Korean J. of Chem. Eng., **6**(3) (1989) *206-211*

CONSTRAINT RELEASE EFFECTS ON THE DYNAMICS OF POLYMER MELTS

Kwang Sik CHOI and In Jae CHUNG*

Department of Chemical Engineering, Korea Advanced Institute of Science and Technology, P.O. Box 131 Cheongryang, Seoul, Korea

(Received 3 September 1988 • accepted 18 January 1989)

Abstract—The dynamical behavior of polymers with molecular weight distribution is analyzed from the standpoint of reptation and tube renewal. In a binary blend where the entanglements between longer chains are prominent, the shorter chain relaxes only by reptation, whereas the longer chain shows more complex behavior, i.e., reptation in the original tube, short-range tube renewal causing the tube enlargement, and thereafter reptation again in the expanded tube. Dynamic moduli data from literature are used for determining the compositional dependence of the relaxation times. Also on the basis of the relaxation mechanism considered here, the critical composition due to the onset of entanglements between different longer chains is proposed as a function of their component molecular weight ratio.

INTRODUCTION

It is now widely recognized that the polymer chain dynamics in concentrated solutions and melts is dominated by reptation [1,2], the snake-like motion of a polymer through a fixed tube-like region formed by surrounding chains. The chain can move freely along its tube, but cannot escape laterally. For nearly monodisperse linear polymers, the reptation model apparently agrees well with self-diffusion data [3,4].

In a real polymer with a broad molecular weight distribution(MWD), however, the assumption of the fixed-obstacles which is useful in monodisperse system is no more valid. That is, the tube expansion will occur by constraint release. For an example of a polydisperse polymer system, a bimodally distributed system, a blend of shorter(1-) and longer(2-) chains, is the most simple but critical case for accounting the polydispersity effect on chain dynamics and their relaxation. The shorter chain relaxes only by reptation just like monodisperse state irrespective of its composition. But the behavior of the longer chain is affected by some factors such as a blend ratio($R = M_2/M_1$) and its volume fraction. That is to say, if the difference of respective molecular weights is small, $M_2/M_1 \rightarrow 1$, the fixed-tube assumption will be valid. As the R increases, the constraint release accompanying the tube enlargement accelerates the crawling motion of the long chain. Ultimately, in the extreme case, $R \rightarrow \infty$, the shorter polymers constraining the 2-chain act as solvent-like chains.

In addition to the dependence of chain dynamics on the blend ratio, the composition dependence is very important. In the limiting dilute region of 2-chains, $\phi_2 \rightarrow 0$ (where the ϕ_2 means the volume fraction of 2-chains), various theories for the dynamics of a longer chain isolated in short chain matrix have been presented by several authors [5,6], and supported by various experiments [7-11]. At a finite concentration allowing entanglements among the different longer chains, however, the relaxation behavior shows somewhat different mode from the dilute-concentration behavior: after the 1-chains surrounding on a 2-chain diffuse out by reptation, the local tube renewal can take place between two 2-2 entanglement couplings.

So as to study the polymer chain dynamics, there are two experimental ways, i.e., the diffusion coefficient from the tracer diffusion experiments [7-9] and the relaxation time from the dynamic shear measurements in linear viscoelastic region [10,11]. In general, the diffusion coefficient is measured by labeling and embedding a polymer chain as a test chain in unlabeled chain matrix. But the measurement of the diffusion coefficient of the 2-chain in a concentrated region is rather complicated so far. The individual contribution of each component to the chain relaxation behavior can be observed rather directly in the dynamic moduli $G'(\omega)$ and $G''(\omega)$, where G', G'' are respectively the

*To whom all correspondences should be addressed.

storage and the loss modulus and ω is a frequency. At a high frequency region all chains participate in the entanglement network. At a low frequency region only the 2-chain exhibits the viscoelastic response and the 1-chain acts as a solvent-like molecule.

In this paper, we will propose a tube renewal theory in the bimodally distributed polymers. From this model we will discuss the effect of a constraint release on the relaxation behavior of higher molecular weight chain and on the rheological properties of the binary blends from literature data.

THEORY

1. Review of reptation theory

The primary factor controlling the overall molecular motion of polymer in an undiluted system is the effect of entanglements, i.e., chains cannot pass through each other. Because of the restricted transverse motion to the chain contour due to those topological constraints, the reptation theory assumes that each polymer chain is confined in a fixed virtual tube, the envelope of all the obstacles which directly surround it, and can move only along the tube-like region by Brownian motion. The diameter of tube, a, a measure of the span of transverse excursions, is an intrinsic property of the polymer and is governed by the entanglement spacing M_e. The tube diameter is assumed to be independent of the molecular weight (MW) and the tube length, L, directly proportional to MW. Each chain and the path of its associated tube have random walk conformations with the same mean square end-to-end distance, $<R>^2$:

$$N=L/a=<R>^2/a^2=M/M_e \tag{1}$$

where N is the number of primitive steps and is equal to the number of entanglement points per chain, and M means the MW of the polymer. The MW between entanglements, M_e, is proportional to the mean square diameter of tube, a^2.

According to this tube model, the longest relaxation time T_d^o when all memory of the original conformation is lost for the chain is given by

$$T_d^o=K\frac{M^3}{M_e} \tag{2}$$

where K is only temperature-dependent coefficient.

The primitive path at time t will consist of the initial steps survived and the new steps disengaged from its initial tube. The fraction having original tube conformation up to time t, $F(t; T_d^o)$, is given by

$$F(t;T_d^o)=\sum_{p=odd}\frac{8}{\pi^2p^2}\exp(-tp^2/T_d^o) \tag{3}$$

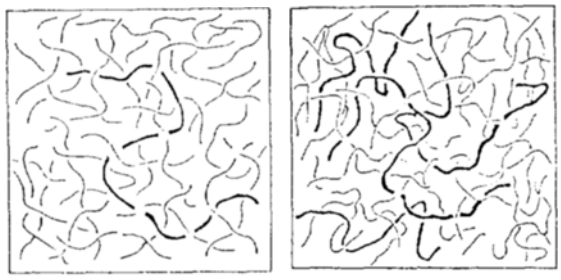
which was first obtained by de Gennes [1].

In a real polymer melt or an entangled solution some surrounding constraints can also diffuse out through reptation. Such a constraint release effect is quite important in a polydisperse system. This point is described in the following section.

2. Dynamics of binary blends

Let us consider a binary blend composed of two monodisperse components with respective molecular weights M_1 and $M_2(M_2>M_1>M_e)$. In their pure states, the longest relaxation times of each chain are designated as T_{d1}^o and T_{d2}^o, respectively. T_{d1} and T_{d2} represent the terminal relaxation time of each chain in blended states. Our primary interest is the interpretation of the intermolecular interactions between 1- and 2-chains by introducing the constraint release mechanism. It is also assumed that each pure component relaxes only by reptation and does not experience the constraint release. While the lower MW one (1-chain) disengages by only reptation and thus the terminal relaxation time T_{d1} is unchanged from its pure state, the motion of higher MW one (2-chain) probably depends on the composition as well as the component molecular weight ratio. Fig. 1 illustrates the entangled states of binary mixtures consisted of shorter (indicated by thin lines) and longer (indicated by thick lines) chains. In dilute region where the 2-chain is isolated in the 1-chain matrix, the relaxation of 2-chain is dominated by tube renewal after the release of 1-chains constraining the 2-chain. In concentrated region where the entanglements among different 2-chains are prominent, the dynamics of 2-chain is quite different from that in the dilute region. Here we put emphasis more on the concentrated region than the dilute region.

Fig. 2 shows schematic illustrations for the relaxation process of a 2-chain in blended state. Up to a time of order T_{c1}, the characteristic relaxation time of 1-



(a) dilute region (b) concentrated region

Fig. 1. Schematic illustration of long-long chains interactions.
(a) At the dilute region a long chain is isolated in short chain matrix. (b) At concentrated region a long chain entangles other chains.

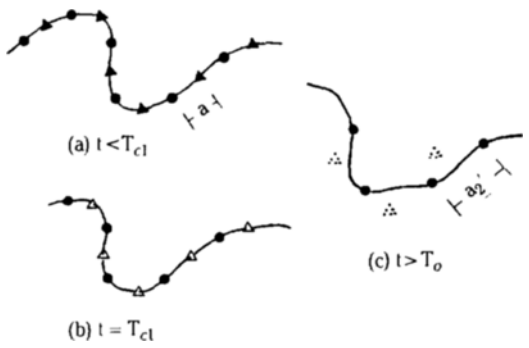


Fig. 2. The relaxation process of the long chain.
(a) The 2-chain disengages the original tube of diameter a by reptation at $t<T_{c1}$. (b) At $t = T_{c1}$, the short constraints begin to evaporate (denoted as open triangles) and cause tube enlargement. (c) After the completion of local tube renewal, the 2-chain disengages the expanded tube with reptation time T_{d2}.

chains upon the 2-chain, the tube conformation is fixed, i.e., the 2-chain relaxes by only reptation in the tube of diameter a. For time larger than $T_{c1}(\simeq T_{d1}^{o})$ [5,6], the 2-chain renews its conformation not only by its own reptation but also by the local constraint release. But the reptation effect is negligible during the tube renewal process.

The tube renewal takes place by Rouse-like motion of local tube segment between the 2-2 entanglements. Thus the effective entanglement spacing during tube renewal is given by [2]

$$M_{e2}(t)=M_e(t/T_{c1})^{1/2} \tag{4}$$

for time larger than T_{c1}. When the tube renewal is completed, the 1-chains begin to act as a somewhat solvent-like molecule and thus the effective entanglement spacing M_{e2}' can be deduced from the effects of polymer concentration in monomeric solvent molecule on the average molecular weight between entanglements, $c^{\alpha}M_e$ = constant, where c is the polymer concentration in solution [12]:

$$M_{e2}'=M_e\phi_2^{-d} \tag{5}$$

where the index d means the degree of departure from the pure solvent-like dependence as a function of the blend ratio and changes from α at $M_1/M_2=0$ to zero at $M_1/M_2=1$:

$$d=\alpha(1-M_1/M_2) \tag{6}$$

where α varies slightly with the polymer species (α = 1~1.25) [10]. It has been confirmed that the dependence of d on the blend ratio is well covered by the above equation without requiring the higher-order approximation [12]. Simultaneously, the effective mean square of tube diameter $a_2'^2$ becomes larger than its original value because the 1-chains constraining the 2-chain diffuse out:

$$a_2'^2=a^2\cdot\phi_2^{-d} \tag{7}$$

Since the M_{e2}' is comparable to eq.(4) when the tube renewal is completed, the tube renewal time is given as

$$T_o=T_{c1}/\phi_2^{2d} \tag{8}$$

After the tube conformation reaches a reequilibrium state accompanying the tube enlargement, the 2-chain disengages by reptation again in the tube expanded with relaxation time T_{d2} which is equivalent to the pure disengagement time of a chain in an original tube of diameter a_2' and entanglement spacing M_{e2}' and number of primitive steps $N_2'=N_2\phi_2^{d}$ [12]:

$$T_{d2}=\frac{M_e}{M_{e2}'}T_{d2}^{o}=\phi_2^{d}T_{d2}^{o} \tag{9}$$

On the other hands, as the composition of 2-chain decreases ultimately to a critical composition ϕ_c owing to the onset of entanglements between long chains, the longest relaxation time T_{d2} probably approaches the local tube renewal time T_o. Thus from eqs. (8) and (9), the critical composition in the binary blend is

$$\phi_c=(M_1/M_2)^{1/d} \tag{10}$$

because T_{c1} is nearly equal to T_{d1}^{o} [5,6]. When $\phi_2>\phi_c$, it is apparent that the 2-chain always finishes its terminal relaxation after the completion of the local tube renewal process.

For time larger than T_{c2} which is the characteristic lifetime of tube constraints formed by 2-chains and nearly equal to T_{d2}, the constraints begin to Rouse-like random jump [5], and the equivalent entanglement spacing during this long-range tube renewal step increases from M_{e2}' to its own molecular weight $M_2=N_2M_e$ at about $T_{r2}=N_2'^2T_{c2}$. After the long-range tube renewal time T_{r2}, all polymer chains including not only 1-component but also 2-component polymers act as a pure viscous liquid.

The time evolution of the effective entanglement spacing $M_{e2}(t)$ on the 2-chain is shown in Fig. 3.

3. Rheological properties

In previous section, the relaxation process of each component chain occurring by reptation and local tube renewal has been visualized as pure reptational disengagement of an equivalent chain whose configurational parameters are time-dependent in relation with the dynamics of surrounding tube constraints. The terminal relaxation times of each component chain are expressed in terms of those at respective pure states, blend ratio and composition.

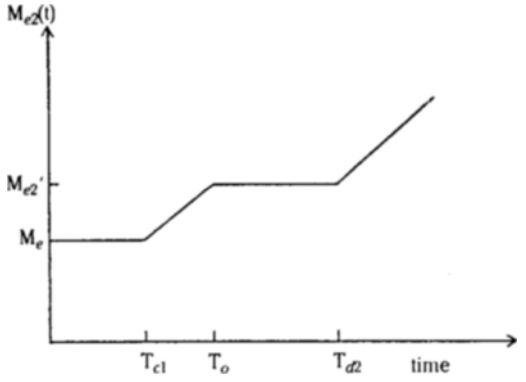


Fig. 3. Log-log plot for the time evolution of effective entanglement spacing on the 2-chain.

Following the single chain approximation of Doi and Edwards that every molecule contributes independently to stress, we can write the shear relaxation modulus G(t), which is conveniently characterizing the rheological properties, from the knowledge of the parameters of equivalent chains [12]:

$$G(t) = \sum_i G_i(t) \tag{11}$$

where

$$G_i(t) = G_N^o\left[\phi_i \frac{M_e}{M_{ei}(t)} F(t; T_{di}')\right] \tag{12}$$

with

$$M_{e1}(t) = M_e \quad \text{for all times} \tag{13}$$

$$M_{e2}(t) = \begin{cases} M_e & \text{for } t < T_{c1} \\ M_e (t/T_{c1})^{1/2} & \text{for } T_{c1} < t < T_o \\ M_{e2}' = M_{e2}^{-d} & \text{for } t > T_o \end{cases} \tag{14}$$

In eq. (12), $M_e/M_{ei}(t)\cdot F(t; T_{di}')$ means the fraction of the configurational memory of the equivalent tube survived up to time t. The configurational relaxation function of respective components are shown in Figs. 4(a) and (b). The G_N^o represents the plateau modulus which is independent of molecular weight. The T_{di}' is given as time dependent value, $M_e/M_{ei}(t)\cdot T_{di}^o$.

Fig. 4(c) shows a typical shape for the relaxation modulus curves of binary blends. Up to a time order T_{d1}, the relaxation modulus is equal to the plateau modulus owing to the participation of each component to viscoelastic response or entanglement network. On the time scale $t > T_{d1}$, the G(t) shows a wedge type relaxation mode because of the Rouse-like tube renewal of shorter constraints on the 2-chain. After tube reorganization, i.e., for time larger than T_o the stress is contributed only by 2-chains since the short chains behave as solvent-like molecule.

From the shear relaxation modulus function, the terminal viscoelastic properties such as zero-shear viscosity and recoverable compliance can be obtained from the linear viscoelastic theory [13].

DISCUSSION

The reptation model can be rheologically tested because the average relaxation time for a monodisperse linear polymer is proportional to the zero shear viscosity η_o which has been measured accurately for a number of polymer with different molecular weights. The experimental results have shown the 3.4-power law of the molecular weight, which is in discord with the reptation model following the 3.0-power law. The discrepancy of the relaxation time between theory and experimental observations is mainly caused by the thermal fluctuation of the primitive chain [14]. Because the contour length fluctuation is one of the intramolecular interactions, however, it does not influence the constraint release which is one of the intermolecular interactions. Since we are interested only in the constraint release effects on the relaxation of 2-chain, the contour length fluctuation can be put aside. Here we demonstrate the ϕ_2 and R-dependence on the relaxation time of 2-chain using literature data [10, 16-18].

In order to determine the characteristic relaxation

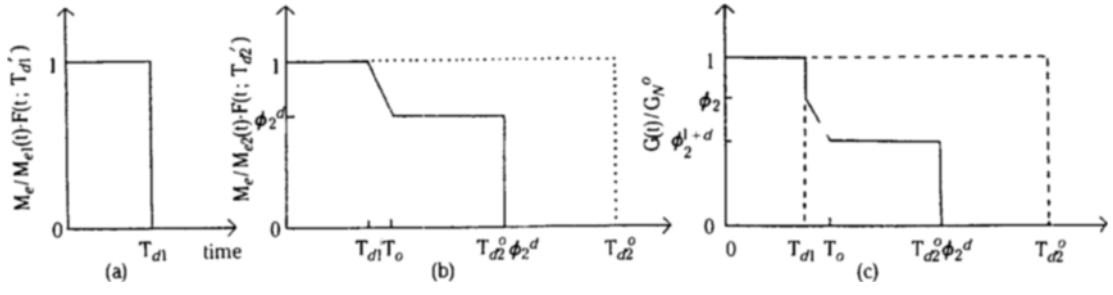


Fig. 4. Orientational relaxation functions for each component in a blend (a, b) and shear relaxation modulus of the blend (c). These are plotted logarithmically against time.

time of each chain, the Cole-Cole plot, η'' vs. η', has been used [10]. The reciprocal of the frequency at maximum, $1/\omega_i^o$, is taken as the average relaxation time in a nearly monodisperse polymer fraction. And in a binary blend, the right and left maximum describe the relaxation time of 2-component ($1/\omega_2$) and 1-component ($1/\omega_1$), respectively.

Fig. 5 shows the variations of $\log(\omega_2^o/\omega_2)$ with $\log \phi_2$ in the concentrated region, where the ω_2^o/ω_2 defines the ratio of the relaxation times of 2-component in blended state and in pure state. Triangles, rectangles, and open circles denote the data for polystyrene binary mixtures with R = 27(△), 5.5(○), and 3.6(□), respectively [10, 15, 16]. The relaxation time of long chain increases with increasing ϕ_2 because the interactions among the 2-chains increase more and more. As the blend ratio R increases, the slope increases also. The variation of the slope with R is similar to that of eq. (5). This means that T_{d2} increases with decreasing R ultimately to its pure component value T_{d2}^o at R→1. Thus the compositional dependence of the terminal relaxation time of 2-chain is well predicted by eq. (9).

On the other hand, the dependence of steady state compliance J_e^o on the molecular weight distribution has received much attention because of its importance of polymer processing. The compliance of binary mixture is very sensitive to the tail of higher component.

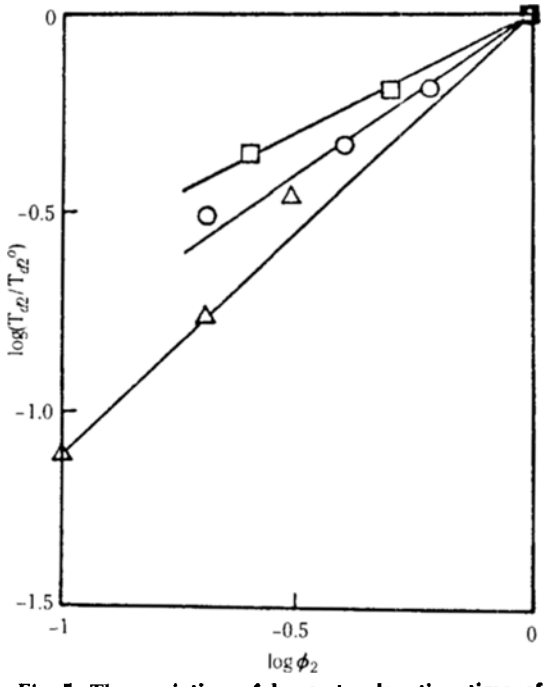


Fig. 5. The variation of longest relaxation time of the long chain with its composition.

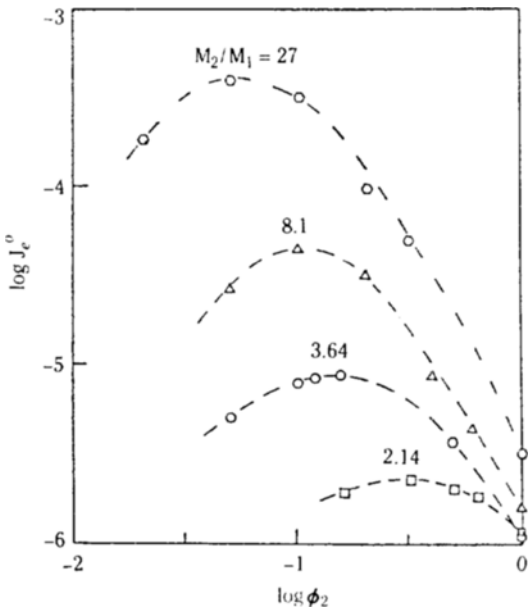


Fig. 6. The compositional dependence of recoverable compliance of binary blends.
Symbols denote the literature data by Montfort et al. (○,○) [10,15], Zang et al.(△) [17], and Akovali(□) [18].

The relationship between J_e^o and ϕ_2 is shown in Fig. 6 for the polystyrene binary blends [10, 15, 17, 18]. As the composition of 2-component increases in an 1-chain matrix, the J_e^o increases rapidly and reaches the maximum value, and thereafter it approaches the compliance of pure state of 2-chains, $(J_e^o)_2$, along the power law, $J_e^o = (J_e^o)_2/\phi_2^\beta$ $(1<\beta<2)$ [16]. The max-

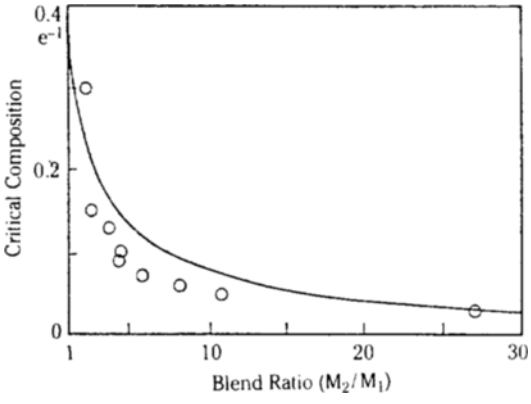


Fig. 7. The critical composition due to the onset of entanglements between long chains.
The symbols and line represent the maximum ϕ_2's in compliance data and the ϕ_c in eq. (10), respectively.

imum composition decreases as the blend ratio R increases. This behavior has not been explained theoretically until now. Choi et al. summarized the maximum composition data on polystyrene and polybutadiene reported by several authors [19]. Fig. 7 shows the comparison of the critical composition of eq. (10) and the maximum composition. The theoretical value shifts to smaller one with increasing R similarly to experimental data. From this figure, it is considered that the maximum composition represents the beginning of entanglement between 2-chains.

CONCLUSION

We have presented a tube renewal mechanism by considering the Rouse-like motion of the long chain after the release of shorter constraints and analyzed the rheological properties in the light of tube model.

The terminal relaxation time of the longer component increases with increasing its composition which results in the increase of entanglement among long chains. And it is concluded that the appearance of maximum value in compliance data of binary mixture is due to the onset of long-long chain entanglements.

Finally, we have not tested the local tube renewal time experimentally. It can be analyzed from the dynamic moduli data [10]. In the future work, we will demonstrate the experimental method to elucidate the local tube renewal process.

REFERENCES

1. de Gennes, P.G.: *J. Chem. Phys.*, **55,** 572 (1971).
2. Doi, M. and Edwards, S.F.: "The Theory of Polymer Dynamics", Oxford Univ. Press, Oxford, 1986.
3. Klein, J.: *Nature,* **274,** 143 (1978).
4. Bartels, C.R., Crist, B., and Crist, W.W.: *Macromolecules,* **17,** 2702 (1984).
5. Klein, J.: *Macromolecules,* **11,** 852 (1978).
6. Graessley, W.W.: *Adv. Polym. Sci.,* **47,** 67 (1982).
7. Green, P.F., Mills, P.J., Palmstrom, C.J., Mayer, J.W., and Kramer, E.J.: *Phys. Rev. Lett.,* **53,** 2143 (1984).
8. Green, P.F., Palmstrom, C.J., Mayer, J.W., and Kramer, E.J.: *Macromolecules,* **18,** 501 (1985).
9. Green, P.F. and Kramer, E.J.: *Macromolecules,* **19,** 1108 (1986).
10. Montfort, J.P., Marin, G., and Monge, Ph.: *Macromolecules,* **17,** 1551 (1984).
11. Struglinski, M.J. and Graessley, W.W.: *Macromolecules,* **18,** 2630 (1985).
12. Kim, H.Y. and Chung, I.J.: *J. Polym. Sci., Polym. Phys. Ed.,* **25,** 2039 (1987).
13. Ferry, J.D.: "Viscoelastic Properties of Polymers", 3rd ed., Wiley, New York, 1980.
14. Doi, M.: *J. Polym. Sci., Polym. Lett. Ed.,* **19,** 265 (1981).
15. Montfort, J.P.: *Polymer,* **17,** 1054 (1976).
16. Kim, H.Y.: Doctoral Thesis, KAIST, 1987.
17. Zang, Y.H., Muller, R., and Froelich, D.: *Polymer,* **28,** 1577 (1987).
18. Akovali, A.: *J. Polym. Sci.,* Part A-2, **5,** 875 (1967).
19. Choi, K.S., Kim, H.Y., and Chung, I.J.: *Macromolecules,* **21,** 3171 (1988).