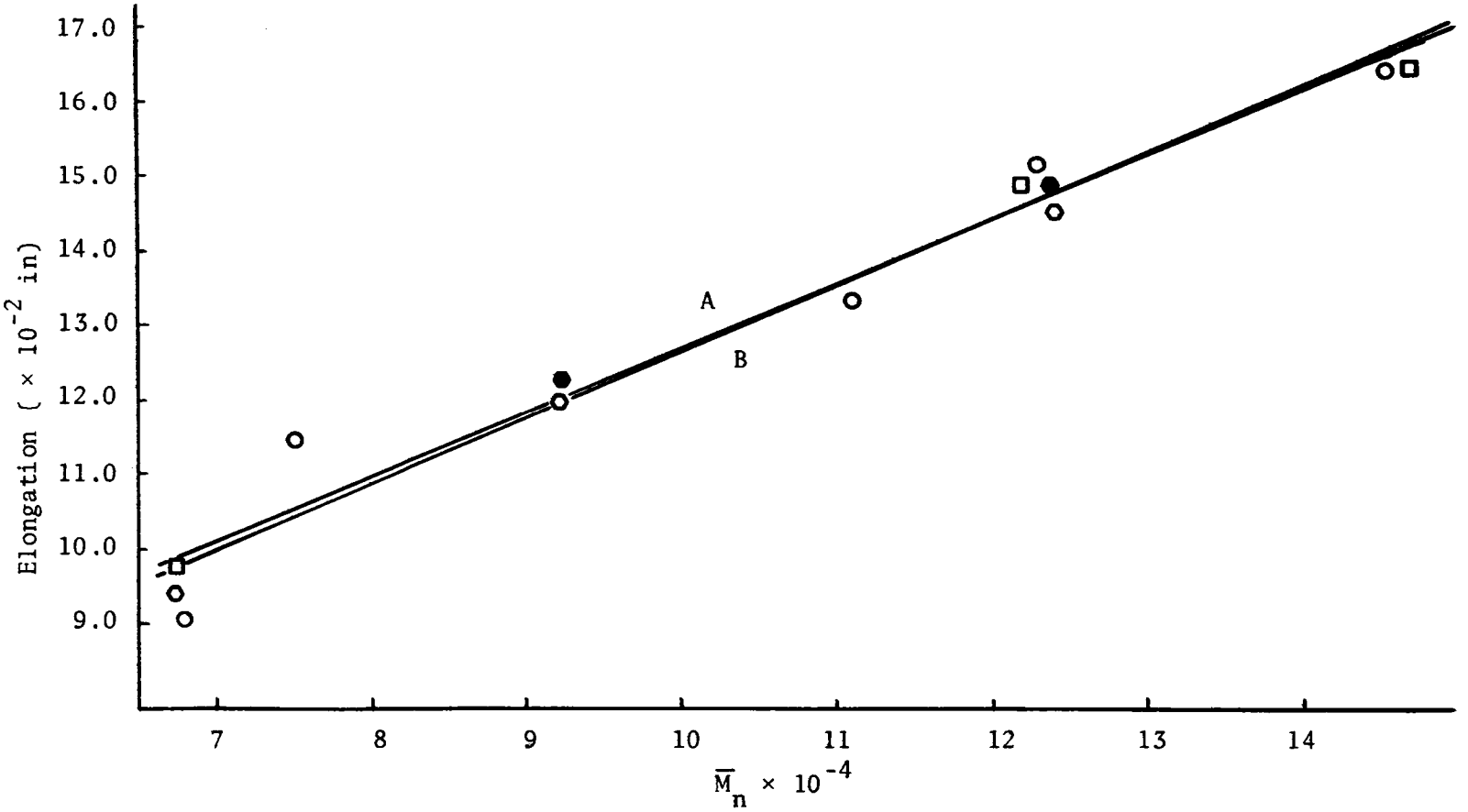


Figure 4-3. Fracture elongation versus molecular weight. A: ACVA polymers. B: AIBN polymers. (○) AIBN. (□) cyclohexanol end groups. (⬡) rubidium end groups. (⬢) eicosanol end groups. (△) Styron 678.

An apparent modulus is calculated based on the slope of the extrapolated line in Appendix E. The slope is converted to stress (psi) divided by strain (inches per inch). The results from Table 3-6, page 37, are plotted versus molecular weight in Figure 4-4. The apparent modulus appears to be relatively independent of the molecular weight as well as the end groups. The average apparent modulus for the bulky end group polymers and the AIBN polymers are within experimental error or one another. The modulus is called apparent because the amount of true strain is not known and can only be estimated. An extensometer was used on one tensile sample of Shell TC 3-30 to find the true strain and an elastic modulus of 450,000 psi. was calculated. The value obtained for the apparent modulus was 228,000 psi. Both the apparent modulus and the fracture elongation can only be used for an internal comparison of data. Since the data relating molecular weight and elongation, and molecular weight and stress are linear in most of the regions tested, it is consistent that the modulus should be relatively constant. The data obtained for the modulus and fracture elongation are good enough to substantiate the stress data.

Glass transition temperatures. The glass transition temperatures were determined directly from the graphs drawn by a Perkin Elmer differential scanning calorimeter. Several runs were made with each sample at different heating rates, but generally no differences in T_g due to the rate were seen. The T_g's for a given polymer were within two or three degrees of one another so the values were averaged and reported

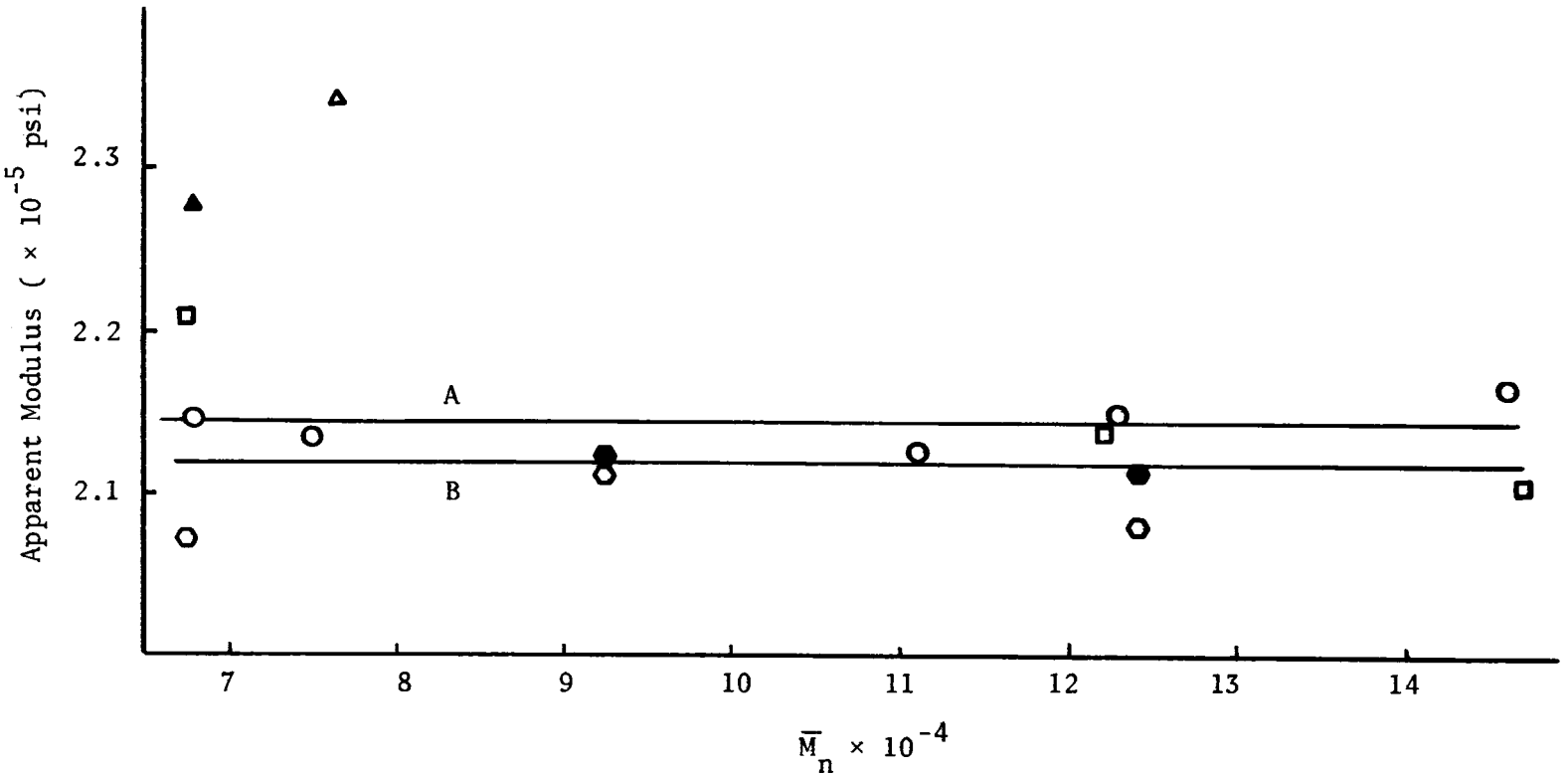


Figure 4-4. Molecular weight versus apparent modulus. A: AIBN polymers. B: ACVA polymers. (○) AIBN. (□) Cyclohexanol end groups. (⬡) rubidium end groups. (●) eicosanol end groups. (△) Styron 678.

in Table 3-5, page 33. When this data was plotted versus molecular weight, a smooth curve was obtained with T_g increasing proportional to molecular weight. No apparent differences are found between polymers with or without bulky end groups (Figure 4-5).

Commercial Polymers

General. The commercial polystyrenes tested were not directly comparable to the laboratory synthesized polymers. The processing conditions were different as well as the molecular weight distributions were generally broader. The broad distribution might indicate a high molecular weight polymer with some low molecular weight polystyrene added to increase processability. It is also possible that other ingredients such as lubricants were added to the commercial pellets. The sheet of polystyrene manufactured by Commercial Plastics and Supply Corporation was probably cast formed. Tensile bars made from this material were cut and machined, not injection molded. Nevertheless, the data from these tests are in the same range as the laboratory polymers.

Strain rate effects. The effect of strain rate was studied on Styron 678 injection molded tensile bars and on tensile bars cut from the Commercial Plastic's sheet polystyrene. The results plotted in Figure 3-2, page 38, indicate a substantial increase in yield strength and craze initiation strength with increasing jaw separation rates. For an increase in jaw separation rate from 0.02 in. per min. to o.20 in.

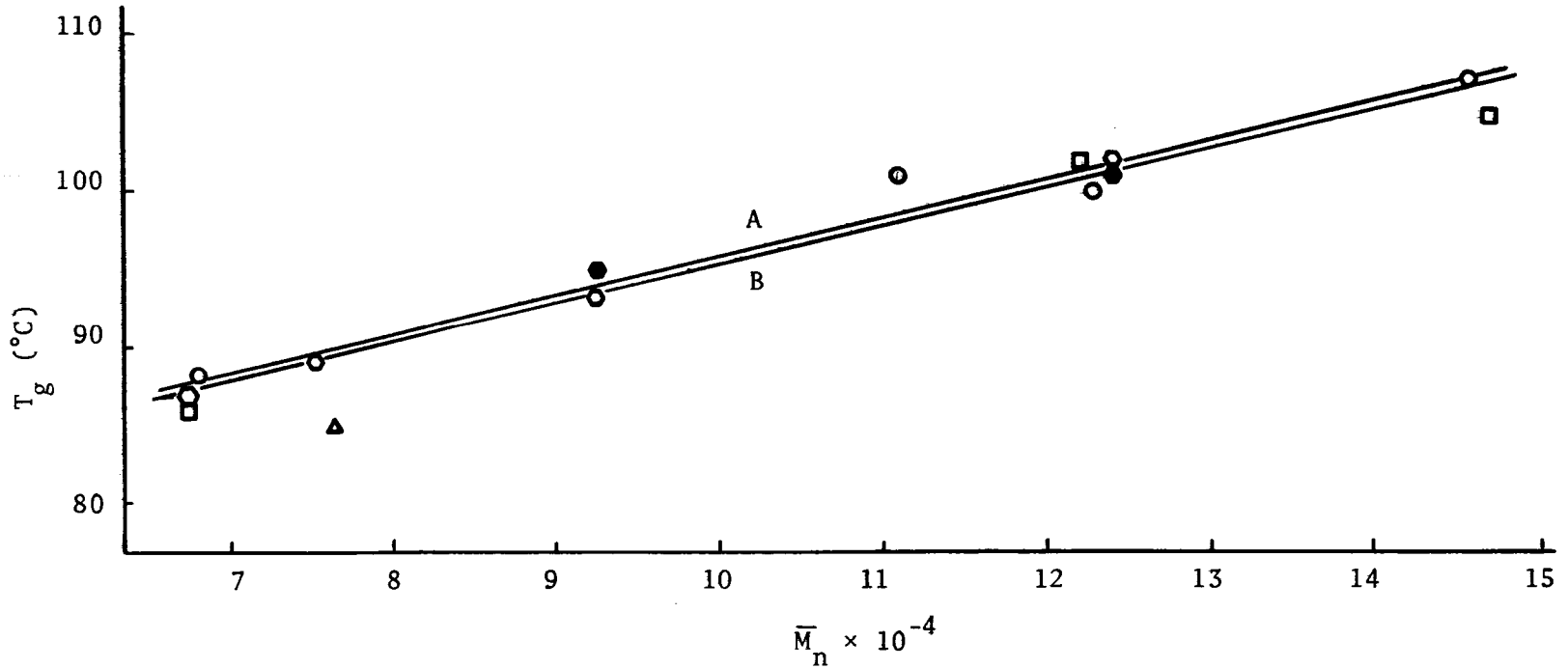


Figure 4-5. Glass transition temperature versus molecular weight. A: AIBN polymers. B: ACVA polymers. (○) AIBN. (□) cyclohexanol end groups. (⬡) rubidium end groups. (⬢) eicosanol end groups. (△) Styron.

per min., both the yield stress and craze stress increase several hundred pounds per square inch. The results show the same trends reported by others[50] and provides useful information in comparing stress results obtained at different strain rates.

Molecular Weight Effects

A good correlation was developed for yield stress and crazing stress versus molecular weight in Figure 4-2, page 49. It is a well-known fact that higher molecular weight polystyrenes have higher yield stresses and that somewhere in molecular weights below 70,000 (depending on molecular weight distribution) the strength of polystyrene rapidly diminishes. The curve of yield stress exhibited this fact very well. Using a least mean squares fit, polystyrene with a number average molecular weight greater than 70,000 has a yield stress given by the following equation:

$$\sigma y = 0.0245\ (MW) + 3600\ \text{psi}. \tag{4.12}$$

Crazing stress for the same range and distribution of molecular weights is represented by the equation:

$$\sigma c = 0.00295\ (MW) + 4130\ \text{psi}. \tag{4.13}$$

The craze initiation stress curve has a smaller slope than one would expect. This curve indicates the amount of stress required to start crazing is approximately the same in the range of molecular weights tested, but crazes are much more stable in higher molecular weight

polystyrenes. One way to interpret this phenomenon may be to think that approximately the same amount of force is needed for molecular flow in both low molecular weight polystyrene and high molecular polystyrene. However, the long chain molecules become entangled[28] after a limited amount of flow and the crazing process stops until the force is increased sufficiently to untangle the molecules or initiate fracture elsewhere. Perhaps this also explains why crazes in high molecular weight polystyrene appear uniform and thin, while lower molecular weight polystyrenes have uneven crazes. For molecular weights in the 60,000 to 70,000 range, crazing occurs at approximately the same stress level as fracture if crazing even occurs. In fact, half of the specimens in this region did not craze before failure.

Comparison of Other Literature

McCormick, Bower, Kin. The literature most comparable to the molecular weight versus stress work presented was done by H. W. McCormick, F. M. Bower, and L. Kin.[51] This group concluded that tensile strength increases with molecular weight to an asymptotic maximum. Thus increasing molecular weight above approximately 130,000 provides diminishing returns in tensile strength while decreasing moldability. A relationship for molecular weight versus physical property between polymers with similar molecular weight distributions may be obtained but no overall relationship for polystyrene in general exists. Using anionic initiated polystyrene of narrow distribution, a conclusion was made that the narrower the distribution the poorer the property.

The main differences between the work of McCormick et al. and the work presented in this paper seem to be in the range of molecular weights used and the elongation rate. McCormick et al. placed more emphasis on higher molecular weight polymers in the 150,000 to 160,000 range. No polymer of significance was tested below 99,000 molecular weight. And only one polymer between 110,000 and 156,000 was tested. A line drawn parallel to the line determined for the AIBN initiated polymers in Figure 4-2, page 49, and about 600 psi. above it shows a reasonable fit for all the points except perhaps the point at 130,000 molecular weight. The line may be extended to pass close to a point obtained for Styron 678 at the same elongation rate. The curve presented by McCormick et al. is drawn on Figure 4-6. It intersects the line obtained in the work here at a molecular weight of 94,000. The two lines should not intersect in this region based on information from the strain rate experiments. A reasonable expectation would be that the yield curve run at a jaw separation rate of 0.2 in. per min. show an increase of 600 to 800 psi. throughout the linear portion of the curve. If the point for Styron may be added, the data for these two experiments agree very well.

McCormick et al. conducted their work under ASTM D-638 conditions with a strain rate of 0.2 in. per min. The samples are prepared with an injection using the following conditions:

1. Plasticizing Temperature 480°F,
2. Mold Temperature 125°F,
3. Injection Pressure 26,600 psi.

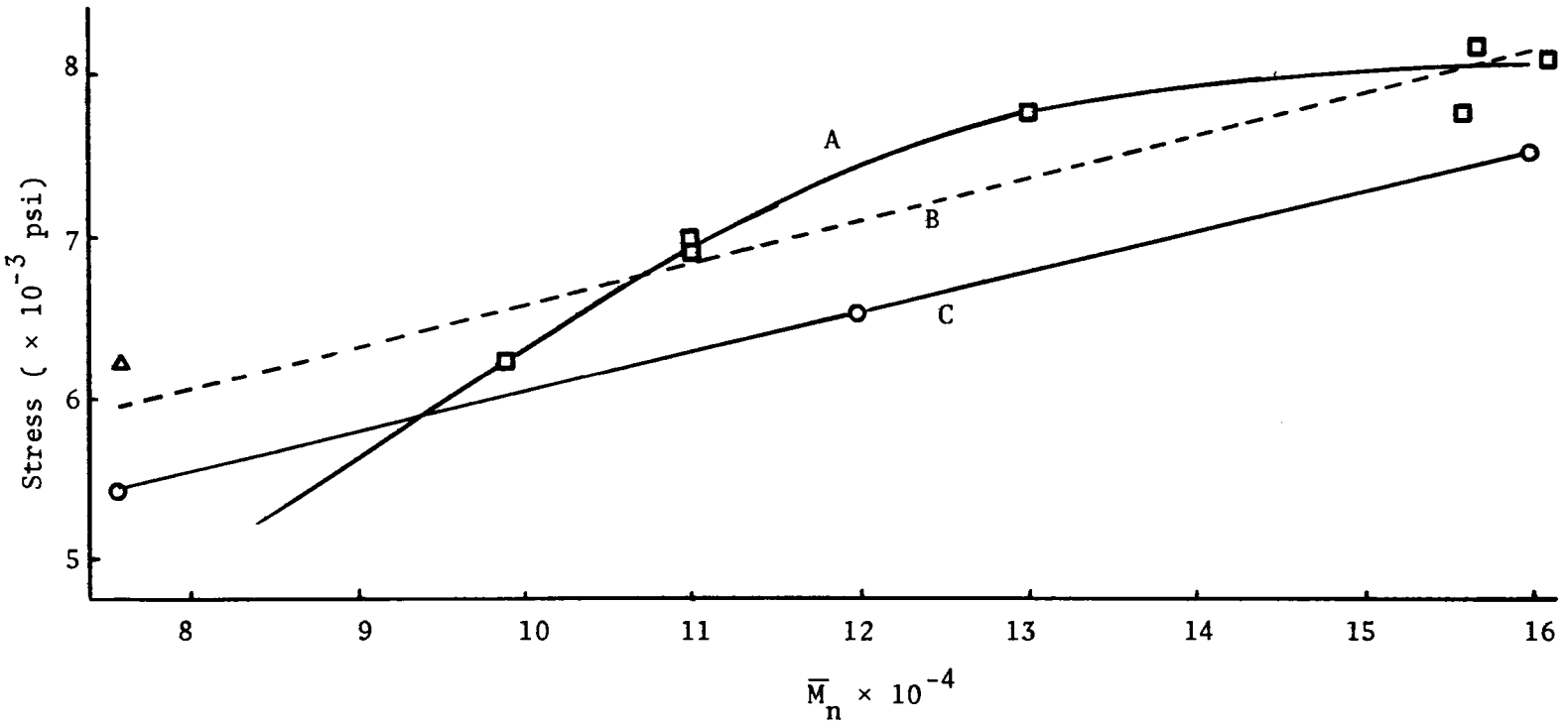


Figure 4-6. Comparative yield stress versus molecular weight data. A: McCormick et al. line. B: AIBN line corrected for strain rate. C: AIBN line. (○) AIBN points. (□) McCormick points. (△) Styron point.

Table 4-1 gives the results obtained and Figure 4-6, page 59, shows these results plotted. The molecular weights were determined by sedimentation velocity analysis of ultra centrifuge data.

The elastic moduli reported in Table 4-1 show no molecular weight dependence.

Haward, Murphy, White. Haward, White, and Murphy[52] tested injection molded samples of Clairex heat resistant polystyrene. At a similar temperature and strain rate to the tests presented here, a yield stress of 12,000 psi. and a craze initiation stress of 4,700 psi. was found. Using Equations (4.12) and (4.13) with a molecular weight of 230,000[53] a yield stress of 9200 psi. and a craze initiation stress of 4800 psi. were calculated. The craze initiation stresses agree very well, however the extrapolated yield stress is slightly low for this particular polymer. It does tend to confirm that the polymer strength does not level off above a molecular weight of 130,000 as has been suggested.[51] Not enough experimental details were given to conduct a full comparison and determine why the yield stresses are 25 percent different.

Haward and Bough. R. N. Haward and I. Bough[53] did not publish any stress-strain curves, however a marked change in fracture mechanisms is noted between the molecular weights of 35,000 and 82,000. The 35,000 molecular weight material is extremely brittle while the higher molecular weight polymer is easily handled without fracture. The reason suggested for this behavior is a lack of molecular entanglements in the low molecular weight material. The higher molecular weight polymers have

TABLE 4-1

McCORMICK ET AL. TENSILE DATA

$\bar{M}_n \times 10^{-3}$	$\bar{M}_w / \bar{M}_n$	Yield Stress (psi)	Elastic Modulus (psi) $\times 10^{-5}$
49	2.41	1580	5.14
99	1.90	6250	4.50
110	1.94	6980	4.51
130	1.96	7760	4.52
161	1.77	8070	4.75
157	2.85	8170	4.64
110	2.38	6950	4.58
156	2.23	7760	4.66
168	2.47	8100	4.53

more entanglements and thus have more strength. This agrees with the data presented in Figure 4-2, page 49, and Table 3-6, page 37.

C. Summary of Conclusions and Suggested Further Work

Block Copolymers

No actual conclusions were made on this work, except that another reaction scheme must be used to obtain the block copolymer. The condensation reactions tried did not produce the high molecular weight product needed. Work on synthesizing the block copolymer using anionic polymerization is scheduled to begin shortly.

End Group Modifications

Several conclusions may be made from the data obtained in these experiments. First, above a molecular weight of 70,000, the craze initiation stress shows only a slight molecular weight dependence, Equation (4.13). Apparently the size of the molecule has little effect on crazing stress. This indicates that crazing occurs from segments of chains slipping past each other and not from motions of entire chains. On the other hand, glass transition temperatures and yield stresses are related to the total chain length as indicated in the sections in Chapter IV on Glass Transition Temperatures and Molecular Weight Effects, respectively. Figure 4-2 indicates that crazes in higher molecular weight materials are more stable than the ones in the lower molecular weight ranges. This supports that the chain motion is stopped after a limited amount of flowing. The most likely cause for the chains to stop

flowing is they are restricted by entanglements with other chains. The higher molecular polymers have more entanglements and therefore should stabilize crazes better. In relating this to the block copolymers it indicates that a minimum of one flexible end group should be put between entanglements. For polystyrene there are approximately 700 chain atoms between entanglements.[54,55] This corresponds to a prepolymer molecular weight of about 35,000.

The bulky end groups tested showed no effect on the polymer yielding properties or glass transition temperatures as indicated in the section on the Effects of End Groups on Polystyrene in Chapter IV. Apparently the end groups were just too small to have any influence on the large polymer chains. Any further work in this area should explore the effects of larger end groups. Perhaps if the molecular weight of the end groups were 2 to 5 percent of the weight of the polymer chain, then a plasticizing effect would be realized.

Further work may also be done in extending the range of molecular weights tested for crazing and yielding properties. However, higher pressure must be made available to the injection molding machine before much higher molecular weight samples may be molded.

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APPENDIXES

APPENDIX A

CALCULATION OF INITIATOR

Styrene monomer: $CH_2 = CH$ (C$_6$H$_5$) M. W. 104 g/mole

density = 0.903 g/ml.

Benzene: C_6H_6 M. W. 78 g/mole

density = 0.879 g/ml.

2 moles styrene monomer = 208 g.

208 g/0.903 (g/ml) = 230 ml.

4 moles benzene = 312 g.

312 g/0.879 (g/ml) = 355 ml.

Total volume = 585 ml.

Concentration of monomer = 2 moles/0.5851 = 3.42M

Concentration of benzene = 4 moles/0.5851 = 6.84M

To get a prepolymer of the desired M.W. a D.P. of 80 is required.

Assume: $f = 0.60$ $C_m = 0.7 \times 10^{-4}$

$k_d = 5.0 \times 10^{-5}$ sec^{-1} $C_p = 3 \times 10^{-4}$

$k_p = 200$ 1/mole sec $C_s = 0.121 \times 10^{4}$

$k_t = 72 \times 10^{6}$ 1/mole sec

(values from Brandrup-Immergut's Polymer Handbook[42])

$$R_d = R_t = R_i = 2fk_d(I) = 2k_t(M\cdot)^2$$

$$R_p = k_p(M)(M\cdot) = k_p(M)\left[\frac{fk_d(I)}{k_t}\right]^{1/2}$$

For a coupling termination

$$\overline{X}_n = R_p/[R_t/2 + k_{tr,m}(M\cdot)(M) + k_{tr,s}(M\cdot)(S) + k_{tr,i}(M\cdot)\ (I)]$$

$$1/\overline{X}_n = k_t R_p/[k_p(M)]^2 + C_m + C_s(S)/(M)$$

$$1/80 = (72 \times 10^6\ \text{1/mole sec})R_p/(200\ \text{1/mole sec})^2\ (3.42\text{m/1})^2 + .7 \times 10^{-4} + .121 \times 10^{-4}\ (2)$$

$$0.125 = 154\ R_p$$

$$R_p = 81.2 \times 10^{-6}\ \text{mole/1 sec}$$

$$R_p = k_p(M)\ [fk_d(I)/k_t]^{1/2}$$

$$81.2 \times 10^{-6}\ \text{moles/1 sec} = (200\ \text{1/mole sec})(3.42\text{m/1})\ \left[\frac{.6(5 \times 10^{-5}\ \text{sec}^{-1}(I)}{72 \times 10^6\ \text{1/mole sec}}\right]^{1/2}.$$

$$(I) = 0.0338\ \text{M}$$

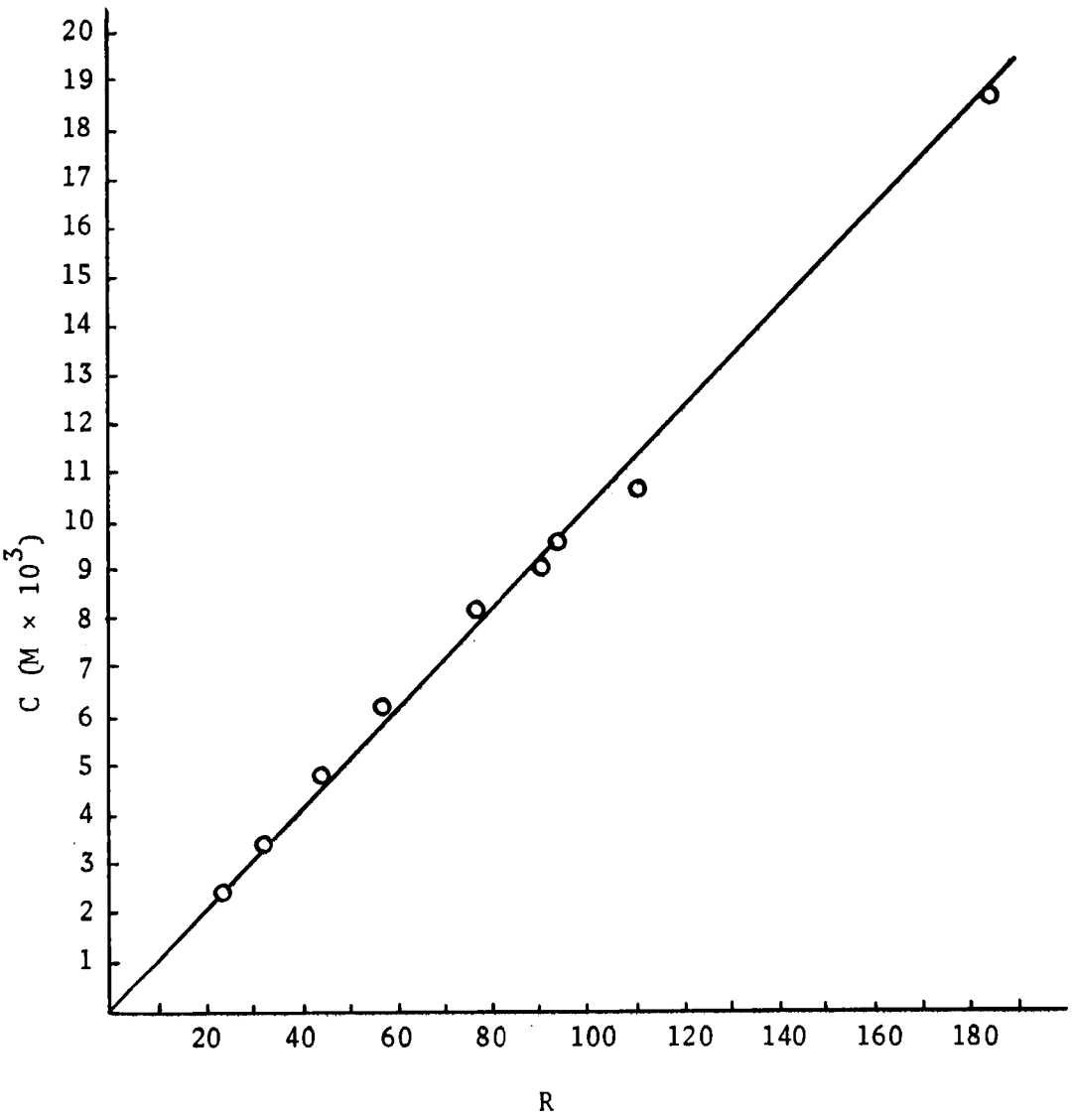
$$(0.0338\text{M})(0.5851) = 0.0198\ \text{moles initiator}$$

For ACVA M.W. = 280.28 g.

$$(0.0198\ \text{moles})(280.28\ \text{g/mole}) = 5.6\ \text{g. ACVA.}$$

APPENDIX B

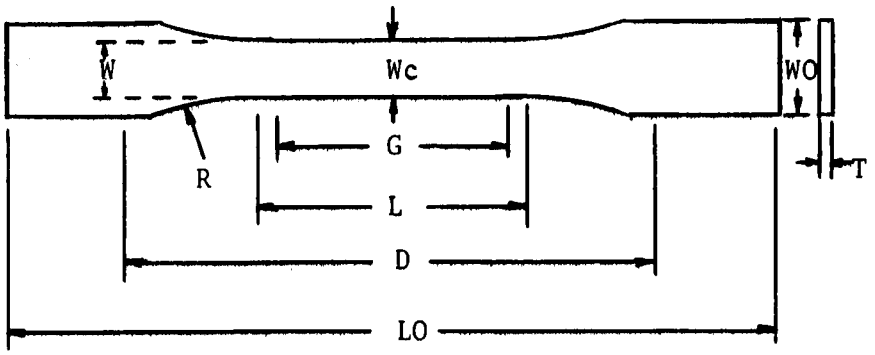
CALIBRATION CURVE FOR THE VAPOR PHASE OSMOMETER



T_m = 55°C.
T_s = 51.6°C.
Solvent - methyl isobutyl ketone.

APPENDIX C

TENSILE BAR SPECIFICATIONS

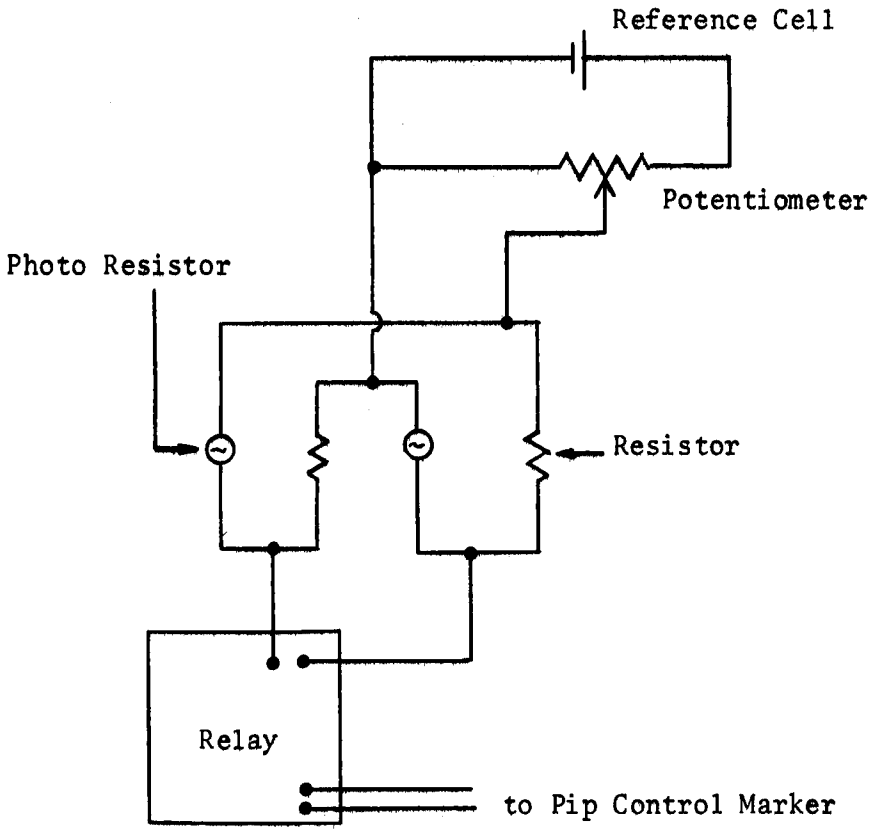


D638 ASTM

W -Width of narrow section	0.50"
L -Length of narrow section	2.25"
WO-Width overall minimum	0.75"
LO-Length overall minimum	6.50"
G -Gauge length	2.00"
D -Distance between grips	4.50"
R -Radius of fillet	3.00"
T -Thickness	0.125"

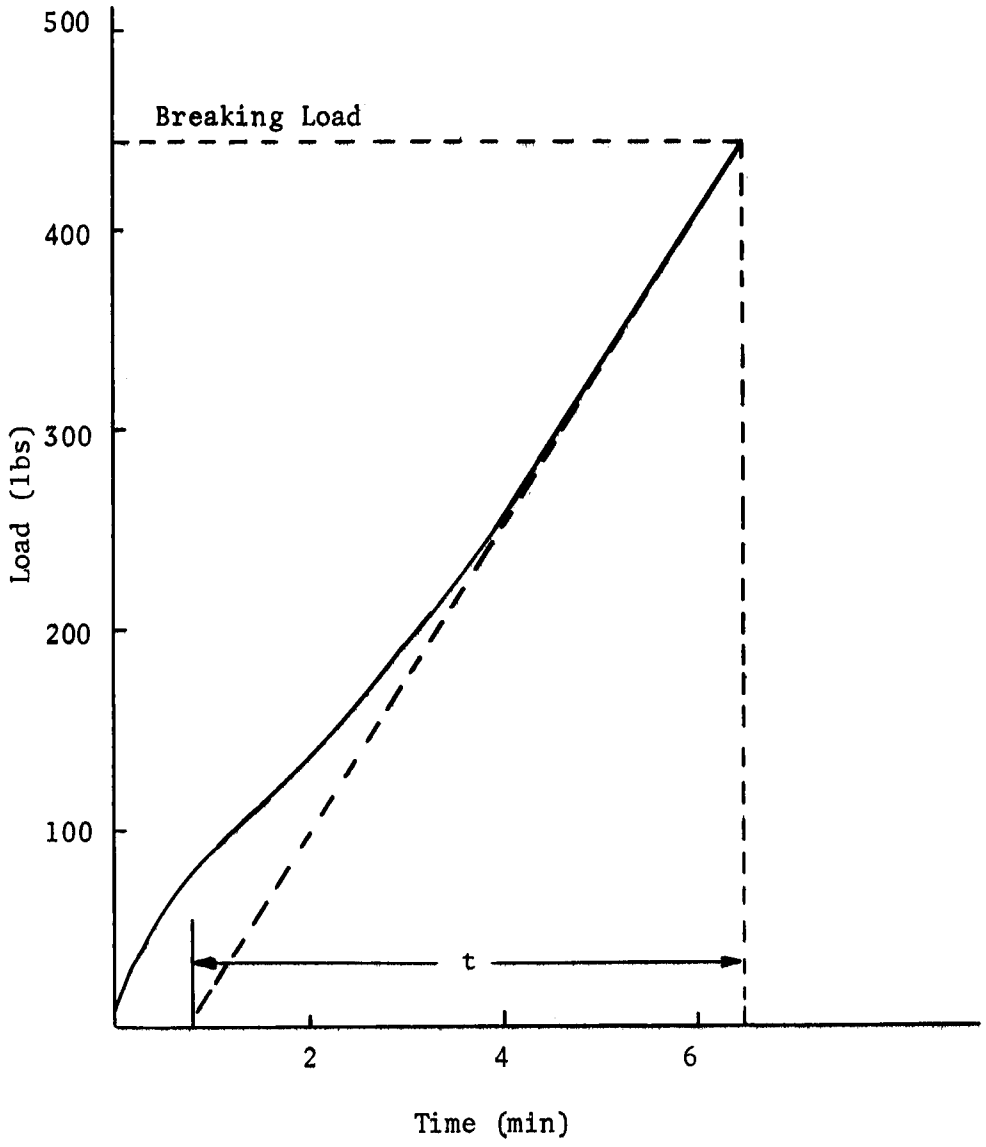
APPENDIX D

CIRCUIT DIAGRAM OF CRAZE DETECTION MECHANISM



APPENDIX E

ACTUAL LOAD-TIME EXTENSION CURVE



Fracture Strain = t × (Elongation Rate)

Apparent Modulus = Breaking Stress × (4.5")/Fracture Strain

VITA

The author, Bennie F. Kee, was born in Jackson, Tennessee on July 23, 1948. He attended both elementary and high school in that city. Upon graduation from high school in 1966, he enrolled at The University of Tennessee Martin in Chemical Engineering. He was a participant in the cooperative engineering education program. He worked in Columbia, Tennessee for E. I. DuPont making celulose sponges. In 1968 he transferred to The University of Tennessee Knoxville where he completed his B.S. in Chemical Engineering in 1971. He was awarded a fellowship at U. T. to continue his studies in chemical engineering. After graduation he went to work for E. I. DuPont in Chattanooga, Tennessee.