

## Dynamic Mechanical Study of Polycarbonate-Based Block Copolymers

MARK D. HARTLEY and H. LEVERNE WILLIAMS, *Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto M5S 1A4, Ontario, Canada*

### Synopsis

The dynamic-mechanical properties of some multi-ABA-type block copolymers were studied using the Rheovibron viscoelastometer. Records of  $\tan \delta$ , loss moduli, and storage moduli were obtained over the temperature range of  $-100^{\circ}\text{C}$  to  $200^{\circ}\text{C}$  (or the upper glass transition temperature) for samples cast from different solvents. Separate glass transitions were apparent when there was phase separation. Under the test conditions, the soft segment or block formed the continuous phase and the associated glass transition was independent of the solvent used. The hard-segment phase was either continuous or discretely aggregated, depending on the solvent used. For hard segments from large monomer molecules, the discretely aggregated phase displayed a greater modulus. The reverse was true when the monomer molecules were small.

### INTRODUCTION

The increased service temperature range exhibited by block and graft copolymers created an upsurge of interest and research in these types of thermoplastic copolymers. The properties of block copolymers are determined by three factors: the glass transition temperatures of the homopolymer segments; the bulkiness of the plastic or hard segment, and of the monomer units acting as tie-down points and filler; and the degree of phase separation of the two segments. It is apparent that below the lower glass transition temperature of the soft segment, the thermoplastic copolymer will exist as a glassy plastic and that above the higher glass transition temperature of the hard segment it will be a viscoelastic liquid. Therefore, in general the temperature range between the two glass transitions is the effective service range of the copolymer as an elastomer.

The hard segment and its monomer unit are generally bulky. Because of these factors, the hard segment will resist movement through the continuous soft-segment phase of the copolymer. This will impede the viscous flow of the soft segment to which it is chemically bound and thus acts as a cross-link.<sup>1,2</sup> In a physical sense, the rigid hard segment also acts as a reinforcing filler which increases the modulus.

For some time it has been established that block copolymers undergo domain formation, each segment type comprising a separate phase. This phenomenon is also considered to be dependent on the relative solubility of the segments in the solvent from which the copolymer film is cast. Commonly,

the hard phase is less soluble and tends to aggregate into discrete domains within the more continuous soft segment, resulting in a reinforced elastomer. Although not as common, the reverse may be true, the product being a toughened plastic. The extreme case of complete phase separation is rare. Normally there is some degree of interpenetration, i.e., mixing of the more continuous soft phase and a network of the hard phase. This hard network carries much of the initial stress on the thermoplastic elastomer.<sup>3</sup> There may be a considerable interfacial or third, blended phase.

The objective was to study block copolymers over a wide temperature range with respect to their dynamic mechanical properties, service range, glass transition temperatures, and moduli. This represents a continuation of the investigations by Memon<sup>1,2</sup> and Wismer<sup>4</sup> on block copolymers of polycarbonates and hydroxy-terminated elastomers.

### EXPERIMENTAL

Three typical copolymers prepared by Memon et al.<sup>1,2</sup> were available. These were multiblock. Polymer A was 60 weight per cent hydroxy-terminated polybutadiene and 40 weight per cent bisphenol A polycarbonate. Polymer B was 60 weight per cent poly(ethylene adipate) and 40 weight per cent cyclohexanediol polycarbonate. Polymer C was 65 weight per cent poly(ethylene adipate) and 35 weight per cent cyclohexylidene bisphenol polycarbonate. The structures are shown diagrammatically in Figure 1. The solubility parameter for polybutadiene is about 8.5 (cal/ml)<sup>1/2</sup>, but comparable values for the other polymers were not located. Assuming that they range from 9 to 11 according to composition and can be arranged in increasing order with increasing glass transition temperature, the solubility parameters would be in the order poly(ethylene adipate), cyclohexanediol polycarbonate, bisphenol A polycarbonate, and cyclohexylidene bisphenol polycarbonate, and all very close to 10 (cal/ml)<sup>1/2</sup>. Three solvents were used to prepare solution for casting films. These were methylene chloride (solvent 1) methyl ethyl ketone (solvent 2), and benzene (solvent 3), the solubility parameters for which are respectively 9.7, 9.3, and 9.2 (cal/ml)<sup>1/2</sup>. Thus, while methylene chloride appears to be a good solvent for all of the polymers, methyl ethyl ketone and benzene tend to be better solvents for the elastomeric portions. Solubility tests were also performed according to Kline et al.<sup>6</sup> to determine the relative values of the solubilities of the homopolymers in the solvents.

The elastomers with aromatic hard segments were prepared by the method outlined by Perry et al.<sup>5</sup> The reactants in the required proportions were dissolved in 100 ml of methylene chloride, and excess pyridine was added. At a constant temperature of 30°C, 75% of the stoichiometric amount of phosgene in solution in benzene was added at a rate of 2 ml/min, the remaining 25% at a rate of 1 ml/min, and a 25% excess at a rate of 0.2 ml/min. The solution of the product was washed with water, dilute hydrochloric acid, and water. Finally the polymer was precipitated with excess 50:50 acetone:methanol mixture. When alicyclic diols were used, the procedure was modified<sup>1,2</sup> by dissolving the reactants in 100 ml of toluene and excess pyridine and refluxing under nitrogen for 10 min. The phosgene in solution in benzene was added 66% at a rate of 1 ml/min at 45°C, 34% at a rate of 1 ml/min at 75°C, and a

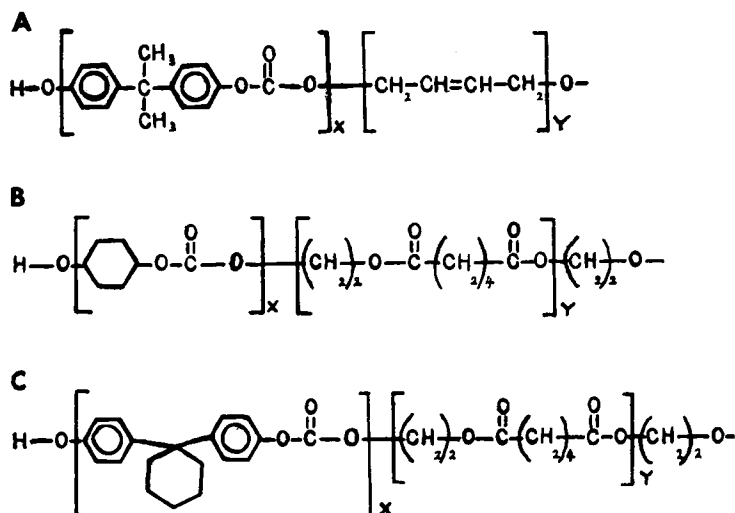


Fig. 1. Molecular formulae.

25% excess at a rate of 0.5 ml/min at 85°C. The product was washed as before and then precipitated with excess methanol.

The block copolymers with alternating units were to be made to low molecular weight deliberately for ease of processing. The intrinsic viscosities measured in methylene dichloride indicated comparatively high molecular weight relative to the 5000 to 8000 molecular weight range for the initial hydroxy-terminated elastomers. An exact calculation of the molecular weights of the products was not possible from the data available, but the products were obviously multiblock. Based on the values shown, the products were chain extended several fold with 1.2 moles of toluene diisocyanate for each mole of polymer to yield products of greater chain length by dissolving in methylene dichloride, adding toluene diisocyanate and antioxidant, evaporating the solvent under slow agitation on a clean mercury surface, and finally drying the films at 60–65°C and 30 mm pressure overnight. In general, the final products were soluble, thermoplastic elastomers, probably branched, but not crosslinked. Strips of the film were prepared and tested on a Rheovibron,<sup>7</sup> a direct-reading, low-frequency, nonresonance, forced-vibration viscoelastometer. Data on damping ( $\tan \delta$ ), loss moduli  $G'$ , and storage moduli  $G''$  were obtained at 110 Hz over the temperature range  $-100^\circ\text{C}$  to  $+200^\circ\text{C}$  (or to the higher glass transition temperature). The nuclear magnetic resonance traces<sup>1,2</sup> for the copolymers based on aromatic diols showed the same ratio of aromatic to aliphatic hydrogen atoms as in the reactants used in the synthesis. It was assumed that the same held true for the cyclohexane diol-based copolymer.

## RESULTS AND DISCUSSION

### Polymer A

“Damping” is the amount of energy dissipated as heat during the deformations of the material<sup>3</sup> and is measured directly as  $\tan \delta$ . Figure 2, damping

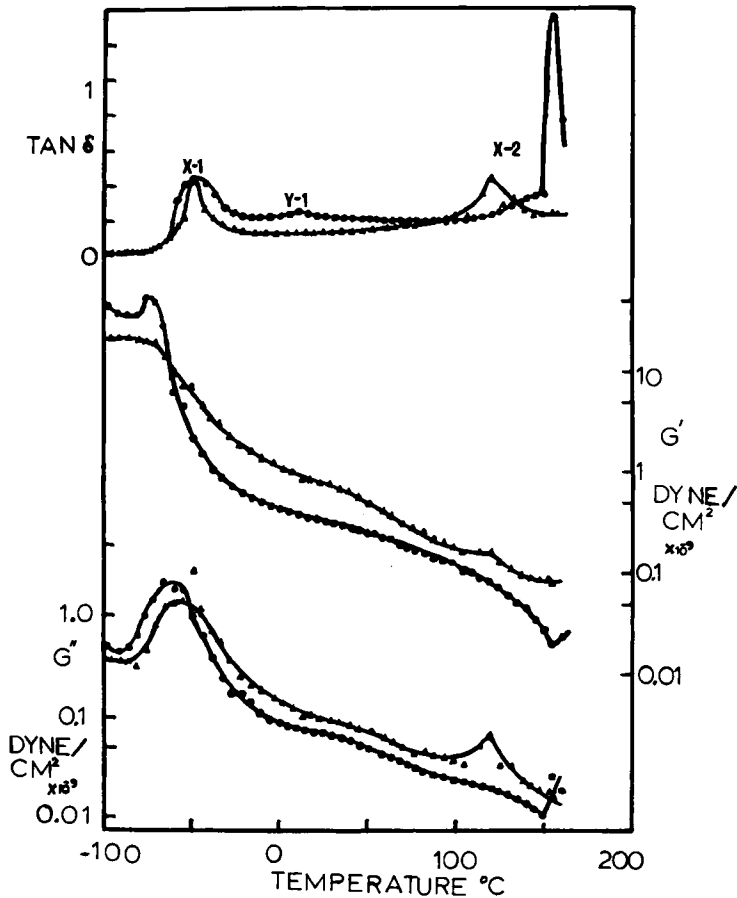


Fig. 2.  $\tan \delta$ ,  $G'$ ,  $G''$  vs. temperature for  $A_1$  (●) and  $A_3$  (Δ).

versus temperature, for samples  $A_1$  (polymer A cast from solvent 1) and  $A_3$  (polymer A cast from solvent 3) confirms the existence of the two glass transitions expected for a block copolymer system. The presence of the two phases of different polymer segments is apparent, but the influence of each on the other is not straight forward.

The two soft segment glass transitions (X-1) in Figure 2 have similar magnitudes and occur at the same temperature, indicating that the soft segment constitutes a continuous phase in both samples  $A_1$  and  $A_3$ . These transition temperatures are significantly higher than the glass transition temperatures for the homopolymers (Table I). This may be attributed to restrictions imposed on segmental motion by the hard segment and appears to be independent of the type of aggregation of the hard segment. The breadth of the peak (X-1) appears significantly greater in case  $A_1$  than in case  $A_3$ . The rapid precipitation of sample  $A_1$  from methylene dichloride results in occlusion of the hard phase causing a wider distribution of relaxation times for the softer segment.

The glass transitions (X-2) of the hard segments, however, differ significantly. For sample  $A_1$ , it is approximately the same as for the homopolymer, while for  $A_3$  it is lower. In preparing sample  $A_1$ , both hard and soft segments

TABLE I  
Experimental and Reference Data

Sample	Hard Segment		Soft Segment		Secondary $T_g$ Exp, °C	Intrinsic Viscosity
	$T_g$ Exp, °C	$T_g$ Ref, °C	$T_g$ Exp, °C	$T_g$ Ref, °C		
A <sub>1</sub>	155	150 <sup>a</sup>	-50	-90 <sup>a</sup>	10	0.75
A <sub>3</sub>	130	150 <sup>a</sup>	-50	-90 <sup>a</sup>	—	
B <sub>1</sub>	200+	178 <sup>b</sup>	-20	-70 <sup>a</sup>	70	0.51
B <sub>2</sub>	185	178 <sup>b</sup>	-20	-70 <sup>a</sup>	—	
C <sub>1</sub>	—	175 <sup>c</sup>	—	-70 <sup>a</sup>	25	1.23
C <sub>3</sub>	—	175 <sup>c</sup>	—	-70 <sup>a</sup>	23	

<sup>a</sup> Reference 3.

<sup>b</sup> Reference 14.

<sup>c</sup> References 1 and 2.

precipitate at about the same time. This allows the hard segment to form an equally continuous network throughout the sample. Since the separation is reasonably complete and the soft segment adds no apparent restrictions, it would seem the free volume<sup>8</sup> of the hard segment is no different than in the homopolymer and therefore has the same glass transition temperature. In sample A<sub>3</sub>, the hard segment phase precipitates first as coiled chains in discrete domains with interpenetration of the soft phase. These domains would possess greater free volume<sup>8</sup> than the homopolymer and therefore a lower glass transition temperature and a much broader range of relaxation times.

Another difference between the two samples is the broad, shallow, secondary glass transition (Y-1) in sample A<sub>1</sub>. Miyamoto et al.<sup>9</sup> and Beecher et al.<sup>10</sup> expressed the opinion that this type of transition is caused by a new phase with the onset of chain mobility different than either homopolymer domain. This phase probably results at the interface from incomplete phase separation, since the high volatility of methylene dichloride solvent causes rapid precipitation of the copolymer and possibly the formation of a mixed phase resembling a solid solution of mixed and varying composition. This may be analogous to the transition zone described recently.<sup>11-13</sup>

On examining the storage and loss moduli for the two samples, it may be seen that the storage modulus for sample A<sub>1</sub> is 50% higher in the glassy region than sample A<sub>3</sub>, in all likelihood due to the greater homogeneity of this sample. However, in the elastomeric region for the copolymer, sample A<sub>3</sub> exhibits 100% greater storage modulus than does sample A<sub>1</sub>. This demonstrates that the discrete hard-segment domains, which act as reinforcing filler and crosslinks in case A<sub>3</sub>, support a greater amount of the initial stress than the more continuous hard phase with partial occlusion of the hard segment in the soft segment. The moduli for A<sub>1</sub> display sharp peaks about 5°C lower than the first glass transition temperature, which could be attributed to the presence of traces of solvent.

### Polymer B

The damping data for specimens B<sub>1</sub> and B<sub>2</sub> (Fig. 3) support the conclusions reached in the previous cases. The lower glass transitions (X-1) are located at the same temperature and approach the same values. This temperature of -20°C is again higher than the glass transition temperature of -70°C for the

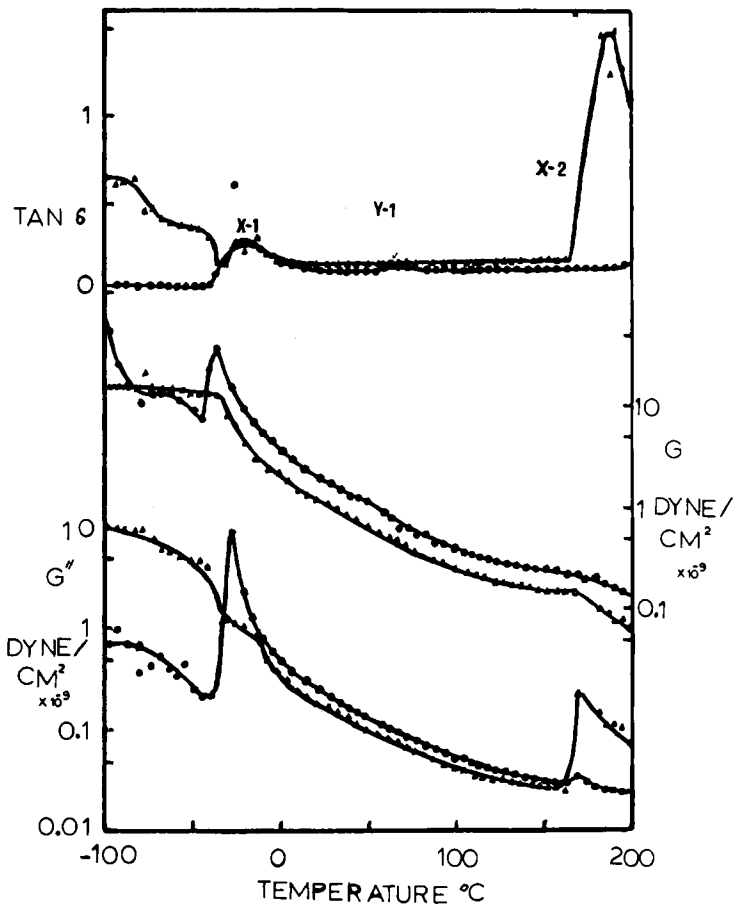


Fig. 3.  $\tan \delta$ ,  $G'$ ,  $G''$  vs. temperature for  $B_1$  (●) and  $B_2$  (Δ).

homopolymer. Data on the glass transitions of the hard segment (X-2) are vague in sample  $B_2$  and beyond the measured temperature range in  $B_1$ . They both appear to be above the glass transition temperature for the homopolymer, 178°C. The reasons for this cannot readily be accounted for. However, glass transition values obtained by DSC methods are generally lower than those obtained by mechanical means. The effect of the chain-extending urethane groups on the glass transition temperatures (particularly the  $T_g$  of the hard segments) has not been investigated, but it is probably a factor contributing to the high values. The upper glass transition temperature may not be as unusual as it first appears. However, it remains an area in which more experimentation is required. Nevertheless, it does, in fact, corroborate the findings that the (X-2) glass transition occurs at a lower temperature when the hard segment precipitates first. A secondary glass transition (Y-1) is also found in sample  $B_1$  as expected from sample  $A_1$ . One notable difference between A and B copolymers is the high degree of damping found in the glassy region in sample  $B_2$ . The chemical similarity (carbonyl groups) between the solvent and copolymer make the presence of residual solvent a likely cause of this.

The trace of solvent may be responsible for the high loss modulus in this

region. The storage and to a lesser extent the loss modulus for sample  $B_1$  are greater in the rubbery region than for sample  $B_2$ . This indicates that the discrete domains of hard segment in  $B_2$  are less effective in supporting stress than the more continuous hard-segment phase in sample  $B_1$ . The small monomer units of the hard segment would give smaller reinforcing domains, which would be less effective as tie-down points and filler than the hard-segment domains in sample  $A_3$ .

### Polymer C

Figure 4 shows virtually identical properties for the two samples  $C_1$  and  $C_3$ ; therefore, the solvents used have resulted in samples of similar morphology, and a single discussion suffices for both. This copolymer exhibits a single, broad damping peak (Y-1) not directly associated with either homopolymer

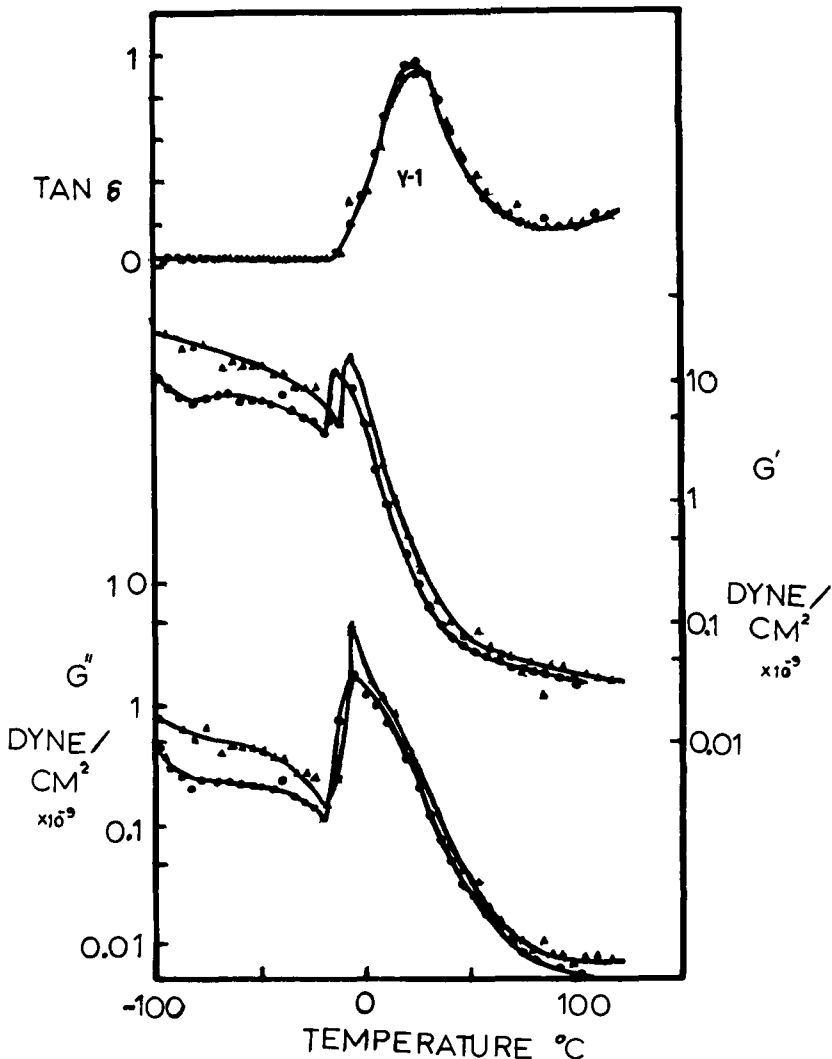


Fig. 4.  $\tan \delta$ ,  $G'$ ,  $G''$  vs. temperature for  $C_1$  (●) and  $C_3$  (Δ).

segment. It is interpreted as being a secondary glass transition,<sup>9,10</sup> similar to those in samples A<sub>1</sub> and B<sub>1</sub>. No glass transitions associated with homopolymer segments were found. The conclusion drawn from these observations is that no phase separation occurred and a homogeneous system was the result. The similarities between samples C<sub>1</sub> and C<sub>3</sub> indicate that this is probably a phenomenon of the copolymer and not of the casting solvent. However, other solvents would have to be tested to verify this conclusion.

The copolymer exhibits a sharp increase in the moduli at about 35°C below the secondary glass transition temperature of 25°C (Y-1). This has been observed to a lesser degree in the more homogeneous samples of the other copolymers (A<sub>1</sub> and B<sub>1</sub>) at a temperature preceding the first glass transition (X-1). Although the copolymers tested are generally amorphous, they do possess some crystalline properties. When they are cooled rapidly (as in this study), no crystalline structure has time to form. However, when the samples warm slowly, during testing, enough mobility is obtained (at a temperature just below the lower glass transition) for some crystallization to occur. This increases the stiffness and is responsible for the sharp increase in moduli.

The samples tested in this paper displayed properties combining those found in polymers mixtures and random copolymers. This can be explained in part by a degree of occlusion of the two blocks within each other, but it is also felt that, although the copolymers are chain extended to high molecular weights, the individual segments in these multiblock copolymers may contain only a few monomer units, insufficient for the copolymers to display the separate characteristic properties of the homopolymers.

Financial assistance from the Defense Research Board of Canada was available through a grant in aid of research. Testing apparatus was donated by Polysar Limited. This paper was taken from the B.A.Sc. Thesis of M. D. Hartley, the University of Toronto, 1972. Helpful discussions were held with Dr. N. A. Memon.

## References

1. N. A. Memon, Doctoral Thesis, Dept. of Chemical Engineering and Applied Chemistry, University of Toronto, 1972, *Chem. Abst.*, 79, 42877c (1973).
2. N. A. Memon and H. L. Williams, *J. Appl. Polym. Sci.*, 17, 1361 (1973).
3. L. E. Nielsen, *Mechanical Properties of Polymers*, Reinhold, New York, 1962.
4. K. H. Wismer, B.A.Sc. Thesis, Dept. of Chemical Engineering and Applied Chemistry, University of Toronto, 1969.
5. K. P. Perry, W. J. Jackson, Jr., and J. R. Caldwell, *J. Appl. Polym. Sci.*, 9, 3415 (1965).
6. G. M. Kline, Ed., *Analytical Chemistry of Polymers*, Part III, Interscience, New York, 1962.
7. Rheovibron, Toyo Measuring Instruments Co. Ltd., Tokyo, 1969.
8. F. Bueche, *Physical Properties of Polymers*, Reinhold, New York, 1962.
9. T. Miyamoto, K. Kodoma, and K. Shiboyama, *J. Polym. Sci.*, 8, 2095 (1970).
10. J. F. Beecher, L. Marker, R. D. Bradford, and S. L. Aggarwal, *Polym. Prepr.*, 8, 1532, (1967).
11. D. Stefan and H. L. Williams, *J. Macromol. Sci.-Phys.*, B4, 853 (1970).
12. D. Stefan and H. L. Williams, *J. Appl. Polym. Sci.*, 18, 1279 (1974).
13. D. Stefan and H. L. Williams, *J. Appl. Polym. Sci.*, 18, 1451 (1974).
14. D. W. Van Krevelen, *Properties of Polymers*, Elsevier, Amsterdam, 1972.

Received May 1, 1974

Revised February 3, 1975