Macromolecules **1991,** *24,* 850-854

Dynamic Mechanical Measurement of Crystallization-Induced Gelation in Thermoplastic Elastomeric Poly(propylene)

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Received February 2, 1990; Revised Manuscript Received July 17, 1990

ABSTRACT: The thermoplastic elastomeric poly(propylene) (TPE-PP) of this study has a linear structure comprised of multiple blocks of stereoregular and stereoirregular sequences. Above a melting temperature of about 65 °C, the TPE-PP is a liquid. In our experiments, the samples were first melted by heating to a prescribed temperature T_p (75, 100, or 150 °C) and then cooled to 40 °C and held there for observation of the crystallization. Upon this cooling into a supercooled state, TPE-PP undergoes a gradual liquid–solid transition as the stereoregular sequences crystallize and hence form physical network junctions. At the gel point of this physical gelation process, the TPE-PP exhibits the typical scaling behavior expressed in power law relaxation, $G(t) = St^{-n}$ with a prefactor S of about 2.0 MPa s^n and a relaxation exponent n close to 0.13. S is constant, while the value of n decreases slightly with the degree of crystallinity at the gel point. The degree of crystallinity at the gel point depends on the thermal history. If T_p is too low (e.g., 75 °C), some of the microphase-separated solid-state structure persists into the melted state and the subsequent gelation is characterized by the absence of scaling behavior.

Introduction

During physical gelation of polymers, long lasting physical bonds form between the macromolecules and connect them into a three-dimensional network. Examples of such bonds are crystallites, hydrogen-bonding association, ionic clusters, and phase-separated microdomains in the crystalline state, mesophase state, liquid state, or glassy state.[1-11] They find applications in thermoplastic elastomers, adhesives, polymer modifiers, and plastisols. For most systems, the rate of formation of physical bonds and their lifetime depend on temperature history. Physical gelation is, in many respects, similar to chemical gelation. However, formation and dissolution of physical cross-links are reversible, cross-link functionality is very high, cross-link size is very large, and the junctions have a finite lifetime. The free variables of physical network formation are temperature and time (for transient network) as compared to the extent of reaction, which determines chemical gelation processes.

Mechanical properties are often monitored as an indicator of a progressing gelation process. However, little is known about the mechanical properties of physical gels. The purpose of this study is to examine whether the mechanical properties of physical gels follow the same well-understood evolution as chemical gels.

For chemically cross-linking systems, the gel point (GP) is defined as the instant at which the weight-average molecular weight diverges to infinity (infinite sample size) or the largest molecular cluster extends across the sample (finite sample size). Mechanically, the GP marks the transition from liquid to solid state. Chemically cross-linking systems at GP, termed at "critical gels",[12] are characterized by a self-similar limiting behavior for both the viscoelastic liquid in the pregel region and the viscoelastic solid in the postgel region.[13] The gel equation of Winter and Chambon[14,15]

$$\tau(t) = S\int_{-\infty}^{t}(t-t')^{-n}\,\dot{\gamma}(t')\,\mathrm{d}t';\quad 0 < n < 1 \qquad (1)$$

describes the stress in a critical gel that is deformed at a rate $\dot{\gamma}(t')$, $-\infty < t' < t$. The prefactor, S (Pa s^n), and the relaxation exponent, n, are characteristic properties of a critical gel independent of frequency. Physically, the prefactor S should be written as $S = G_0\lambda_0{}^n$, where the modulus G_0 and the short relaxation time λ_0 are network-specific material parameters.[16] For this study, we do not have sufficient information to separate S into its components.

As a consequence, the dynamic mechanical behavior at GP is characterized by a scaling relation between dynamic moduli and frequency

$$G'(\omega) \sim G''(\omega) \sim \omega^n \qquad (2)$$

and a frequency-independent loss angle

$$\delta_c = n\pi/2 \quad \text{or} \quad \tan\delta_c = G''/G' = \tan(n\pi/2) \qquad (3)$$

These distinct mechanical properties of critical gels provide an easy tool for determining GP of chemical cross-linking systems. It also seems to apply to physically cross-linking systems.[1,2] The universality of this phenomenon in physical gelation remains to be examined by studying a wider variety of polymers.

Recently, we designed and synthesized a new titanocene complex having two dissimilar η^5 groups, *rac*-ethylidene-(1-η^5-tetramethylcyclopentadienyl)(1-η^5-indenyl)dichlorotitanium, which together with methylaluminoxane (MAO) polymerizes propylene into chains comprised of about 20% crystallizable (stereoregular) and noncrystallizable (stereoirregular) sequences. The new thermoplastic elastomer of poly(propylene) (TPE-PP) exhibits superior mechanical and elastic properties. The strain recovery ratio is up to 92% after 1260% elongation to break. Such high elasticity is obviously due to the crystallization of the stereoregular sequences, which form physical cross-links between the amorphous atactic sequences. The formation of these thermoreversible cross-links can be viewed as physical gelation.

Experimental Section

Materials and Preparation. The synthesis of *rac*-ethylidene-(1-η^5-tetramethylcyclopentadienyl)(1-η^5-indenyl)dichlorotitanium was described previously,[17] as also are the preparation of MAO,[18] procedure for propylene polymerization,[19] and determination of $\bar{M}_n$, $\bar{M}_w$, and X-ray crystallinity.[20] For this study, the polymerization temperature was 25 °C.

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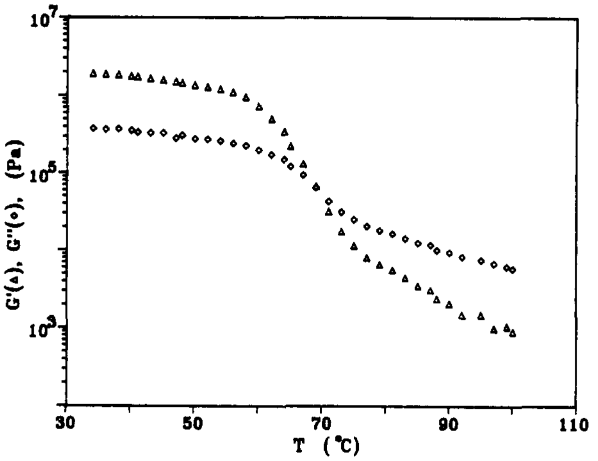

Figure 1. Temperature sweep on an RDS at 1 rad/s and a strain amplitude of 0.5%. The heating rate was 1 K/min.

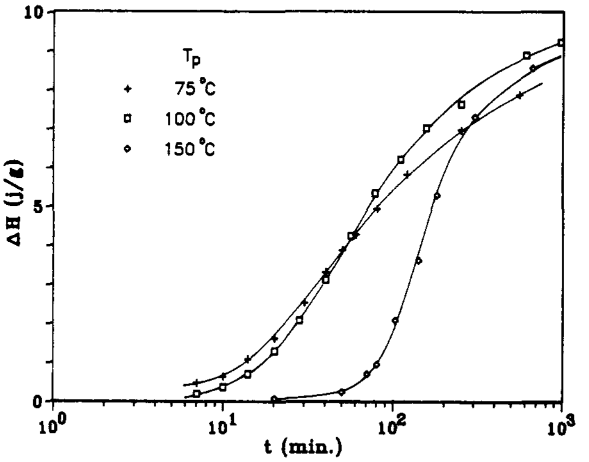

Figure 2. Growth of the degree of crystallinity during isothermal crystallization at 40 °C. The parameter is the prescribed preheating temperature. The crystallinity was measured by melting in a DSC at 20 K/min. Each point is a separated experiment.

Apparatus. Dynamic mechanical measurements on a Rheometrics dynamic spectrometer (RDS Model 7700) used cone/plate geometry. Samples were molded in the rheometer at 75 °C. Differential scanning calorimetry was carried out on a Perkin-Elmer calorimeter (DSC-4), at a heating rate of 20 K/min.

Results

The storage modulus, G', and the loss modulus, G'', at 1 rad/s decay by 2 and 1 orders of magnitude, respectively, during the melting transition around 65 °C when TPE-PP is heated in a temperature sweep (Figure 1). The observed melting temperature is in agreement with DSC results. The low melting temperature of the TPE-PP, compared to $T_m \approx 160$ °C for isotactic poly(propylene), is due to the short length of the stereoregular sequences.

When a melted sample is cooled from a prescribed heating temperature T_p (75, 100, or 150 °C) to a temperature below T_m for isothermal crystallization, the rate of crystallization depends not only on the degree of supercooling but also on T_p. We chose 40 °C as the crystallization temperature in the present study for the reason that the rates of crystallization at 40 °C are convenient for the measurements. In Figure 2, each point belongs to a separate experiment. Higher T_p leads to an extended nucleation stage, indicating that high-temperature heating is required for melting residual solid-state structure, which otherwise would act as nuclei. The crystallization at 40 °C has been monitored by dynamic mechanical measurements at 1 rad/s and a strain amplitude of 0.5%. The dynamic moduli and the relative elasticity grow with annealing time (Figure 3), indicating a gradual transition from viscoelastic liquid to viscoelastic solid. Repeated experiments at rest and during shear confirmed that oscillatory shear at a small-strain amplitude ($\gamma_0 = 0.5\%$) does not influence the rate of crystallization. There is a good agreement between the shapes of the modulus growth curves (Figure 3) and the crystallinity increase curves (Figure 2).

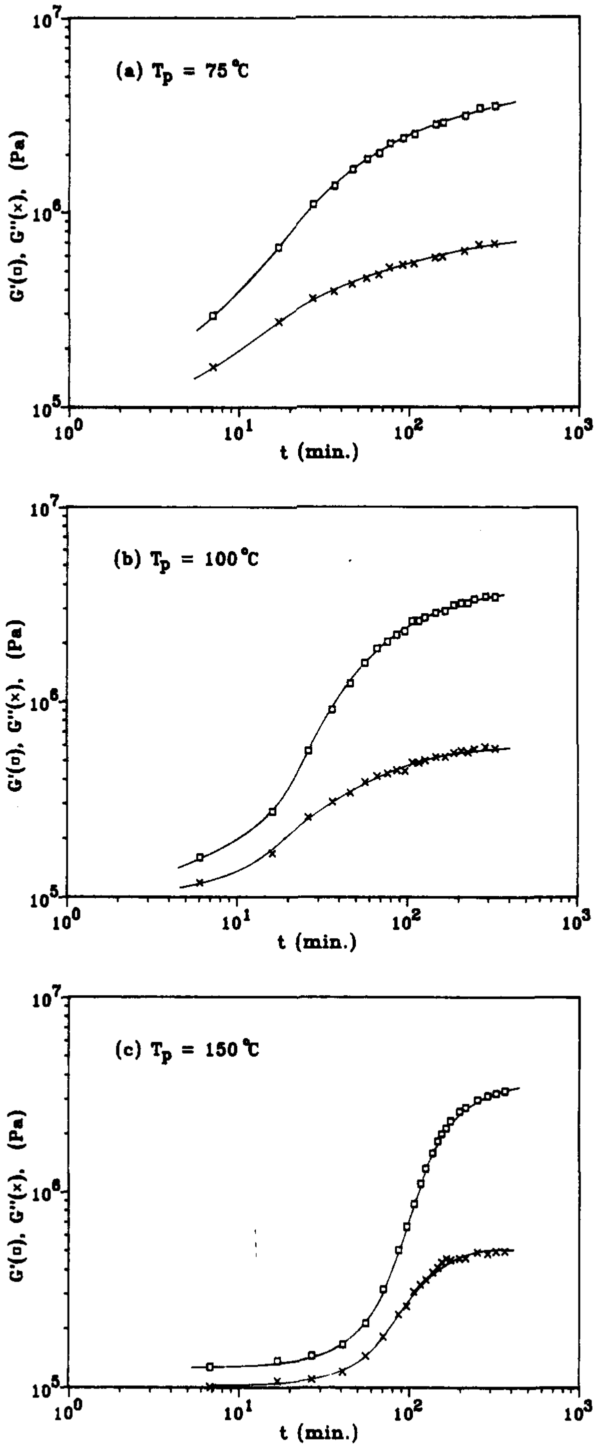

Figure 3. Modulus growth during crystallization at 40 °C, measured at 1 rad/s. The samples had been molten upon heating to (a) 75 °C, (b) 100 °C, and (c) 150 °C, respectively.

According to eq 3, GP is distinct by a loss tangent (tan $\delta = G''/G'$), which is independent of frequency. To find GP, tan δ was measured at 0.0316, 1, and 31.6 rad/s as a

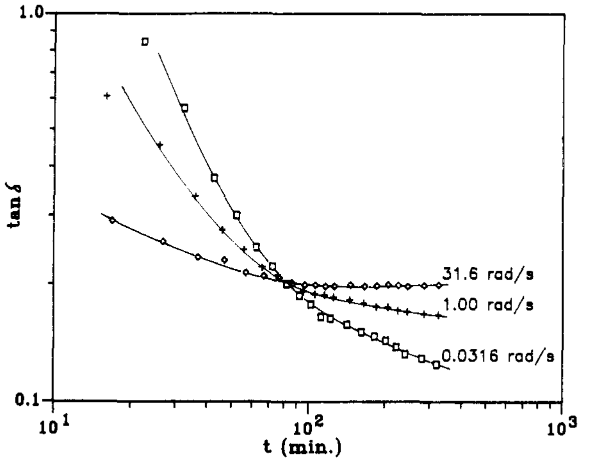

Figure 4. Evolution of loss tangent during crystallization at 40 °C. The parameter is frequency. T_p = 100 °C.

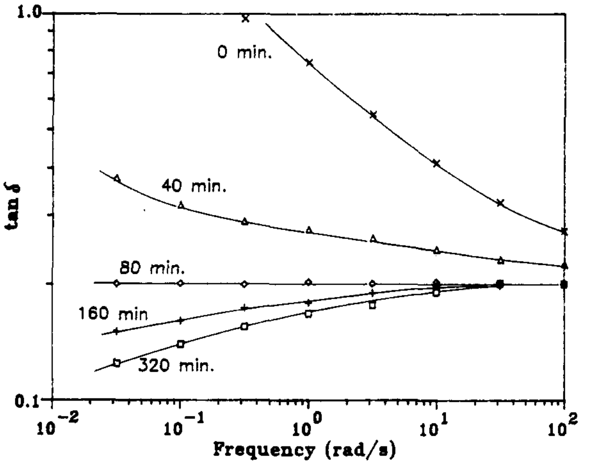

Figure 5. Frequency sweep for loss tangent. The sample has been heated to 100 °C and then cooled to 40 °C for the indicated time.

function of annealing time. The sample of T_p = 100 °C shows a GP at 80 min (Figure 4). Before the gelation time, tan δ decreases as the frequency increases (Figure 5), as is typical for a viscoelastic liquid. After the gelation time, tan δ increases with frequency (Figure 5), indicating that the polymer has changed into the viscoelastic solid state. At GP, tan δ_c equals 0.20, which corresponds to a relaxation exponent of n = 0.125. The evolution of $G'(\omega)$ and $G''(\omega)$ is shown in Figure 6.

The preheating temperature, T_p, has a large influence on the developing structure. When preheating to T_p = 150 °C, the crystallizing sample at 40 °C exhibits power law relaxation behavior after 160 min (Figure 7). Compared to the sample of T_p = 100 °C, gelation needs about twice as long and the relaxation component of n = 0.133 is slightly larger. However, the prefactor, S = 2.0 MPa s^n, is the same for both samples. From the intersection of the curves in Figure 2, the melting enthalpic changes of the critical gels are determined to be 5.4 and 4.5 J/g for the samples with T_p at 100 and 150 °C, respectively. This implies that a critical gel would form at a lower degree of crystallinity in a sample of higher T_p.

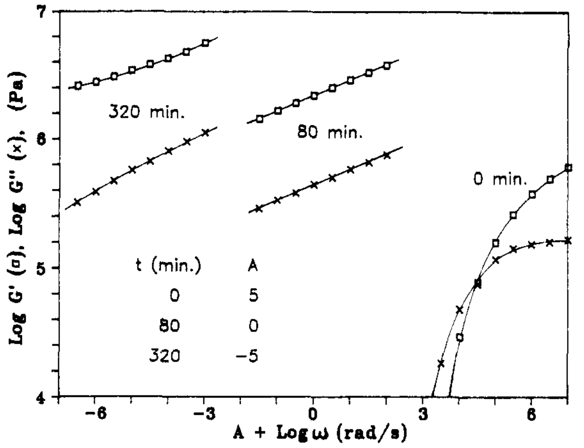

Figure 6. Frequency sweep for storage modulus and loss modulus. The sample has been heated to 100 °C and then cooled to 40 °C for the indicated time.

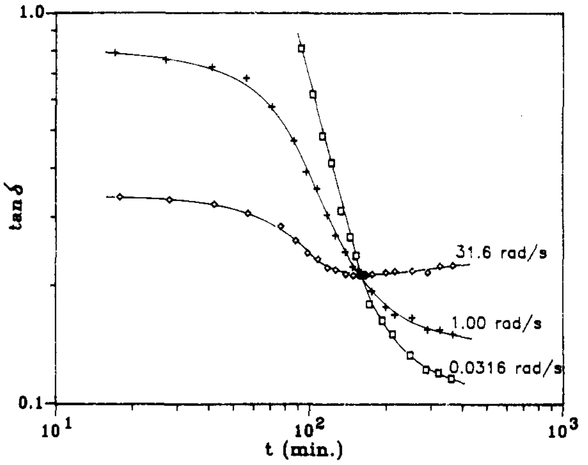

Figure 7. Evolution of loss tangent during crystallization at 40 °C. The parameter is frequency. T_p = 150 °C.

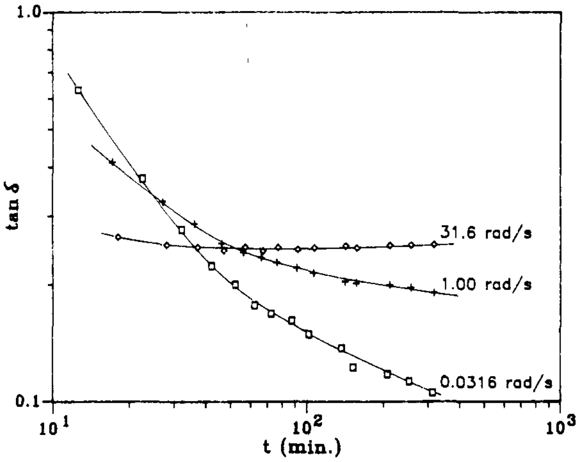

Figure 8. Evolution of loss tangent during crystallization at 40 °C. The parameter is frequency. T_p = 75 °C.

T_p = 75 °C leads to a qualitatively different gelation process. The curves of tan δ measured at different frequencies during crystallization do not intersect at a single point (Figure 8). Apparently, the sample has become a viscoelastic solid within 60 min of crystallizing at 40 °C, because tan δ is already increasing monotonically with frequency (Figure 9). However, for times shorter than 60 min the sample does not show constant tan δ or power law relaxation at any time. Surprisingly, the curves of tan $\delta(\omega)$ at different times show a peak at $\omega \approx 2$ rad/s (Figure 9).

Discussion

The wide frequency range of power law behavior at the gel point is remarkable. The long lifetime of the crystals gives the appearance of a permanently cross-linked system. It therefore is expected that the power law region extends

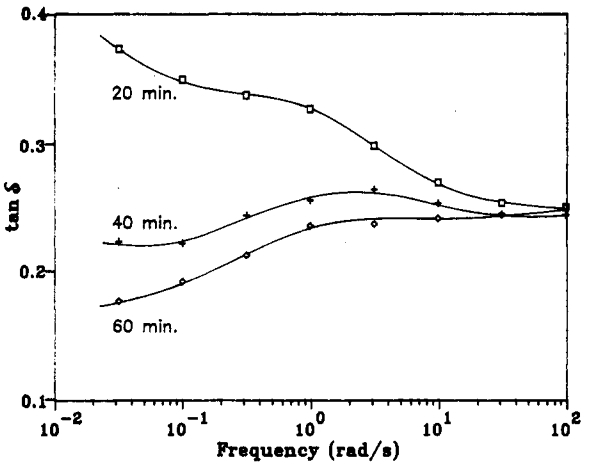

Figure 9. Frequency sweep for loss tangent. The sample has been heated to 75 °C and then cooled to 40 °C for the indicated time.

to very low frequencies much beyond the experimental frequency window. On the other hand, at very high frequencies there is no indication of a glass transition, which is expected to occur as the scale of observation decreases at increased frequencies. The very low glass transition temperature of TPE-PP agrees with this observation.

The rheological experiment integrates the response of the entire sample. Power law relaxation can only be observed if sample inhomogeneities are much smaller than the sample size. Macroscopic structural fluctuations will lead to deviations from the power law. This seems to be an important consideration for TPE-PP gelation.

Apparently, the sample of T_p = 100 °C already exhibits uniform gelation. More so, heating to 150 °C destroys any possible residuals of solid-state structure. This is indicated by the very low initial moduli and the extended nucleation stage during the subsequent crystallization (Figures 2 and 3). T_p = 150 °C leads to a lower degree of crystallinity at the GP, which implies a lower cross-linking density. The fact that gelation occurs at a lower degree of crystallinity suggests a higher functionality of the cross-links or a larger average size of the crystals at GP. This could explain why critical gels from T_p = 150 °C relax faster (slightly larger n) than those prepared with T_p = 100 °C.

The absence of melted-state microphase separation seems to be an important condition for a uniform gelation process. For the present TPE-PP, microphase separation might persist in the melted state slightly above T_m. The presence of residual high-melting crystallites decreases the molecular mobility and hinders the mixing of stereoregular sequences with stereoirregular sequences. When TPE-PP is heated to 100 °C or above, the separated microphases may disappear due the melting of residual crystallites and the increased thermal motion of the molecules.

Crystallizing multiblock copolymers with strong microphase separation always display solidlike dynamic spectra during the whole crystallization process.[6-8] At small strains and low stresses, the microphase-separated domains even in the liquid state act as cross-links in these copolymers. Crystallization that occurs within the microphase-separated domains only increases the strength of these physical cross-links but does not significantly change the physical network structure. For these multiblock copolymers, the transition from liquid to solid state is not marked by power law relaxation behavior. It is unclear whether these multiblock copolymers would exhibit power law relaxation behavior in a transient state of microphase separation. When a copolymer is cooled across the microphase-separation temperature, T_s, the high rate of phase separation does not allow one to measure the dynamic spectra of transient states. In comparison, for an amorphous phase-separated diblock copolymer, a power law relaxation has been reported in the terminal frequency range.[21]

In this context, the observed deviation from the power law relaxation for T_p = 75 °C can be understood. Microphase separation and residual high-melting crystals mask the classical gelation process. The distribution of block length and perfection of the stereoregular sequences broaden the melting transition. The presence of residual structure after preheating to only T_p = 75 °C is responsible for the relatively high dynamic moduli at the initial state (Figure 3a). During gelation, the persisting morphological heterogeneity results in regional differences in the degree of crystallinity and hence in the degree of cross-linking. The sample is a mixture of liquidlike and solidlike regions within the same time period. Consequently, the whole sample exhibits complicated dynamic mechanical properties and a masking of the power law relaxation (Figure 9).

Conclusions

When crystallization of a polymer leads to the formation of a three-dimensional network structure, power law relaxation behavior can be observed at the GP. This observation is a further implication that the scaling behavior of critical gels could be a universal phenomenon for all cross-linking systems, although there is a large difference between chemical and physical cross-linking in functionality and size of the cross-links. The lifetime of the crystalline cross-links below T_m is so long that they can be considered permanent.

On the other hand, nonuniform samples do not show the characteristic properties of a critical gel at a transient state due to heterogeneity-induced regional difference in the degree of cross-linking. This phenomenon is observed in the present crystallization/gelation study and is also believed to happen in inhomogeneous chemical gelation processes. For crystallization/gelation systems, the absence of melted-state microphase separation seems to be a necessary condition for the polymers to exhibit power law relaxation behavior at a critical time.

Acknowledgment. J.C.W.C. and D.T.M. acknowledge the support from the donors of the Petroleum Research Fund, administered by the American Chemical Society. H.H.W. and Y.G.L. acknowledge support from the NSF (Grant MSM 86-01595 and equipment grant DMR 88-06556) and the ONR.

References and Notes

(1) Te Nijenuis, K.; Winter, H. H. *Macromolecules* **1989**, *22*, 411.
(2) Cuvelier, G.; Peigney-Nourry, C.; Launay, B. *Gums and Stabilisers for the Food Industry. 5*; Phillips, G. O., et al., Eds.; IRL Press: Oxford, 1990; p 549.
(3) Gan, Y. S.; Francois, J.; Guenet, J. M. *Makromol. Chem., Rapid Commun.* **1985**, *6*, 225.
(4) Jo, W. H.; Kwon, I. H.; Seoul, C. *Polym. Eng. Sci.* **1989**, *29* (22), 1569.
(5) Eldridge, J. E.; Ferry, J. D. *J. Phys. Chem.* **1954**, *58*, 992.
(6) Lin, Y. G.; Zhou, R.; Chien, J. C. W.; Winter, H. H. *Macromolecules* **1988**, *21*, 2014.
(7) Lin, Y. G.; Jin, P. W.; Chien, J. C. W.; Winter, H. H. *Polymer* **1989**, *30*, 831.

(8) Lin, Y. G.; Zhou, R.; Chien, J. C. W.; Winter, H. H. *Polymer* **1989**, *30*, 2204.
(9) Arnauts, J.; Berghmans, H. *Polym. Commun.* **1987**, *28*, 66.
(10) Te Nijenhuis, K. *Colloid Polym. Sci.* **1981**, *259*, 522.
(11) Morton, M. *Rubber Chem. Technol.* **1983**, *56*, 1096.
(12) Winter, H. H. *Prog. Colloid Polym. Sci.* **1987**, *75*, 104.
(13) Chambon, F.; Winter, H. H. *Polym. Bull.* **1985**, *13*, 499.
(14) Winter, H. H.; Chambon, F. *J. Rheol.* **1986**, *30*, 367.
(15) Chambon, F.; Winter, H. H. *J. Rheol.* **1987**, *31*, 687.
(16) Scanlan, J.; Winter, H. H. *Macromolecules*, in press.
(17) Mallin, D. T.; Rausch, M. D.; Lin, Y. G.; Dong, S.; Chien, J. C. W. *J. Am. Chem. Soc.* **1990**, *112*, 2030.
(18) Chien, J. C. W.; Wang, B. P. *J. Polym. Sci., Part A: Polym. Chem.* **1988**, *26*, 3089.
(19) Gieger, B.; Chien, J. C. W. *Polym. Bull.* **1989**, *21*, 159.
(20) Rieger, B.; Mu, X.; Mallin, D. T.; Chien, J. C. W. *Macromolecules*, in press.
(21) Bates, F. *Macromolecules* 1984, *17*, 2607.

Registry No. PP (homopolymer), 9003-07-0.