Crazing Studies of Polystyrene.
I. A New Phenomenological Observation

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Synopsis

This paper reports a new phenomenological observation regarding the stress crazing of glassy polystyrene. It was found that the applied stress to initiate a craze, often called the critical crazing stress, is independent of molecular weight. Further, the gross structure of the craze does depend on molecular weight, and other phenomenological aspects previously reported have been reaffirmed. These observations are interpreted in the light of knowledge from the literature and provide a better understanding of the crazing process.

INTRODUCTION

The subject of crazing in glassy polymers has been extensively studied, and it is fitting to give an introductory summary to the current understanding of the crazing process. Two recent review articles are available,[1,2] so these remarks will be brief and limited in scope primarily to craze initiation and development.

It is now well established that crazes are regions of extreme (40–60%) local plastic deformation.[3] The craze has the appearance to the eye of a fine hair-like crack. In reality, the craze contains plastically deformed highly oriented polymeric material possessing a different density and refractive index than the glassy polymer from which it was produced.[4-6]

Further, it has also been established that a critical stress must be reached before crazing will occur and the stress must have a tensile component.[5,7-13] To date, crazes have not been observed to form unless the deformation mode contains a tensile component, i.e., shear or compression will not produce crazing.[2] Also, craze formation is known to show time-dependent characteristics such as applying a load and then waiting a given period of time for a craze to appear.[6,9,10,12,14,15] Or, viewed in another way, the crazing process is sensitive to the rate of deformation.[5,16-18]

Another extremely interesting result is the fact that the critical stress to produce a craze is dependent on the test temperature.[5,10,11,16,18,19] Some quantitative data are available for both polystyrene[5] and poly(methyl methacrylate).[10]

A rather consistent, but as yet not complete, physical model is generally agreed upon by most researchers in this area. An attempt is made here to outline the salient features of this model. First of all, the glassy polymer is said to not be entirely homogeneous. That is, the structure of the glassy polymer contains certain disruptions and defects, such as voids, dust particles, collections of polymer chain ends, microvariations of density, etc. These defects play the role of stress concentrators when a load is applied to a sample.[9,14,20] This leads to a very localized stress build-up, and when a certain stress level is attained, crazes initiate and then propagate through the sample. It is important to point out that Sternstein has developed a good analytical view of the stress conditions present and necessary for crazing to occur.[10,11,21]

While Sternstein's analysis draws attention to the fact that crazes always form perpendicular to the applied stress, no further understanding in this regard beyond the phenomenological description is available. It is, of course, very interesting to note from this observation that crazing is thus dependent on normal stresses. This is not typical of plastic deformation processes in most materials, and by way of contrast it is pointed out that many other very commonly observed plastic deformations such as Luder's bands and "slip mechanisms" in metals are dependent on shear stresses. The model does appear to be lacking in this sense, at least until further explanation can be developed.

Finally, the model for glassy state behavior has been extended to include the coalescence of voids in the craze to form a crack which can propagate through the sample to produce catastrophic failure.[6,22−32] Many details of this model are of interest to the entire craze behavior but are not salient to our further discussion here.[1,2,33,34,35]

The main purpose of the above introduction is to provide a perspective to later base a discussion of the crazing phenomenon and its relationship to the molecular weight of glassy polystyrene. The observations of the critical crazing stress being independent of molecular weight, tensile strength considerations in different molecular weight ranges, and gross structural features of the crazes will all be dealt with.

EXPERIMENTAL PROCEDURES AND RESULTS

A number of polystyrene samples were synthesized. These polystyrenes varied both in molecular weight and endgroup structure.

Standard Polystyrene Homopolymers

Styrene monomer was solution polymerized in refluxing benzene (80°C) using 2,2'-azobis(2-methyl propionitrite) as the initiator. A nitrogen atmosphere was maintained in a standard glass reactor, fitted with reflux condensor and stirrer. The ratio of styrene monomer to initiator was varied to produce different molecular weight polystyrenes. (Table I sum-

TABLE I
Basic Characterization Data for Polystyrene Samples[a]

Polymer no.[b]	Endgroup	$\bar{M}_n \times 10^{-3}$, g/mole	$\bar{M}_w/\bar{M}_n$	T_g, °C
1	Cyclohexanate	67.5	2.39	86
2	Cyclohexanate	122	2.58	102
3	Cyclohexanate	147	2.36	105
4	Eicosonate	92.5	3.11	95
5	Eicosonate	124	3.51	101
6	Rubidium ion	67.5	2.39	87
7	Rubidium ion	92.5	3.11	93
8	Rubidium ion	124	3.51	102
9	2-Methyl propionitrile	68	2.64	88
10	2-Methyl propionitrile	75	2.78	89
11	2-Methyl propionitrile	111	3.20	101
12	2-Methyl propionitrile	123	2.71	100
13	2-Methyl propionitrile	146	2.81	107

[a] Molecular weight data are based on gel permeation chromatography measurements.[39]

[b] These numbers identify the polymer samples in Figures 3, 4, and 5.

marizes synthesis and characterization data for all polymers described in this section.)

After completion of the polymerization, the polymer was coagulated in n-heptane, dried, and stored until further use.

Carboxyl-Terminated Polystyrene

The same polymerization procedure was used as described above, with the exception that 4,4'-azobis(4-cyanovaleric acid) was employed as the initiator. Since free-radical solution polymerizations of styrene undergo termination by combination of free-radial species, the polystyrene produced here contains a carboxyl group at each end of the chain.[36,37] This was verified by acid titration and molecular weight measurements.[38]

Modified Polystyrenes

A number of attempts to modify the polystyrene structure were undertaken through the use of the carboxyl endgroups. Some block copolymer structures were tried via condensation of carboxyl groups with various diamines, diols, diepoxides, etc. The general result was a block structure $(-A-B-)_n$, where n only equaled 2 to 4. Since the starting block segments were low molecular weight (polystyrene $M_n \sim 10,000$ and cosegment 200–1000), the polyblock structure never had a high enough molecular weight to be useful in the crazing studies.

Another alternative was available in that at least the endgroup structure could be changed. In order to determine if various endgroup structures, ranging from bulky to long-chain alkyl to ionic, would affect the crazing behavior, the following products were synthesized. The carboxyl groups were reacted with cyclohexanol, eicosanol, or rubidium hydroxide. This

TABLE II

Tensile Measurements for Polystyrene at 25°C and a Nominal Strain
Rate of $1.7 \times 10^{-4} \sec^{-1}$

Polymer no.	Breaking stress, psi	Crazing stress,[a] psi	Breaking elongation, in.	Modulus,[b] psi $\times 10^{-5}$
1	4410 ± 320	3920 ± 200[c]	0.0978	2.21
6	3840 ± 190	3710 ± 200[c]	0.0941	2.07
3	6960 ± 700	4570 ± 90	0.1644	2.11
2	6560 ± 230	4700 ± 280	0.1490	2.14
5	6580 ± 140	4330 ± 310	0.1491	2.11
8	6300 ± 390	4430 ± 480	0.1453	2.08
4	5900 ± 140	4560 ± 340	0.1230	2.11
7	5860 ± 70	4230 ± 550	0.1200	2.12
9	4330 ± 210	3750 ± 70[c]	0.0909	2.15
12	6670 ± 500	4270 ± 400	0.1515	2.15
13	7200 ± 570	4610 ± 250	0.1641	2.17
10	5740 ± 280	4290 ± 240	0.1148	2.14
11	6160 ± 320	4400 ± 430	0.1336	2.13

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

[b] This is an apparent modulus.

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

potential variable can be disposed of quickly. Note in the data presented in Tables I and II and Figures 3, 4, and 5 that, whenever the endgroup structure was changed, the property under examination did not respond to the change in endgroups, within the limits of measurement and detection used in this study.

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 machined into it. The molded tensile specimens were very close to this configuration, differing by only a few thousandths of an inch. The tensile bars had a gauge length of 2 in. and a cross section of 0.500 in. by 0.125 in.

When the tensile bars were viewed through polarized lenses, some color was apparent which indicates residual stress or orientation. Murphy[18] showed that the residual stresses in his moldings of polystyrene were 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 catastrophically. Annealing

produced gross contractions in the tensile bars. This was also thought to be an orientation effect.

Another study by Thomas and Hagan[39] showed that molecular weight and molecular weight distribution influences the orientation of injection-molded polystyrene and its crazing behavior. They demonstrated that different crazing patterns formed depending on the orientation developed during molding. The point of interest here is that the orientation depended on molecular weight and its distribution.

In order to minimize this effect in our studies, the highest practical melt temperature and lowest flow rate necessary to make a full tensile bar were used. These laboratory polymer tensile bars were then tested exactly as fabricated.

Testing the Samples

Glass Transition Temperature

The glass transition temperatures were determined for each polymer using a Perkin-Elmer differential scanning calorimeter Model 1B. Most determinations were made at scanning speeds of 5°C/min and 10°C/min. Several runs were made with each polymer at different speeds, and the results were 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 I and Figure 5.

Tensile Testing

The polystyrene specimens were tested for tensile strength and crazing properties on an Instron tensile testing machine. Craze initiation was detected using the reflective properties of crazes. A light was focused to a 1-in. circle on the specimen. Until crazing occurred, the light shined through the specimen. At the onset of crazing, the light was reflected up to a photoresistor which was connected through an adjustable bridge circuit to a relay. The relay activated a Pip Control even marker on the Instron chart. The craze detection equipment (Fig. 1) was mounted on
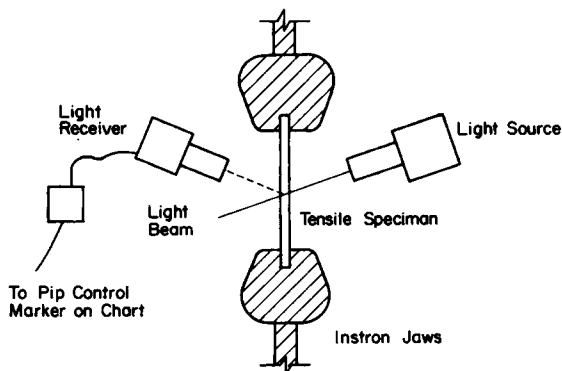

Fig. 1. Schematic representation of the craze detection mechanism.

the Instron frame with a bracket.   The photoresistor 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 stan-
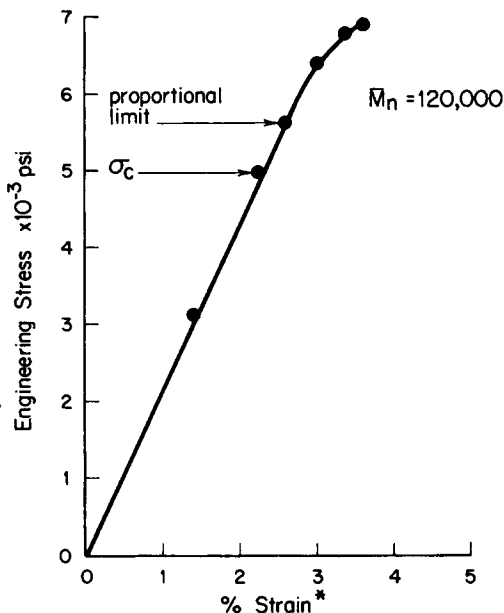

Fig. 2. Engineering stress–strain curve for polystyrene at 25°C and a nominal strain rate of 1.7×10^{-4} sec^{-1}. (*Based on Instron jaw separation.)
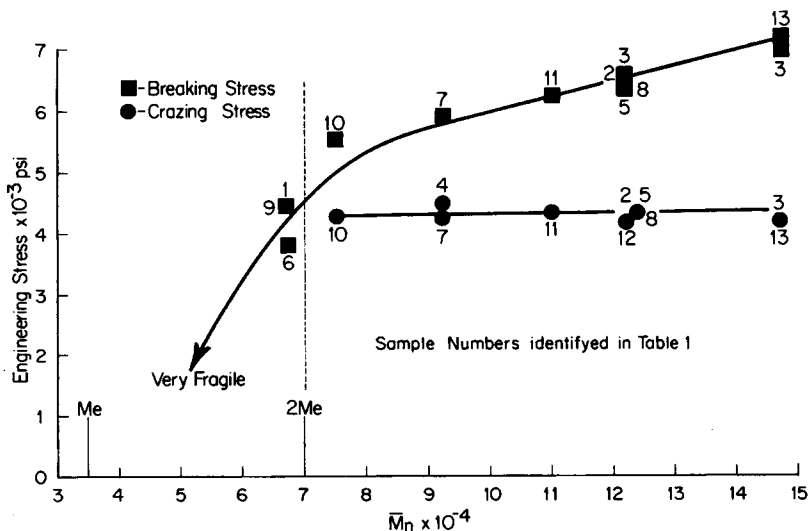

Fig. 3.   Breaking stress and crazing stress vs. molecular weight for polystyrene at 25°C and a nominal strain rate of 1.7×10^{-4} sec^{-1}.
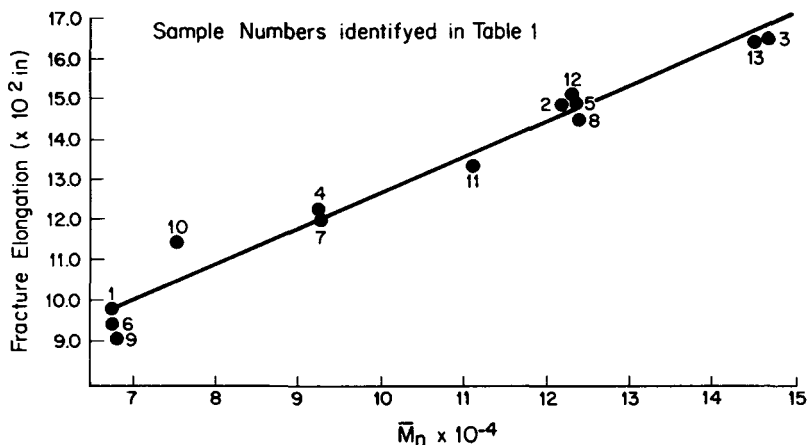
Fig. 4. Fracture elongation vs. molecular weight for polystyrene at 25°C and a nominal strain rate of 1.7×10^{-4} sec^{-1}.

dard $1\frac{1}{2}$ 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[9] and Haward et al.[5]

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 engineering 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 in. 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 weight material. The tensile data are reported in Table II and plotted in Figures 2, 3, and 4.

DISCUSSION

Much of the following discussion is concerned with the influence of molecular weight on the deformation processes in glassy polystyrene. The major point of interest is that the initiation of a craze is independent of molecular weight, in contrast to craze development and breakdown which are highly dependent on molecular weight. As demonstrated in Figure 3, the deformation behavior greatly depends on whether the polymer $\bar{M}_n$ is greater or less than $2 M_e$.
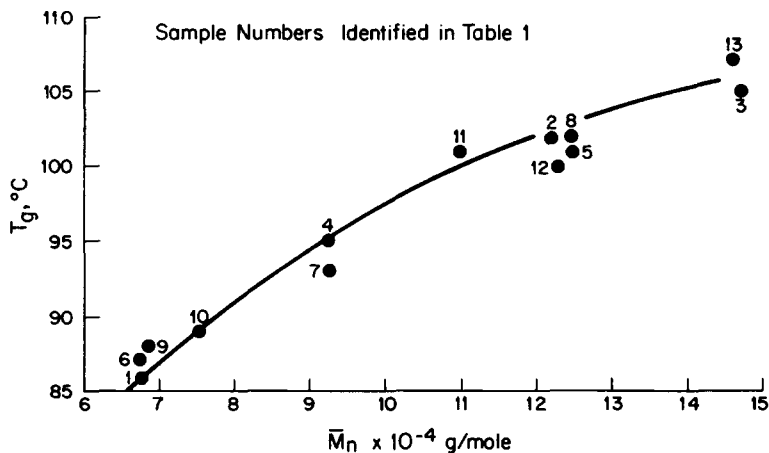
Fig. 5. Glass transition temperature of polystyrene vs. molecular weight.

Deformation vs. Molecular Weight

The first specific issue to examine is the relationship between plastic deformation and the molecular weight of the polystyrene. It is known that a craze is a region of considerable plastic strain, ca. 40% to 60%.[3] Other plastic events also occur. Some homogeneous plastic flow occurs in all of these test pieces as evidenced by the nonlinearity of the stress–strain curves. Parameters such as stress at break and strain at break, then, are related to plastic deformation.

Now, plastic deformation in polymeric materials is closely related to the movement of the polymer segments under an applied load. Since these segments are connected within a single polymer chain, one expects plastic deformation events to show a dependence on molecular weight. This is consistent with most plastic events, e.g., strain to break, stress at break, and strain hardening all show the common feature of an increasing dependence on molecular weight (see Figs. 3 and 4).

However, the important new finding presented here is that the crazing stress is independent of molecular weight when the polystyrene $\bar{M}_n > 2\,M_e$. Clearly, then, craze initiation is not a plastic event.

We offer the following interpretation to explain the nature of the craze initiation step. In the arguments presented in the introductory section, it was pointed out that the flaws in glassy materials act as stress concentrators. These stress concentrators, acting in a very localized region, raise the stress level above the resistance barrier to plastic flow. Thus, the nominal stress required to initiate a craze, when it is enhanced by a flaw, then signifies for the craze-prone region the transition from elastic to plastic deformation. Now, of course, if this is truly a localized transition from elastic to plastic response, then little if any plastic flow of polymer segments has occurred. This then explains why the observed crazing stress is independent of molecular weight.
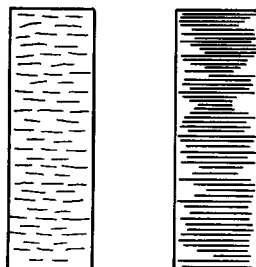
Other Molecular Weight Effects

Since molecular weight is a key molecular variable for a polymer, it should not be surprising to observe its influence on other deformation related phenomena. There are, thus, two more molecular weight considerations that will be developed here. One is the effect of molecular weight on the gross crazing pattern. The other is the junction of the breaking stress and crazing stress at $2 M_e$ (see Fig. 3).

Both the frequency of craze formation and the gross structure of the craze are sensitive to the molecular weight of the polystyrene. This was observed in this work and also under conditions of solvent stress crazing by Rudd.[40]

In the case of high molecular weight polystyrene, the crazes are very numerous, fine in texture, long, and very straight. When the $\bar{M}_n$ is decreased to 70,000–80,000 g/mole, comparatively few crazes are formed; they are coarse in texture, somewhat shorter than the former case, and can be jagged. (This is illustrated in Fig. 6.) At an $\bar{M}_n$ less than 70,000 g/mole, the tendency for craze formation is greatly decreased to where few if any crazes form.

The following facts form an interesting pattern of behavior: (1) Polystyrene shows a sudden drop in strength when its molecular weight is decreased below about 70,000 g/mole (Fig. 3); (2) the tendency to form crazes is greatly diminished below 70,000 g/mole; (3) the entanglement molecular weight for polystyrene is around 35,000 g/mole.[41,42]

The junction of the breaking stress and the crazing stress at $2 M_e$ suggests this view of deformation in polystyrene. Below $2 M_e$, where no network of entangled chains exists and the polymer is of low tensile strength and ductility,[43–45] the first flaw that concentrates stress to a critical level causes catastrophic failure because no plastic deformation mechanism is available. However, when $2 M_e$ is exceeded, stress is locally relieved by craze propagation. Then the breakdown of crazes and propagation of true cracks is the predominant deformation process leading to failure. (A note by Gent and Thomas[46] provides an apparently compatible view of molec-

$\bar{M}_n \sim 80,000$ $\bar{M}_n \sim 150,000$

Fig. 6. Illustration of gross craze structure vs. molecular weight for polystyrene.

ular weight effects on crazing and fracture when considered in the context of the experimental findings presented here.)   The ratio, polystyrene $\bar{M}_n/2 M_e$, is a critical parameter.   A value of less than one leads to brittle tensile fracture.   A value greater than one means the possibility exists for significant plastic flow to occur prior to fracture.

References

1. R. P. Kambour and R. E. Robertson, General Electric Report No. 70-C-104, 1970.

2. S. Rabinowitz and P. Beardmore, *CRC Critical Reviews in Macromolecular Science*, **1**, 1 (1972).

3. R. P. Kambour, *J. Polym. Sci. A*, **2**, 4159 (1964).

4. J. P. Berry, *J. Polym. Sci.*, **50**, 107 (1961).

5. R. N. Haward, B. M. Murphy, and E. F. T. White, Symposium on Fracture, Paper 45, Session IV, Brighton, England, 1970.

6. R. P. Kambour, *J. Polym. Sci. A*, **3**, 1713 (1965).

7. M. Bevis and D. Hull, *J. Mater. Sci.*, **5**, 357 (1970).

8. R. J. Bird, G. Rooney, and J. Mann, *Polymer*, **12**, 742 (1971).

9. B. Maxwell and L. F. Fahm, *Ind. Eng. Chem.*, **41**, 9, 1948.

10. S. S. Sternstein, L. Ongchin, and A. Silvermann, *Appl. Polym. Symposia*, **7**, 175 (1968).

11. S. S. Sternstein and L. Ongchin, *ACS Polym. Preprints*, **10**(2), 1117 (1969).

12. E. E. Ziegler and W. E. Brown, *Plast. Technol.*, 409 (1955).

13. E. E. Ziegler and W. W. Brown, *Plast. Technol.*, 341 (1955).

14. C. C. Hsiao and J. A. Sauer, *J. Appl. Phys.*, **21**, 11, 1071 (1950).

15. O. K. Spurr, Jr., and W. D. Niegisch, *J. Appl. Polym. Sci.*, **6**, 585 (1962).

16. P. Beardmore and T. L. Johnston, *Phil. Mag.*, **23**, 119 (1971).

17. J. Murray and D. Hull, *J. Polym. Sci. A2*, **8**, 1521 (1970).

18. B. M. Murphy, *Chem. Ind.*, **8**, 298 (1969).

19. G. S. Sadakne, Master's Thesis in Chemical Engineering, University of Tennessee, Knoxville, Tennessee, 1972.

20. L. Nielson, *J. Appl. Polym. Sci.*, **1**, 24 (1959).

21. L. D. Cessna, Jr., and S. S. Sternstein, *Fundam. Phenom. Mater. Sci.*, **4**, 45 (1967).

22. P. Beardmore and S. Rabinowitz, *J. Mater. Sci.*, **7**, 720 (1972).

23. P. Beardmore and S. Rabinowitz, Ford Motor Co. Scientific Paper, (1971).

24. P. S. Beardmore, S. Rabinowitz, and A. R. Krouse, Ford Motor Co. Scientific Research Staff Report No. SR 71-123 (1971).

25. A. N. Gent, *J. Mater. Sci.*, **5**, 925 (1970).

26. D. Hull, *J. Mater. Sci.*, **5**, 357 (1970).

27. R. P. Kambour, *J. Polym. Sci. A2*, **4**, 17 (1966).

28. R. P. Kambour, *J. Polym. Sci. A2*, **4**, 349 (1966).

29. R. P. Kambour, *J. Polym. Sci. A2*, **4**, 359 (1966).

30. R. P. Kambour, *Polym. Eng. Sci.*, **8**(4), 281 (1968).

31. J. Murray and D. Hull, *Polymer*, **15**, 451 (1969).

32. J. Murray and D. Hull, *J. Polym. Sci. A2*, **8**, 583 (1970).

33. R. P. Kambour and R. W. Kopp, *J. Polym. Sci A2*, **7**, 183 (1969).

34. G. Rehage and G. Goldbach, *Angew. Makromol. Chem.*, **1**, 125 (1967).

35. P. I. Vincent and S. Raha, *Polymer*, **13**, 283 (1972).

36. C. H. Bamford, A. D. Jenkins, and R. P. Wayne, *Faraday Soc. Trans.*, **56**(1), 932 (1960).

37. J. C. Bevington, H. W. Melville, and R. P. Taylor, *J. Polym. Sci.*, **12**, 449 (1954).
38. Kee, B. F., Master's Thesis in Chemical Engineering, University of Tennessee, 1973.
39. D. Thomas and R. Hagan, *Polym. Eng. Sci.*, **9**, 164 (1969).
40. J. F. Rudd, *Polym. Lett.*, **1**, 1 (1963).
41. R. S. Porter and J. F. Johnson, *Chem. Rev.*, **66**, 1 (1966).
42. R. S. Porter, W. J. MacKnight, and J. F. Johnson, *Rubber Chem. Technol.*, **41**(1), 1 (1968).
43. R. N. Haward and I. Brough, *Polymer*, **10**, 724 (1969).
44. R. N. Haward and J. Mann, *Proc. Royal Soc. A*, **282**, 120 (1964).
45. H. W. McCormick, F. M. Brower, and L. Kin, *J. Polym. Sci.*, **39**, 87 (1959).
46. A. Gent and G. Thomas, *J. Polym. Sci. A-2*, **10**, 571 (1972).