Mechanical Relaxation in Polycarbonate–Polysulfone Blends

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Synopsis

Lexan polycarbonate and polysulfone P-1700 were blended to various weight percentages by dissolution in methylene chloride. The blended material was reclaimed in the form of evaporated thin films which were dried, ground, and molded. Low-frequency mechanical relaxation tests were run on specimens machined from this material as a function of composition and thermal treatment. In addition to the β-peak, a second peak, β', was resolved in unannealed 75 wt/o P-1700 specimens. These results are presented and a possible interpretation is discussed and compared with previously proposed mechanisms.

INTRODUCTION

Bisphenol A polycarbonate and poly(arylene sulfones) are members of the class of polyesters and polyethers which contain phenyl groups in the main chain. These materials are of commercial prominence due to their relatively high glass transition and their superior ductility and impact resistance below T_g. The toughness of these polymers has been attributed to molecular motions of the main chain at temperatures below T_g. This motion is evidenced by the broad relaxation β-peaks in these materials. While the β-peak in polycarbonate has been extensively studied,[1-6] little research on mechanical relaxation has been reported on the polysulfones.[7] The results of the low-frequency mechanical relaxation experiments on injection- and compression-molded specimens of General Electric's Lexan polycarbonate, Union Carbide Corporation's polysulfone P-1700, and blends of these two polymers are discussed in this paper.

MATERIALS AND EXPERIMENTAL PROCEDURES

Lexan polycarbonate and polysulfone P-1700 injection-molding resins were used in these experiments. The homopolymers were blended to the desired weight percentages by dissolution in methylene chloride to a total

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concentration of 250 g/l. The blended material was reclaimed from solution by evaporation of thin films cast on Pyrex plates. Film thickness was maintained at approximately 0.005 in.

The cast films were dried and ground for molding. Molding was done by both compression and injection techniques. The compression molding was done with a modified Buehler specimen press which yielded a cylindrical shot weighing of approximately 90 g with a diameter of 1.15 in. and a length of approximately 6 in. The molding parameters used were 315°C mold temperature, 10,000 psi molding pressure, and a dwell time of 10 min at temperature and pressure. At the end of the dwell time, the power to the mold heaters was turned off and the mold was allowed to cool to 100°C, with the pressure being maintained during cooling. The shot was then pressed from the mold and specimens were machined from its central section.

The injection molding was done with a small ram-type injection press designed and built for this work. A number of temperature profiles and ram speeds were investigated. The bulk of the material tested was molded with cylinder and nozzle temperatures of 315°C, mold temperature of 175°C, ram speed of 2 in./min, final molding pressure of 9500 psi, and a dwell time at pressure of 1 min. The inside diameter of the cylinder was 1.15 in. and the nozzle diameter was 0.25 in. The resulting shot was of rectangular cross section, $0.875 \times 0.625 \times 3.000$ in. long. As with the compression-molded material, specimens were machined from the central areas of the shots.

Intrinsic viscosity measurements were made on material at various stages of the processing. There was no indication of molecular weight breakdown, either as a result of the grinding or the molding.

The data were taken by a free decay technique on apparatus designed by Carnahan and Buch.[8] The bulk of the data were taken at 6 cycles/sec. To determine the peak shift with frequency, a limited number of tests were run at frequencies above and below this value. The variation of frequency was accomplished by changes in the inertia member and specimen geometry. The standard specimen was a rectangular parallelpiped $0.250 \times 0.125 \times 1.250$ in. long with 0.375 in. between the upper and lower grips.

In addition to Lexan and P-1700, specimens of 5, 10, 25, 50, 60, 75, 80, 90, and 95 wt/o P-1700 were tested. The β-peak was investigated as a function of composition and as a function of thermal history for each composition. In each case an unannealed, as-machined specimen was run. This was followed by a series of anneals under 25-micron vacuum for 36 hr at temperature. Each anneal was preceeded by a 24-hr drying period at 125°C, also under vacuum. The annealing temperatures selected were 140°C, 160°C, 175°C, 190°C, and 200°C. Not all compositions could be annealed at all of these temperatures. Excessive flow was found to occur in low P-1700 compositions during the higher temperature anneals and in P-1700 specimens at temperatures above 200°C. These temperatures were selected to give anneals: below T_g of Lexan, between T_g of Lexan and T_g of P-1700, and above T_g of P-1700. Specimens were taken through the

sequence of anneals until it was found that the next-higher anneal resulted in no change in the loss curve.

The relaxation parameter obtained as a function of temperature from these tests was the internal friction, Q^{-1}, which is defined by

$$Q^{-1} = (1/n\pi)\ln(A_0/A_n) = \tan\delta$$

where A_0 = the peak-to-peak amplitude of the first cycle counted, A_n = the peak to peak amplitude of the nth cycle counted, n = the number of cycles counted, and δ = the angle by which the strain lags the stress in the specimen. The data were all taken in the amplitude-independent region of the internal friction, with n equal to between 30 and 90 cycles.

RESULTS

Figures 1 through 5 are Q^{-1}-versus-$1/T$ curves for Lexan, 50 wt/o, 60 wt/o, 75 wt/o P-1700, and P-1700 material with results from unannealed specimens, partially annealed specimens, and fully annealed specimens. "Fully annealed" means here the highest temperature anneal which resulted in a change in test results. These specimens were run at 6 hertz. The curves for Lexan and polysulfone compare very well with previously published data. The small intermediate peak reported for Lexan at $1/T$ = 0.003 by Illers and Breuer[6] and Muller and Huff[3] is apparent in Figures 1 and 2 for unannealed Lexan and 50 wt/o specimens.

From Figures 1 and 5, qualitative differences in the results for Lexan polycarbonate and polysulfone are evident. On the high-temperature side of the β-peak, between $1/T$ = 0.0030 and $1/T$ = 0.0055 (60° to −90°C), the curve for Lexan is concave from below while the curve for P-1700 is linear to convex. The results for the polyblend specimens containing 5%
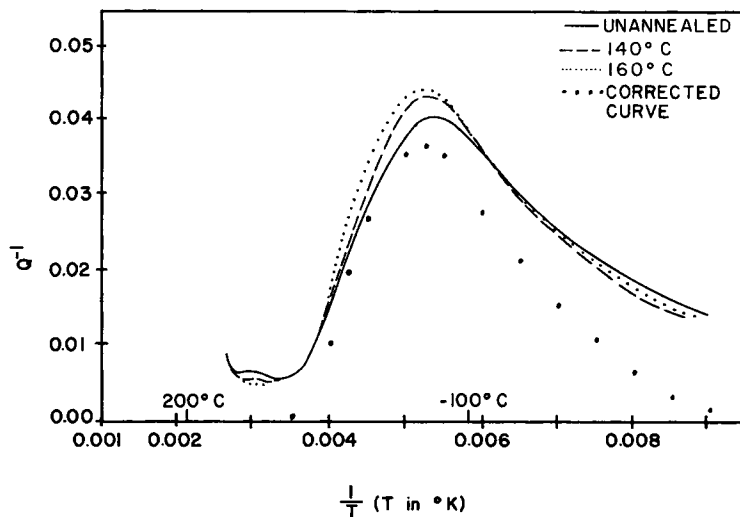

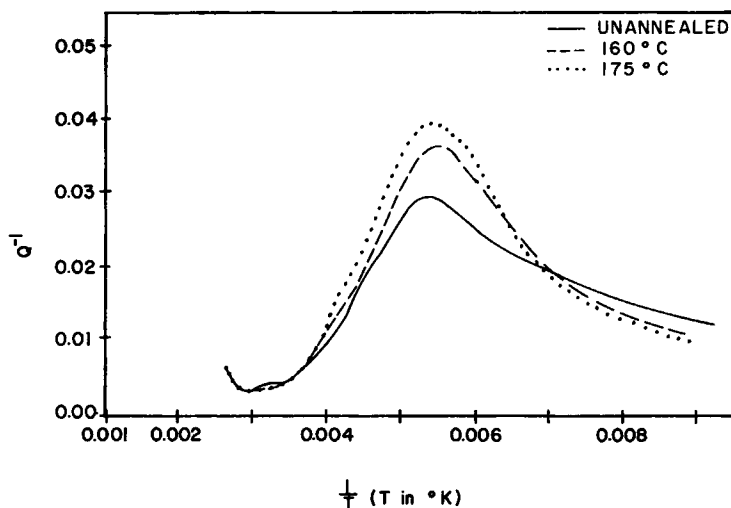Fig. 1. Q^{-1} vs. $1/T$ for polycarbonate run at 6 hertz.

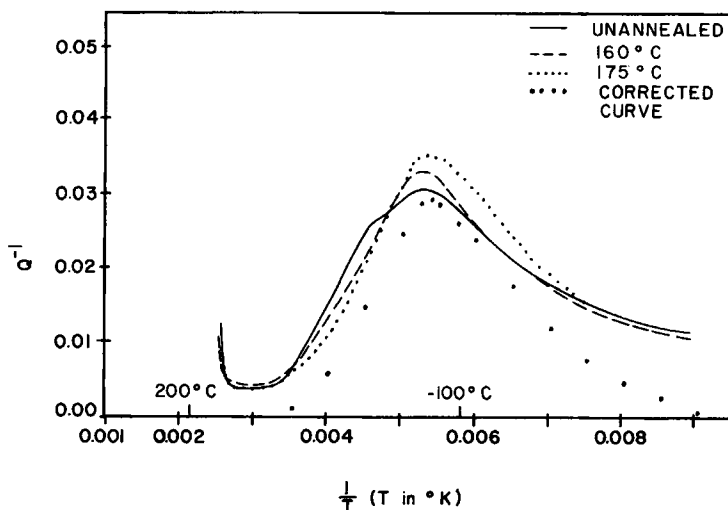Fig. 2. Q^{-1} vs. $1/T$ for 50 wt/o P-1700 run at 6 hertz.

Fig. 3. Q^{-1} vs. $1/T$ for 60 wt/o P-1700 run at 6 hertz.

to 50% P-1700 were found to be similar to the results obtained for the Lexan specimens. The results for specimens with compositions from 80 wt/o through P-1700 were similar to that of Polysulfone. The 60 wt/o specimens yielded results similar to Lexan in the unannealed state, but took on the linear to convex aspects of P-1700 with annealing. In 75 wt/o material, the most interesting effects of blending were noted; a very distinct second peak with maximum at $1/T = 0.00410$ ($T = -20°C$) was found in the unannealed specimen. This peak has been designated β', and the major peak at $1/T \cong 0.0055$ ($T \cong 90°C$) was designated β. It was found
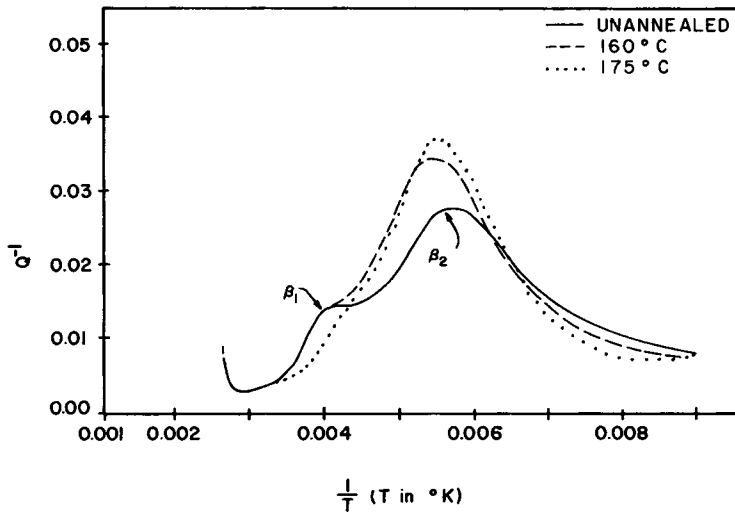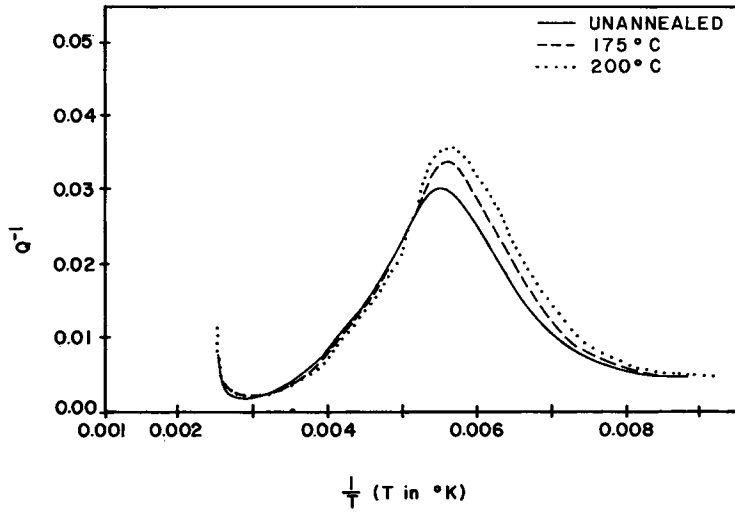
Fig. 4. Q^{-1} vs. $1/T$ for 75 wt/o P-1700 run at 6 hertz.

Fig. 5. Q^{-1} vs. $1/T$ for polysulfone run at 6 hertz.

TABLE I
Activation Energies from Peak Shift Data

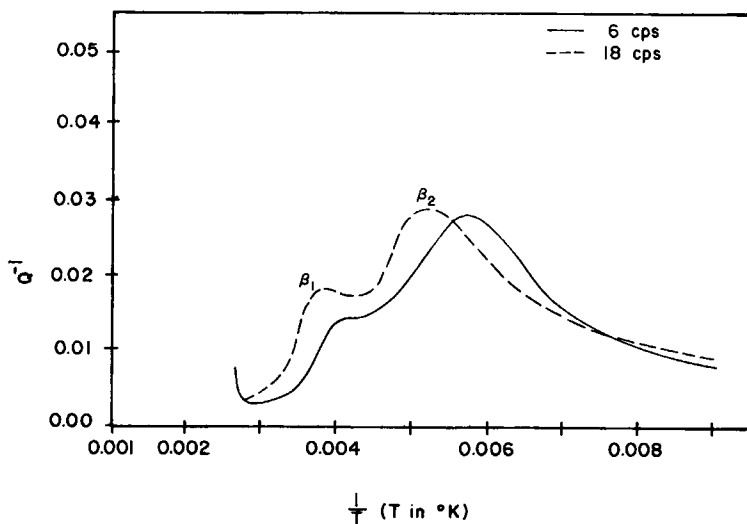| Composition, wt-% P-1700	Frequency #1, rdn/sec	Frequency #2, rdn/sec	Peak shift $\Delta(1/T)_{max}$	H, kcal/mole
Lexan	37.7	24.5	0.00023	3.5
5	66.0	24.5	0.00035	3.4
75,β'-peak	113.1	37.7	0.00030	7.3
75,β-peak	113.1	37.7	0.00050	4.4
P-1700	37.7	24.5	0.00019	4.2

Fig. 6. Q^{-1} vs. $1/T$ for 75 wt/o P-1700 unannealed material run at 6 and 18 hertz.

that with annealing, the β'-peak was absorbed into the high-temperature side of the β-peak.

The effect of a change in frequency on the location of the peak maximum was investigated on Lexan, P-1700, and 5 and 75 wt/o material. The results of these tests are tabulated in Table I. The Q^{-1}-versus-$1/T$ data for the 75 wt/o unannealed material at 6 and 18 hertz are shown in Figure 6.

DISCUSSION

From investigations of a number of poly(methylene terephthalates) and bisphenol A polycarbonate by mechanical relaxation techniques, Illers and Breuer[6] assigned the β-peak in polycarbonate to the motion of the carbonyl group. Kurz, Woodbury, and Ohta[7] assigned the corresponding relaxation in P-1700 to the motion of the SO_2 group. From work on phenyl-containing polyurethanes, Kajiyama and MacKnight[9] suggested that similar peaks were due to the torsional motion of the phenyl groups. Matsuoka and Ishida[4] conducted dielectric relaxation and nuclear magnetic resonance studies on bisphenol A polycarbonate and divided the β-peak into a contribution from the movement of the carbonate groups and a contribution from the motion of the benzene rings.

It seems reasonable to attribute the differences in the relaxation spectra of P-1700 and Lexan to the differences in the configuration of these two polymers. The two repeat units are depicted in structural formulas in Figure 7. These units differ in the polar groups, SO_2 in P-1700 and CO_3 in Lexan, and the polysulfone ether linkage which is not found in Lexan. If the relaxation process is assumed to be a combination of motions of the polar group and the benzene rings, the differences in the loss curves should
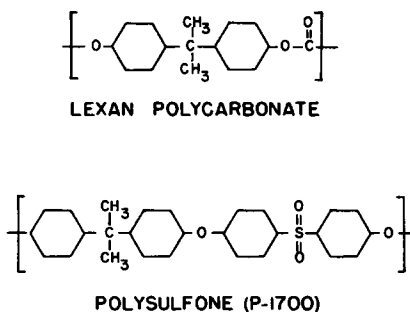
LEXAN POLYCARBONATE

POLYSULFONE (P-1700)

Fig. 7. Structural formulas of Lexan and P-1700 repeat units.

be attributable principally to the difference in the polar groups. As previously discussed, the difference in the loss curves of the two homopolymers is most pronounced on the high-temperature side of the β-peak. It is also in this temperature interval that the β'-peak appears in the unannealed 75 wt/o polyblend and is incipient in the 60 wt/o polyblend. The activation energies for the β- and β'-relaxation for Lexan, P-1700, P-1700, 5 wt/o and 75 wt/o specimens were calculated from the shift of the temperature of peak maximum with frequency and are listed in Table I. An estimate of activation energies for the other compositions was obtained as follows: A tangent line was drawn between the low- and high-temperature tails of the loss curve, and the area below this line was treated as "background." This background was subtracted from the experimental curve to give a corrected curve as indicated by the bottom-most curves in Figures 1 and 3. The half-width, Δ, of the peak of the corrected curve were determined, and Δ was then used to calculate activation energies on the assumption of a standard linear solid model.

The activation energies estimated from the peak half-widths are tabulated in Table II. An approximately constant value of ~ 2.0 kcal/mole was found through 60 wt/o P-1700, and a second constant value of approximately 2.7 kcal/mole was found for the specimens with greater than 60 wt/o P-1700.

Comparison of the activation energies in Tables I and II indicates that values calculated from the peak shift are higher than those calculated from the peak shape. In the case of the β'-peak in the 75 wt/o blend, the activation energies determined by the two techniques are in good agreement. This indicates that the β-peak cannot be described by a standard linear solid. A distribution of relaxation times for standard linear solids leads to a wider peak and, hence, a lower activation energy from peak shape than peak shift as our results show.

In their work on polycarbonate, Matsuoka and Ishida[4] reported an activation energy for the dielectric β-relaxation of approximately 7.0 kcal/mole. Since the CO_5 unit offers the only dipolar group in the repeat unit, it seems plausible that the dielectric relaxation is due solely to the movement of this group and is not notably affected by the movement of the

TABLE II
Activation Energies from Peak Half-Widths

Sample	Peak	Annealing temp., °C	Q^{-1}_{max}	$\frac{1}{T_{max}}$	T_{max}, °K	Δ	H, kcal/mole
Lexan	β	unannealed	0.0329	0.00535	186.9	0.00267	1.970
	β	160	0.0365	0.00528	189.5	0.00252	2.085
5 wt-o	β	unannealed	0.0286	0.00607	164.8	0.00360	1.461
	β	160	0.0344	0.00535	186.9	0.00230	2.285
10 wt/o	β	unannealed	0.0309	0.00535	186.9	0.00275	1.915
	β	160	0.0377	0.00547	182.8	0.00230	2.285
25 wt/o	β	unannealed	0.0227	0.00505	198.0	0.00266	1.975
	β	160	0.0333	0.00540	185.3	0.00220	2.390
50 wt/o	β	unannealed	0.0244	0.00540	185.3	0.00266	1.975
	β	175	0.0339	0.00542	184.5	0.00214	2.460
60 wt/o	β	unannealed	0.0252	0.00540	185.3	0.00257	2.045
	β	175	0.0295	0.00537	186.2	0.00225	2.335
75 wt/o	β'	unannealed[a]	0.0100	0.00410	243.5	0.00080	6.580
	β	[b]	0.0225	0.00570	175.5	0.00200	2.630
	β	175	0.0324	0.00552	181.2	0.00173	3.040
	β'	[c]	0.0147	0.00380	263.5	0.00080	6.580
	β	[d]	0.0237	0.00520	192.3	0.00210	2.505
80 wt/o	β	unannealed	0.0249	0.00530	188.8	0.00205	2.565
	β	190	0.0289	0.00540	185.3	0.00200	2.630
90 wt/o	β	unannealed	0.0252	0.00550	181.9	0.00189	2.780
	β	190	0.0304	0.00555	180.3	0.00175	3.005
95 wt/o	β	unannealed	0.0232	0.00515	194.1	0.00185	2.840
	β	200	0.0300	0.00545	183.6	0.00195	2.695
P-1700	β	unannealed	0.0274	0.00550	181.9	0.00185	2.840
	β	200	0.0323	0.00557	179.5	0.00181	2.905

[a] β' at 6 cps.
[b] β at 6 cps.
[c] β' at 18 cps.
[d] β at 18 cps.

phenyl groups. The activation energies determined via peak half-width measurement for the β'-peak in the unannealed 75 wt/o polyblend ranged between 6.5 and 7.5* kcal/mole, while the peak shift determination resulted in a value of 7.3 kcal/mole. The activation energies calculated from peak shape and peak shift are in good agreement, indicating that it may be possible to describe the β'-peak in 75 wt/o unannealed material by a standard linear solid.

In order to test this possibility, the β- and β'-peaks for the 75 wt/o unannealed specimen run at 18 cycles per second were compared with two standard linear solids. The results are reported in Figure 8. The approximation for the β'-peak is in agreement with the experimental data. The high temperature side of the β-peak agrees with the approximation from the second standard linear solid, but the experimental curve is broader on the low-temperature side. On the basis of the agreement between activation

* Cold rolled specimen.

energies calculated from peak shift and peak shape for the β'-peak, the disagreement between these values for the β peak, and the results illustrated in Figure 8, it appears that the β'-peak may be approximated by a standard linear solid, but the β-peak is the result of a more complex mechanism.

In each of the repeat units, there is one polar group, the carbonyl group in Lexan and the sulfone group in P-1700. In a Lexan repeat unit, the phenyl groups are separated by propyl and carbonyl groups. In P-1700, phenyl groups are separated by three different linkages: propyl, ether, and sulfone. Thus, it would be expected that a relaxation due to the movement of the phenyl groups would be a complex mechanism made up of con-
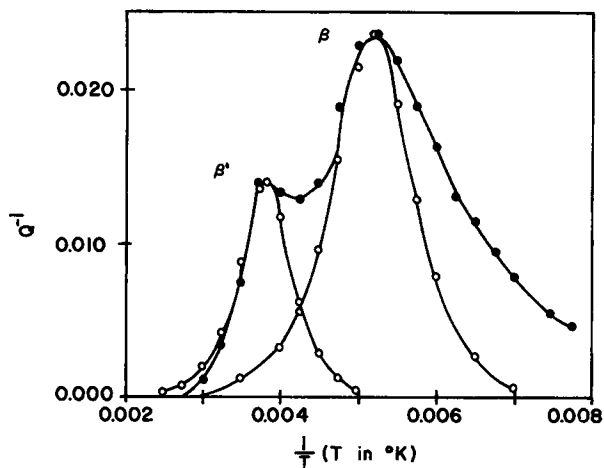

Fig. 8. Standard linear solid approximation to 75 wt/o β'- and β-peaks run at 18 hertz.

tributions differing as a result of these various linkages. It is suggested, therefore, that the β'-peak in the 75 wt/o unannealed specimens can be assigned to the movement of the polar groups and that the β-peak in this material can be assigned to the movement of the various phenyl groups.

The reason for the occurrence of the β'-peak only in 75 wt/o P-1700 material is not at present fully understood. These blends yield two phase structures at all compositions in the range of 5–95 wt/o P-1700, and the phase inversion was found to occur near 75 wt/o. It is speculated that the β'-peak in unannealed material is the result of a more intimate mixing of the chains near the phase inversion than occurs at the other compositions.

References

1. L. E. Nielsen, *Mechanical Properties of Polymers*, Reinhold, London, 1962.
2. H. Schnell, *Angew. Chem.*, **68,** 633 (1956).
3. F. H. Muller and K. Huff, *Kolloid-Z.*, **164,** 34 (1959).
4. S. Matsuoka and Y. Ishida, *J. Polym. Sci., C*, **14,** 247 (1966).
5. F. P. Reding, J. A. Faucher, and R. D. Whitman, *J. Polym. Sci.*, **54,** 556 (1961).
6. E. H. Illers and H. Breuer, *Kolloid-Z.*, **176,** 110 (1961).
7. J. E. Kurz, J. C. Woodbrey, and M. Ohta, *J. Polym. Sci. A-2*, **8,** 1169 (1970).
8. J. D. Buch, R. D. Carnahan, and J. O. Brittain, *Rev. Sci. Inst.*, **38,** 1785 (1967).
9. T. Kajiyama and W. T. MacKnight, *Am. Chem. Soc. Polym. Preprints*, **10,** (No. 1), 65 (1969).