

Melt Rheology of Ion-Containing Polymers. I. Effect of Molecular Weight and Excess Neutralizing Agent in Model Elastomeric Sulfonated Polyisobutylene-Based Ionomers

SHRIRAM BAGRODIA, RAMESH PISIPATI, and GARTH L. WILKES, *Department of Chemical Engineering, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061-6496*, and ROBSON F. STOREY and JOSEPH P. KENNEDY, *University of Akron, Institute of Polymer Science, Akron, Ohio 44304*

Synopsis

Melt rheology of elastomeric triarm sulfonated polyisobutylene model ionomers has been studied. The molecular weights (\bar{M}_n) of the polymers have been varied from 8300 to 34,000. The sulfonated materials were neutralized with potassium hydroxide either to the exact stoichiometric equivalence point or to twice this amount, i.e., 100% excess neutralizing agent was added. For comparison one nonsulfonated precursor of $\bar{M}_n = 8300$ was also studied. It was observed that the introduction of one sulfonate group at each chain end of the triarm polyisobutylene molecule changes the state of matter at room temperature. Specifically, the unsulfonated materials are viscous liquids while the sulfonated ionomers are solid elastomers at room temperature. The zero-shear melt viscosity of the unsulfonated precursor is 900 poise (90 Pa · s), at room temperature while for those materials neutralized with potassium hydroxide to the exact stoichiometric point it is above 9×10^3 poise (900 Pa · s) at 180°C. As expected, the zero shear viscosity increases with an increase in the molecular weight. Significant ionic interactions still persist at 180°C as evident by the high viscosity of the ionomers. However, at higher frequencies (~ 600 rad/s), the melt viscosity decreases to about 5×10^3 poise for the different molecular weight materials. The melt viscosity of ionomers containing 100% excess neutralizing agent shows a dramatic increase. The excess KOH is speculated to be incorporated into the ionic domains rather than uniformly distributed throughout the matrix. This results in an increased strength of the ionic aggregates, thereby increasing the melt viscosities. Thus, due to the very pronounced effect on rheological properties it is important to know not only the extent of neutralization (up to full neutralization) but also the amount of excess neutralizing agent, if any, which is present in the sample.

INTRODUCTION

Hydrocarbon polymers containing typically less than about 15 mol % ionic groups are known as ionomers.¹ Small quantities of ionic moieties attached to a polymer significantly affect both the mechanical and rheological properties of the material.¹⁻³ Regarding melt rheological behavior, it has been pointed out that, due to the coulombic interactions of ionic species following neutralization, the relaxation spectrum shifts to longer times as compared to the precursor polymer devoid of ionogenic moieties.⁴ However, due to the thermal dissociation or weakening of these ionic interactions, ionomers are generally processable at moderately elevated temperatures. This allows the ready fabrication of these materials into coatings,

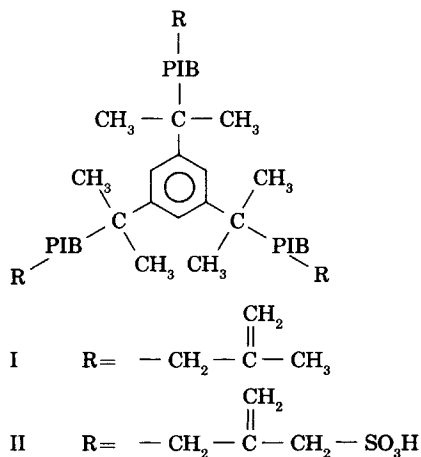
films, etc.⁵ The choice of cation used in neutralization, however, may affect the dissociation process. Specifically, Lundberg et al. have observed that sulfonated EPDM ionomers containing zinc cations exhibit a much lower viscosity than those containing other cations, such as Mg, Ca, etc.¹

According to these researchers^{6,7} sulfonated EPDM ionomers display thermoplastic elastomer behavior and can be processed at moderately elevated temperatures. Processability was greatly facilitated in the presence of an ionic plasticizer such as zinc stearate. However, after cooling the melt, the zinc stearate separates, crystallizes and serves as a reinforcing filler.⁶⁻⁸ We have also studied reinforcement of sulfonated EPDM by zinc stearate following thermal treatment, and the results will be forthcoming.⁹ Ionomers also display unique solution behavior.¹⁰⁻¹⁴

Recent work from our laboratory has focused on the solid state properties of model triarm sulfonated polyisobutylene (PIB) ionomers.¹⁵⁻¹⁸ Specifically, it has been shown that by the introduction of about 1-2 mol % $-\text{SO}_3^- \text{x}^+$ (x = cation) groups at the chain termini of low molecular weight (liquid) triarm PIB polymers, interesting elastomeric properties arise, i.e., extensions to over 1000% in conjunction with low permanent set and low hysteresis.¹⁶ The unique feature of these ionomers is that the ionic groups reside exclusively at the terminal points of the molecule, i.e., the triarm polymers contain only three ionic groups per molecule. Since the terminal groups are ionic, "model" end linked ionomeric networks can be constructed.^{16,17} While these model systems display very interesting solid state properties, there is a need to better understand their processing behavior. With this objective in mind we have initiated studies on the rheological behavior of these ionomers. The data presented here represent our initial findings regarding the variable of molecular weight and excess neutralization.

EXPERIMENTAL

Materials. The synthesis of triarm star olefin-telechelic polyisobutylenes having exactly three $-\text{CH}_2-\overset{\text{CH}_2}{\underset{\parallel}{\text{C}}}-\text{CH}_3$ termini (I) has been described previously.^{19,20} The structure before (I) and after sulfonation (II) is shown below:



Mixed hexanes (Fisher Scientific Co.) were refluxed over fuming sulfuric acid, washed with water, dried over anhydrous MgSO_4 and finally distilled over CaH_2 . Tetrahydrofuran (Fisher Scientific Co.) was freshly distilled from CaH_2 . Acetic anhydride and sulfuric acid (both Fisher Scientific Co.) were used without further purification. Potassium hydroxide was ACS-certified reagent.

Sulfonation of I. Heterogeneous sulfonations were carried out in hexane solutions (10 g/100 mL) at room temperature.¹⁸ Five grams of I were dissolved in hexane and stirred at room temperature. Then 1.4 mL of acetic anhydride was added, stirring was continued, and after 10 min 0.65 mL sulfuric acid was added. After stirring for 2 h, the mixture was allowed to separate and the lower sulfuric acid layer was discarded. The number average molecular weights (\bar{M}_n) were 8300, 14,000 and 34,000 ($M_w/M_n \sim 1.7$). The sulfonated products II were neutralized with potassium hydroxide as described.^{17,18} The precursor acid was neutralized with potassium hydroxide to (i) exact stoichiometric equivalence and (ii) 100% excess over exact stoichiometric equivalence.

Nomenclature and Abbreviations. The samples are designated by four symbols, for example, T-8.3-K-0. The first symbol T indicates a triarm ionomer. The second symbol, 8.3, expresses the $\bar{M}_n \times 10^{-3}$. The third symbol, in this case K, indicates the cation the ionomer contains. The fourth symbol, in this case 0, indicates the extent of excess neutralization past the equivalence point. Thus 0 indicates exact stoichiometric neutralization (no excess). The symbolism T-8.3-K-100 would stand for the same material except containing 100% excess of KOH. The following ionomeric materials are discussed within this paper: T-8.3-K-0, T-14-K-0, T-34-K-0, T-8.3-K-100, and T-34-K-100.

For comparison purposes a precursor triarm olefin-telechelic PIB $\bar{M}_n = 8300$ has also been investigated. The structure of this ionomer precursor is shown by the formula I, above. The symbol of this polymer is T-8.3-HC (HC for hydrocarbon). The sulfonic acid precursor could not be studied because it rapidly decomposes (brownish discoloration) particularly at elevated temperatures.

A Rheometrics mechanical spectrometer (RMS) was used to obtain the small-strain response in the dynamic mode with disc and plate geometry. Experiments were performed at a 5% strain amplitude at 180°C, unless otherwise stated. The diameter of the plates was 2.5 cm. A preliminary strain sweep experiment demonstrated a linear viscoelastic response at strain amplitudes up to 20%. The frequency was varied from 10^{-1} to approximately 700 rad/s. Since T-8.3-HC is a viscous liquid at room temperature, it was studied only at room temperature.

RESULTS AND DISCUSSION

Figure 1 shows the dynamic shear viscosity (η^*) as a function of frequency at 180°C (except for T-8.3-HC). It is observed that the viscosity of the ionomers at 180°C are several orders of magnitude higher than that of the precursor T-8.3-HC—the latter being measured at 25°C. The T-8.3-HC system behaves like a newtonian fluid at room temperature.

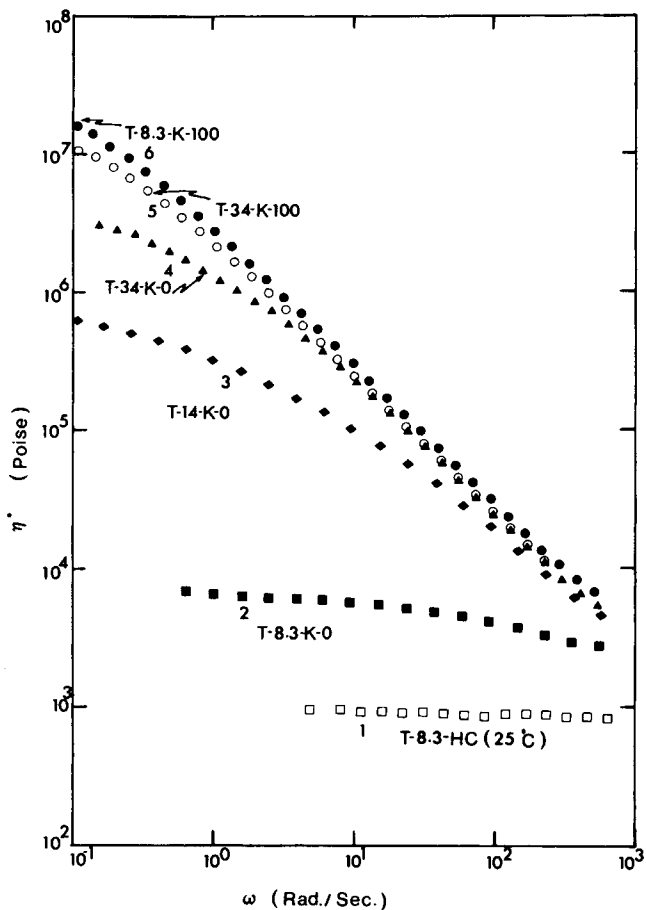


Fig. 1. Dynamic melt viscosity (η^*) as a function of frequency for T-8.3-HC (at 25°C) and T-8.3-K-O, T-14-K-O, T-34-K-O, and T-8.3-K-100 materials at 180°C.

It has been reported in the literature that the melt viscosity of linear PIB fractions of $\bar{M}_n = 12,900$ (M_w/M_n not given) at 182°C is only 14.2 P,²¹ while the viscosity for the above ionomers, even at much higher frequencies, is in the range of 10^3 – 10^4 P, which is an increase by a factor of $(1 \text{ Pa} \cdot \text{s} = 10 \text{ P}) 10^3$! This enhancement is clearly due to the presence of ionic interactions which are of relatively low content. Specifically, the three $\text{SO}_3^- \text{K}^+$ terminal groups correspond to about 2.0, 1.2, and 0.5 mol % ionic contents in the 8300, 14,000, and 34,000 molecular weight materials, respectively.

The effect of molecular weight on the viscosity of these ionomers is shown in Figure 1 by the curves 2, 3, and 4, which correspond to the T-8.3-K-O, T-14-K-O, and T-34-K-O materials, respectively. The viscosity of these ionomers increase with molecular weight at low frequencies as would be expected. It is also noted that the viscosity for the T-34-K-O material is higher by a factor of about 1.7×10^2 than that for the T-8.3-K-O material at the lowest frequency. The extrapolated (approximate) zero shear viscosity for polymers T-8.3-K-O, T-14-K-O, and T-34-K-O are about 10^4 , 8.5×10^5 , and 4.0×10^6 P, respectively.

The critical molecular weight for entanglement (\overline{M}_{uc}) for linear PIB has been reported to be in the range of 9000–17,000.²² For the polymers studied in this paper, the polydispersity (M_w/M_n) is 1.7, thereby leading to weight average molecular weights of 15,000, 25,000, and 61,000 for the three PIB ionomers. The lowest molecular weight material therefore borders M_{uc} while the rest are well above the M_{uc} range. It should be realized, however, that the effect of a triarm architecture on M_{uc} has not been taken into account in this discussion.

For linear polymers, η_0 is proportional to $M_w^{1.0}$ when $M_w < M_{uc}$ while η_0 is proportional to $M_w^{3.4}$ when $M_w > M_{uc}$. This implies that if this rule were to hold for our materials, then the ratio of the estimated zero shear viscosities for T-14-K-O to that for T-34-K-O should be 0.048 but is experimentally observed to be considerably higher and is in fact 0.21. While this ratio rests on our estimates of zero shear viscosities, it is very clear that these polymers do not fit this simple law, and this is likely due to the presence of the coulombic interactions of these materials. Another possible origin or deviation from the 3.4 power relationship may also result from the fact that these systems are triarm rather than linear. However, such a strong deviation is not likely to be due solely to a change in the molecular architecture.

It is of particular interest to compare the behavior of the materials that have been exactly neutralized to those containing a 100% excess of the neutralizing agent. As shown by the data in Figure 1, the addition of 100% excess KOH increases the viscosity of T-8.3-K-100 by a factor of about 10^3 as compared to T-8.3-K-O at the lowest frequency! Yet, the viscosity of T-34-K-O increases only by a factor of only 2.5 at low frequencies when a 100% excess of KOH is used (T-34-K-100). Clearly the effect of excess neutralization on the rheological behavior is much more pronounced for the low molecular weight, $\overline{M}_n = 8300$, material than for the high molecular weight ($\overline{M}_n = 34,000$) material. This, however, is expected since the low molecular weight material contains a relatively higher molar concentration of ionic groups than the high molecular weight material, although this difference is not large. It is postulated that by the addition of excess neutralizing agent the coulombic cohesion of the ionic aggregates increases and thereby causes the behavior of the system to more closely simulate a covalently crosslinked network. In conjunction with our earlier work on the bulk properties of these materials,¹⁷ the present study further substantiates our earlier hypothesis that the excess ions introduced in the system are believed to be incorporated into the ionic domains rather than being uniformly distributed throughout the matrix. The simplified molecular model shown in Figure 2 helps to visualize this proposition.

Referring to Figure 1, it is observed that the viscosity for T-8.3-K-100 and T-34-K-100 is inversely proportional to frequency and the slope of $\log \eta$ vs. $\log \omega$ curve is -1 at high frequencies. This indeed suggests that the materials are more elastic-like rather than viscous fluids at 180°C.

The shear storage modulus (G') as a function of frequency is shown in Figure 3. It is observed that for the T-14-K-O materials, where ($M_w > M_{uc}$) a plateau value is reached at the high frequencies. From this plateau value, M_{uc} is found to be about 14,000 ($M_{uc} = \rho RT/G'$) close to that reported in the literature. In contrast, the value G' for material T-8.3-K-O does not

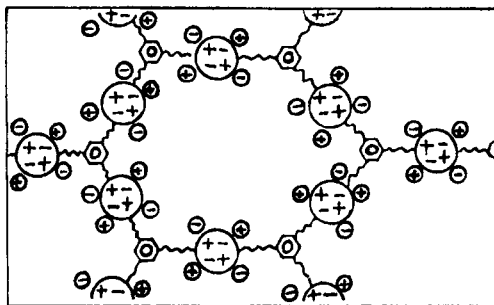


Fig. 2. Simple schematic molecular model used to account for the observed melt rheological behavior of those inomers having an excess of neutralizing agent. The relative sizes of the circles indicating coulombic interaction carry no physical significance.

approach a plateau value. However, when this polymer is neutralized with 100% excess agent to produce material T-8.3-K-100, a very distinct plateau region in the behavior of G' is noted as seen within Figure 3. That is, what was a viscous fluid at 180°C for end-point neutralization is now transformed into a much more elastic or rubberlike system when excess neutralization agent is present. In fact, the reader will note that the shear modulus behavior for T-8.3-K-100 displays this plateau value even at frequencies as low as 10 rad. This behavior is in accord with the earlier hypothesis that the excess neutralizing agent is not uniformly distributed throughout the matrix, but is preferentially incorporated into the ionic multiplet regions that persist even at this high temperature. These additional ions of potassium and hydroxide clearly strengthen these ionic associations and promote the more elastic behavior of the excess neutralized material.

In Figure 4, the loss modulus (G'') as a function of frequency (ω) is presented. It is noted that samples T-14-K-O, T-34-K-O, and T-34-K-100 all display a maximum in G'' . Although G'' does not usually show a maximum for general viscous melt behavior, we speculate that in this system this

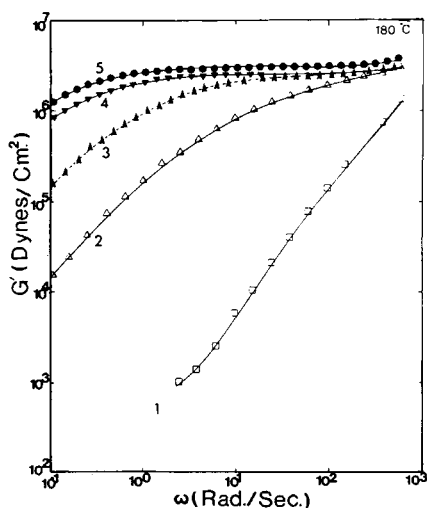


Fig. 3. Shear storage modulus (G') as a function of frequency for (1) T-8.3-K-O, (2) T-14-K-O, (3) T-34-K-O, (4) T-34-K-100, and (5) T-8.3-K-100 materials at 180°C.

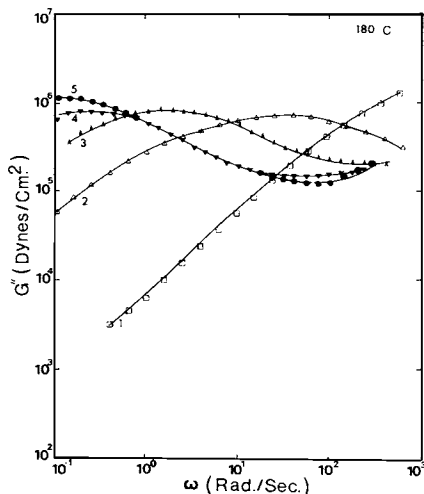


Fig. 4. Shear loss modulus (G'') as a function of frequency for the (1) T-8.3-K-O, (2) T-14-K-O, (3) T-34-K-O, (4) T-34-K-100, and (5) T-8.3-K-100 materials at 180°C.

maximum indicates the transition from the viscous flow region to the rubbery network plateau region. A similar behavior has been previously reported by the authors.^{23,24} Recently, Teyssié et al. have observed a maximum in G'' for carboxy-terminated polybutadiene ionomers neutralized with magnesium salts and have offered a similar explanation.²⁵ Thus it is observed that the melt rheological behavior and hence the processability of these ionomers is strongly dependent on the amount of excess neutralizing agent present in these materials. Addition of excess neutralizing agent adversely affects the processability of these ionomers by virtue of increased viscosity through enhanced ionic associations. We have recently studied the mechanical¹⁷ properties of these ionomers, and it has been shown that they behave as elastomers at room temperature. With the addition of excess neutralizing agent, the resulting mechanical properties of these ionomers at room temperature improve in that for the higher elongation regions (> 400%) the stress values are increased. Thus, the amount of excess neutralizing agent added to these ionomers also plays a very important role favorably influencing the ultimate mechanical properties. However, the melt viscosities increase dramatically with the addition of excess neutralizing agent, which, of course, begins to adversely affect their processability. Based on this mechanical behavior and the present initial rheological data, it must be concluded that there must be a compromise between processability and ultimate material properties.

A more detailed study on the melt rheology of these ionomers is underway. This includes the effect of cation type, the molecular architecture of the base polymer (three-arm vs. linear vs. monofunctional ends, and blends thereof) and the effect of temperature on the viscosity of these materials.

CONCLUSIONS

As expected, the melt viscosity of these ionomers increases with an increase in molecular weight. The ionic interactions, even at 180°C, remain

highly influential and result in very high viscosities when compared to the unsulfonated polymer precursor. The addition of excess neutralizing agent strongly affects the melt viscosities of these ionomers. The effect is much more pronounced for the low molecular weight ionomers since the ion content is greater for these systems. In conjunction with mechanical behavior studies of the same ionomers,¹⁷ this study further reinforces the morphological model and predicts that the excess neutralizing base is preferentially incorporated into the ionic domains rather than being uniformly distributed throughout the matrix. The viscosity displays typical shear thinning behavior at higher frequencies, at 180°C. Both our previous mechanical and thermal studies¹⁵⁻¹⁸ as well as the present study on the rheological behavior of these ionomers, indicate that these sulfonated polyisobutylene-based ionomers can be viewed as thermoplastic elastomeric ionomers. However, the role of excess neutralizing agent in these ionomers on the resulting properties cannot be overemphasized. Effects due to the presence of excess neutralizing agent can easily mask those due to other variables, and one has to be extremely careful with the manner of neutralizing the acid form of these ionomers.

We are grateful to acknowledge financial help by the polymer program of NSF (J.P.K., DMR-81-7536), the partial support from the Army Research Office & Petroleum Research Fund (GLW/SRB), and a grant by the General Tire and Rubber Company to one of us (R.F.S.).

References

1. A. Eisenberg, Ed., *Ions in Polymers*, Advances in Chemistry Series, 187 Am. Chem. Soc., Washington, D.C., 1980.
2. W. J. MacKnight and T. R. Earnest, Jr., *J. Polym. Sci., Macromol. Rev.*, **16**, 41 (1981).
3. C. G. Bazuim and A. Eisenberg, *Ind. Eng. Chem., Prod. Res. Dev.*, **20**, 271 (1981).
4. R. W. Connelly, R. C. McConkey, J. M. Noonan, and G. H. Pearson, *J. Polym. Sci., Polym. Phys. Ed.*, **20**, 59 (1982).
5. H. S. Makowski, R. D. Lundberg, L. Westerman, and J. Bock, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **19**, 292 (1978).
6. H. S. Makowski, P. K. Agarwal, R. A. Weiss, and R. D. Lundberg, *Polym. Prepr.*, **20**, 281 (1979).
7. H. S. Makowski, R. D. Lundberg, L. Westerman, and J. Bock, in *Ions in Polymers*, A. Eisenberg, Ed., Advances in Chemistry Series, 187, Am. Chem. Soc., Washington, D.C., 1980.
8. H. S. Makowski and R. D. Lundberg, *Polym. Prepr.*, **19**(2), 304 (1978).
9. G. L. Wilkes and C. Wood, to appear.
10. R. D. Lundberg and H. S. Makowski, *J. Polym. Sci., Polym. Phys. Ed.*, **18**(9), 1821 (1980).
11. R. D. Lundberg and R. R. Phillips, *J. Polym. Sci., Polym. Phys. Ed.*, **20**(7), 1143 (1982).
12. R. D. Lundberg, *J. Appl. Polym. Sci.*, **27**, 4623 (1982).
13. G. Broze, R. Jerome, and Ph. Teyssie, *Macromolecules*, **14**, 224 (1981).
14. G. Bronze, R. Jerome, and Ph. Teyssie, *Macromolecules*, **15**, 920 (1982).
15. S. Bagrodia, Y. Mohajer, G. L. Wilkes, R. Storey, and J. P. Kennedy, *Polym. Bull.*, **8**, 281 (1982).
16. S. Bagrodia, Y. Mohajer, G. L. Wilkes, R. Storey, and J. P. Kennedy, *Polym. Bull.*, **9**, 174 (1983).
17. S. Bagrodia, Y. Mohajer, G. L. Wilkes, R. Storey, and J. P. Kennedy, *J. Appl. Polym. Sci.*, to appear.
18. Y. Mohajer, D. Tyagi, G. L. Wilkes, R. Storey, and J. P. Kennedy, *Polym. Bull.*, **8**, 47 (1982).
19. J. P. Kennedy, L. R. Ross, J. E. Lackey, and O. Nuyken, *Polym. Bull.*, **4**, 67 (1981).
20. R. Storey, Ph.D. thesis, Department of Polymer Science, The University of Akron, Ohio, 1983.
21. T. G. Fox and P. J. Flory, *J. Phys. Chem.*, **55**, 221 (1951).

22. F. N. Kelley, Ph.D. thesis, The University of Akron, Ohio, 1961.
23. S. Bagrodia, G. L. Wilkes, and J. P. Kennedy, presented at the 55th Annual Meeting of the Society of Rheology, Knoxville, Oct. 1983.
24. G. L. Wilkes, Y. Mohajer, S. Bagrodia, J. P. Kennedy, and R. F. Storey, 28th Macromol. Symposia, IUPAC, Amherst, Mass., 1982, p. 906.
25. G. Broze, R. Jerome, P. Teyssié, and C. Marco, *Polym. Bull.*, **4**, 241 (1981).

Received November 4, 1983

Accepted February 9, 1984