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Triblock Copolymer Based Thermoreversible Gels. 3. Effect of Stereocomplexation with iPMMA

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ABSTRACT: Thermoreversible gelation of syndiotactic poly(methyl methacrylate) (sPMMA)−polybutadiene (PBD)−sPMMA, triblock copolymers in *o*-xylene has been studied in the presence of isotactic PMMA (iPMMA) in a large range of syndio/iso mixing ratio (s/i). Differential scanning calorimetry (DSC) shows that two types of association contribute to the gel formation, i.e., the self-aggregation of the sPMMA outer blocks and the stereocomplexation of the sPMMA outer blocks with iPMMA. At low iPMMA contents (s/i = 30/1), self-association of the outer blocks accounts for the gelation process, although stereocomplexation occurs. Stereocomplexation becomes the dominant gelation mechanism at a high enough iPMMA content (s/i = 2/1). Thus, gelation is observed at a copolymer concentration as low as 1 wt %. The time dependence of the storage (G') and loss (G'') moduli has been measured in the 0.08−1Hz frequency range in order to probe the gelation process. At the gel point, where the loss angle ($\tan \delta_c = G''/G'$) is independent of the probing frequency, the sample fits in the typical power law $G'(\omega) \sim G''(\omega) \sim \omega^{\Delta}$. While the gelation time is greatly influenced by the s/i mixing ratio, the scaling exponent Δ is essentially constant in the range of 0.70−0.75. The Δ value agrees with theoretical predictions as well as with experimental values reported for some chemical gels but it is different from the experimental values reported for most physical gels. The Δ value is also independent of the PBD microstructure and it also holds for sPMMA-polystyrene (PS)−PBD−PS−sPMMA (MSBSM) pentablock copolymers. Therefore, the value of Δ appears to be a typical exponent for thermoplastic gels based on triblock copolymers of the ABA type in *o*-xylene.

Introduction

Stereocomplexation between sPMMA and iPMMA has been the topic of extensive investigations.[1,2] It can occur as well in bulk as in suitable solvents. Dissolved in some solvents, such as *o*-dichlorobenzene, butyl acetate and *o*-xylene,[1] sPMMA can also self-aggregate. Stereocomplexation and self-aggregation manifest themselves by a liquid to solid transition provided that the chain cross-linking exceeds a critical value.

Recently, much attention has been paid to the mechanism of the sol−gel transition, i.e., how the structure and the viscoelastic properties are changing on that occasion. As a rule, gelation may be of a physical or a chemical origin, depending on the structure of the cross-links. In physical gels, the cross-linking is reversible and the cross-linking sites can be of a large size and of a high functionality. In contrast, chemical gels are permanently cross-linked by covalent bonds and the branching point has a well-defined functionality, i.e., one of the cross-linker.

Chemical gelation has been extensively investigated by sophisticated experiments[3] and accounted for by different theories, from the original mean-field theory of Flory[4] to the concept of fractal geometry and the connectivity transition model of percolation.[3,5,6] Particular attention is being focused on the viscoelastic behavior of near-critical gels.[7−14,22,23] Analysis of the dynamics near the critical gelation point has led to predictions for the frequency dependence of shear storage and loss moduli, eq 1, where $G^*(\omega)$, $G'(\omega)$, and $G''(\omega)$

$$G^*(\omega) = G'(\omega) + iG''(\omega) \qquad (1)$$

are the complex, storage, and loss moduli, respectively, and ω the angular frequency. At the gel point, these moduli are predicted[7−9] and observed[7,10,11] to scale with frequency (f) according to eq 2 where $\omega = 2\pi f$; f is the

$$G'(\omega) \sim G''(\omega) \sim \omega^{\Delta} \qquad (2)$$

frequency and Δ is the scaling exponent.

As a rule, the loss angle at the gel point (δ_c) which is a measure of the phase difference between G' and G'' ($G''/G' = \tan \delta_c$), has an universal value at least at low frequencies[10]

$$\delta_c = \Delta(\pi/2) \qquad (3)$$

In contrast to chemical gelation, physical gelation is not so well understood. The transient nature of the physical network junctions makes it difficult to study these systems near the gel point. According to de Gennes,[3] the physical gelation can either fit the universal law for “strong gelation” or be comparable to a “glass transition” which is then referred to as “weak gelation”. Although $\Delta = 0.7$ is reported for chemical gels,[10,11] Δ is observed in the range of 0.1−0.8 for physical gels.[12−14]

Recently, we reported on physical gels formed by sPMMA−PBD−sPMMA, or MBM, copolymers in *o*-xylene, which is a selective solvent of the central block. The intermolecular association of the sPMMA outer blocks is at the origin of this phenomenon.[15,16] At the gel point, where the loss angle $\tan \delta_c$ is independent of frequency, these samples fit the power law expressed by eq 2 , where the scaling exponent Δ is found equal to 0.7, whatever the PBD and sPMMA molecular weight, the copolymer concentration (in the 2−7 wt % investigated range), and the temperature in the 8−24 °C range.[16] It thus appears that the physical gels formed by MBM copolymers exhibit all the characteristic features reported for the chemical gels. This paper addresses the question of the effect that the addition of homopolymers, sPMMA and iPMMA, can have on the viscoelasticity of the MBM copolymers in *o*-xylene.

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Table 1. Molecular Characteristics of Block Copolymers and PMMA Homopolymers

sample	$10^{-3}M_n$ M−(S-)B−(S-)M	M_w/M_n	PMMA s (%)	h (%)	i (%)	PBD 1,2-units (%)
MBM1	25−80−25	1.10	80	20	0	43
MBM2	12−50−12	1.10	78	22	0	15
MBM3	19−61−19	1.10	77	23	0	68
MSBSM	19−18−79−18−19	1.10	79	21	0	44
sPMMA	30	1.15	80	20	0	
iPMMA	30	1.10	6	4	90	

iPMMA is known for stereocomplexation with the sPMMA outer blocks of MBM copolymers.[17] Gelation of MBM copolymers containing PBD of different microstructures and gelation of MSBSM pentablock copolymers in *o*-xylene will also be reported.

Experimental Section

The MBM triblock copolymer was prepared by sequential anionic polymerization of butadiene and methyl methacrylate with the diadduct of *t*-BuLi onto *m*-diisopropenylbenzene (*m*-DIB) as a difunctional initiator. The detailed synthesis was reported elsewhere.[18] Chemical composition, molecular weight, and chain configuration of these copolymers are listed in Table 1. Tacticity of the sPMMA block was quite comparable in all the samples, in contrast to the PBD microstructure which varied from 15 to 68% 1,2-units. All these triblock copolymers were of a very narrow molecular weight distribution.

sPMMA was prepared by anionic polymerization in THF at −78 °C by using the reaction product of s-BuLi with one equivalent of 1,1-diphenylethylene (DPE) as initiator. iPMMA was synthesized by anionic polymerization of MMA initiated by *t*-BuMgBr in toluene at −78 °C.[19] The molecular characteristics of sPMMA and iPMMA are reported in Table 1.

Homogeneous solutions of MBM and MSBSM copolymers, added with sPMMA or not, were prepared in *o*-xylene at 80 °C. Solutions of blends of MBM with iPMMA were prepared in *o*-xylene at 130 °C.

Thermal analysis (DSC) was carried out with a Dupont 910 calorimeter in sealed pans at a heating rate of 20 °C/min. Weight loss less than 1 wt % was observed during these measurements. The dynamic mechanical properties were measured with a Bohlin CS apparatus equipped with coaxial cylinders (d = 25 mm). The polymer solution, preheated at 80 °C (or 130 °C), was rapidly added between the coaxial cylinders thermostated at the requested temperature. Solutions were cooled from 80 or 130 °C down to the requested temperature within ca. 1 min (as measured with a thermocouple) and the measurements were then immediately started. A 1% strain was used, and the linear regime was ascertained as reported elsewhere.[15]

Results and Discussion

The MBM1 triblock copolymer (Table 1) has been used for studying the effect of various amounts of homopolymers (sPMMA and iPMMA) on gelation. Blends of MBM1 with iPMMA have been denoted as MBM1/iPMMA. The other MBM copolymers have been studied in relation to the PBD midblock microstructure. All the solutions and gels are optically transparent.

Effect of iPMMA Addition. *Calorimetric Analysis.* When MBM triblock copolymers are blended with iPMMA in *o*-xylene, two types of intermolecular association may occur: self-association of the sPMMA outer blocks with formation of ordered conformation,[15,20] and stereocomplexation of these sPMMA blocks with iPMMA.[17]

Gels of MBM1 and MBM1/iPMMA blends in *o*-xylene were analyzed by differential scanning calorimetry (DSC) after aging at 0 °C for 1 week. Due to the low sensitivity of DSC, only gels of a high enough polymer concentration (10 wt %) were studied, i.e., at a concentration higher than the samples used for rheological analysis. Figure 1 shows the DSC thermograms typical of three samples, i.e., a MBM1 gel, a MBM1/iPMMA gel with a 10/1 s/i mixing ratio, and the same with a 2/1 mixing ratio. Curve 1 shows a melting endotherm for the MBM1 gel characteristic of the self-aggregation of the sPMMA outer blocks.[15] The melting region extends over ca. 20 °C with a maximum at 39 °C. When the MBM1 copolymer is added with a minor amount of iPMMA with respect to the sPMMA blocks (curve 2), an additional endotherm is observed at a much higher temperature (113 °C), which is the signature of the sPMMA/iPMMA stereocomplexation. When the s/i mixing ratio is decreased from 10/1 to 2/1, which is actually the optimum mixing ratio for the PMMA stereocomplexation,[1,2,17] the melting endotherm for the self-aggregation of the sPMMA blocks completely disappears, in contrast to melting of the stereocomplex which is much better defined (curve 3).

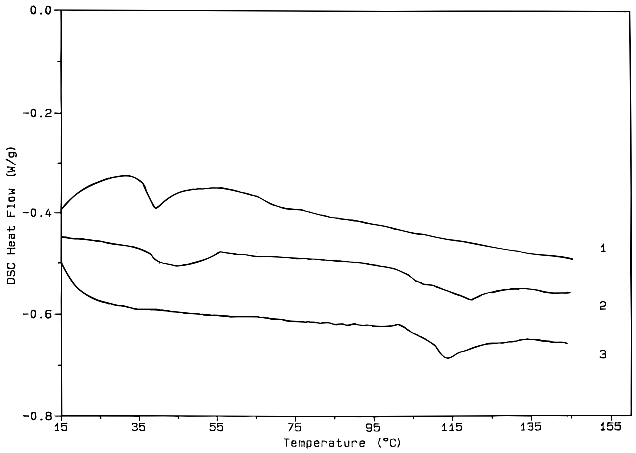

Figure 1. DSC traces of 10 wt % solutions in *o*-xylene of (1) MBM1; (2) MBM1/iPMMA (10/1 s/i, wt/wt) mixture; (3) MBM1/iPMMA (2/1 s/i, wt/wt) mixture.

Rheological Analysis. Rheology of the MBM block copolymer solutions in *o*-xylene is a convenient way to probe the gelation process, which is known to be a time-dependent process.[15] Special attention was paid to the time dependence of the complex shear modulus of 7 wt % solutions of MBM1/iPMMA mixtures of various s/i mixing ratios at 24 °C .

Figure 2A shows how the shear storage modulus (G') and the shear loss modulus (G'') depend on time at three frequencies, 0.05, 0.2, and 1 Hz, for the MBM1 gel (sample B1, Table 2). At a constant frequency, the loss modulus G'' is initially higher than G', which is characteristic of viscoelastic liquids. Both the moduli increase with time as result of the progress of the sPMMA block aggregation. The elastic component of the complex modulus, however, rises more rapidly than the viscous component, so that the two curves intersect ($G' = G''$) at the so-called crossing time. It has been reported that the crossing point is independent of frequency at least for some chemical gels.[11] Figure 2A shows that the crossing time is frequency-dependent for the MBM1 solution in *o*-xylene at 24 °C. Actually, it increases with the frequency and thus with the apparent moduli.

Figure 2B illustrates the time dependence of G' and G'' at three frequencies, 0.1, 0.4, and 1 Hz, for the MBM1 copolymer added with a small amount of iPMMA (s/i = 30/1) (sample B2, Table 2). Although the general behavior is kept unchanged compared to the original MBM1 copolymer (sample B1), the crossing times are

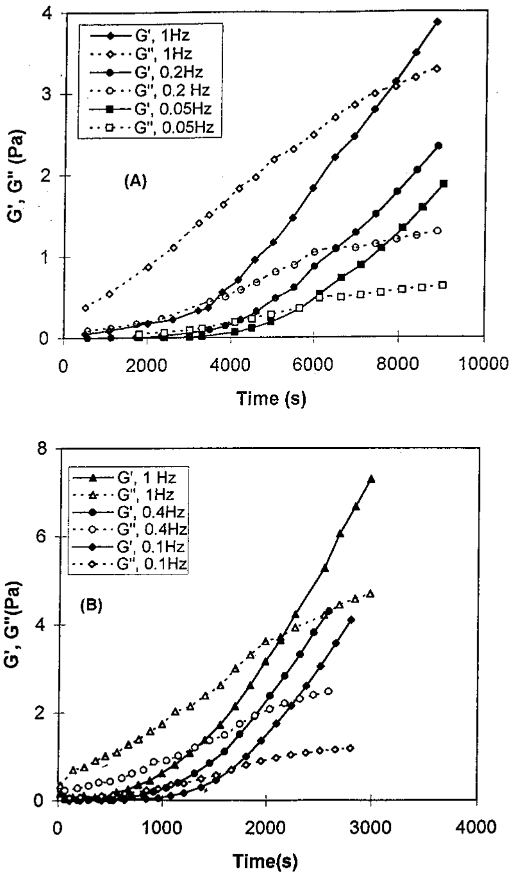

Figure 2. Time dependence of the shear storage (G') and loss (G'') moduli at 24 °C and various frequencies for 7 wt % solutions in *o*-xylene: (A) MBM1 triblock; (B) MBM1/iPMMA(30/1 s/i, wt/wt) mixture.

Table 2. Gelation Time (t_g) and Scaling Exponent (Δ) for Solutions of Copolymers in *o*-Xylene Added with Homo PMMA or Not

sample	block copolymer	homo-polymer	conc. (wt %)	b/h[a]	T (°C)	t_g[b] (s)	Δ[c]
B1	MBM1		7		24	4200	0.70
B2	MBM1	iPMMA	7	30/1	24	1330	0.72
B3	MBM1	iPMMA	7	20/1	24	650	0.74
B4	MBM1	iPMMA	7	15/1	24	180	0.75
B5	MBM1	iPMMA	7	10/1	24		
B6	MBM1	iPMMA	1	2/1	10		
B7	MBM1	sPMMA	7	2/1	24	6440	0.73
B8	MBM2		12		10	300	0.70
B9	MBM3		10		10	3660	0.70
B10	MSBSM		7		15	2000	0.72

[a] Weight ratio of the sPMMA outer blocks with respect to homopolymer. [b] Time characteristic of the point where tan δ is independent of frequency. [c] Scaling exponent defined by eqs 2 and 3.

shorter, all the other conditions being the same. For instance, the crossing time at 1 Hz (2200 s) is more than 3 times smaller than for the neat copolymer (7800 s), which indicates that even a small amount of iPMMA makes the gelation much faster as result of stereocomplexation in addition to the self-association of the sPMMA blocks. The modulus at the crossing point at 1 Hz (3.8 Pa) is only slightly higher compared to B1 sample (3.2 Pa). The gelation rate is increased as the relative amount of iPMMA is larger, and the crossing time at 1 Hz is further decreased down to 1200 s when the s/i ratio is 20/1 (B3, Table 2, Figure 3A). A further decrease in the mixing ratio by a factor of 2 (s/i = 10/1, B5, Table 2) results in a quasi instantaneous gelation (Figure 3B), since as soon as the first measurement is carried out, G' is higher than G'' and the crossing point goes unobserved. G'' is time-independent, whereas G' increases with time in a way which does not strongly depend on frequency at least in the investigated range. At mixing ratios smaller than 10/1, gelation is so fast that time dependence of G' and G'' is no longer observed. Actually, the gel is formed before the measurement cell is filled. In order to collect information for the 2/1 mixing ratio, which is the optimum ratio for stereocomplexation,[1,2] solution of a lower concentration (1 wt %) has been investigated at 10 °C (B6, Table 2). Figure 4

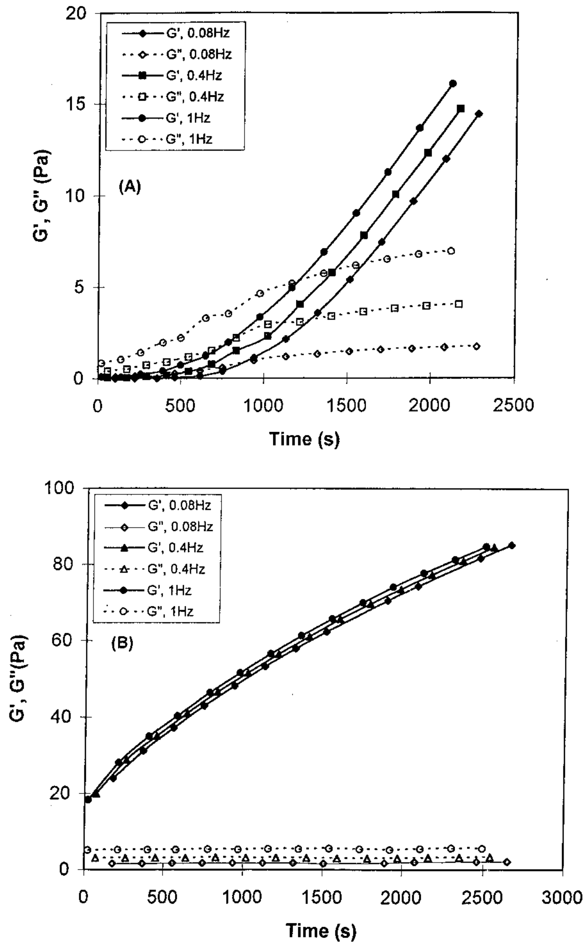

Figure 3. Time dependence of the shear storage (G') and loss (G'') moduli at 24 °C and various frequencies for 7 wt % solutions in *o*-xylene: (A) MBM1/iPMMA (20/1 s/i, wt/wt) mixture; (B) MBM1/iPMMA (10/1 s/i, wt/wt) mixture.

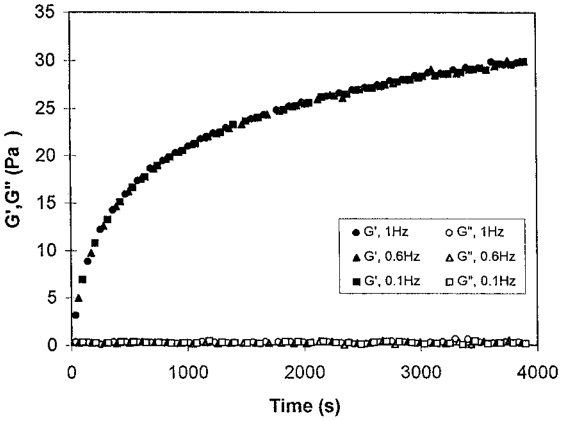

Figure 4. Time dependence of the shear storage (G') and loss (G'') moduli at 10 °C and various frequencies for 1 wt % solution of the MBM1/iPMMA(2/1 s/i, wt/wt) mixture in *o*-xylene.

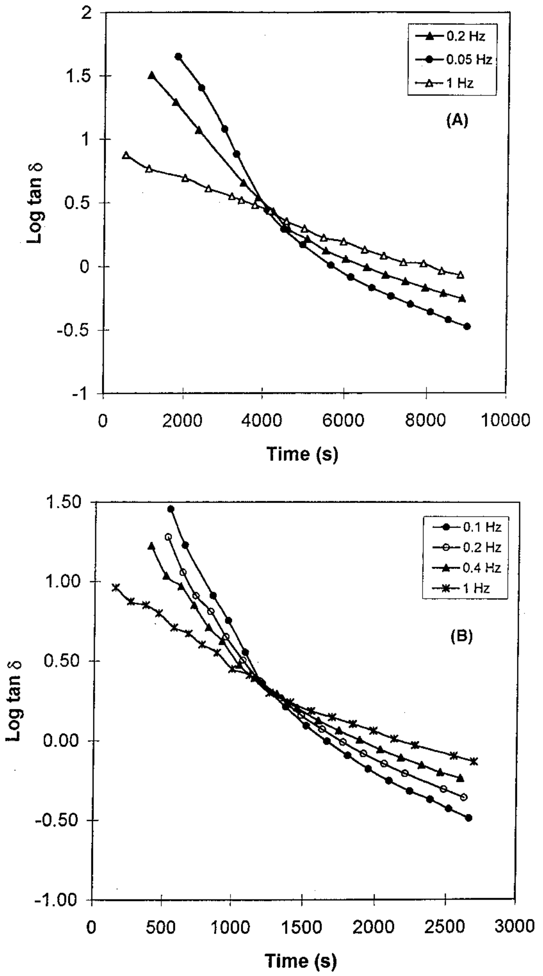

Figure 5. Loss tangent vs time at 24 °C and various frequencies for 7 wt % solutions in *o*-xylene: (A) MBM1; (B) MBM1/iPMMA (30/1 s/i, wt/wt) mixture.

shows that G'' is close to zero, whereas a rapid initial increase in G' is observed, which corresponds to the rapid stereocomplexation between sPMMA blocks of MBM1 and iPMMA. Such a fast gelation is quite surprising for a polymer concentration as low as 1 wt %. It is worth noting that G' is independent of frequency in the 0.1−1 Hz range.

Scaling Properties. Although the crossing point of G' and $G''(G' = G'')$ is designated as the gel point by some authors,[21] a more rigorous definition of the gel point has been given by Winter et al.[10] as the point where $\tan\delta$ ($=G''/G'$) is independent of frequency (eq 2). It is known that the static structure and the relaxation modes of the polymer at the gel point are self-similar and that the dynamic mechanical behavior at the gel point fits a power law for the frequency dependence of the moduli (eqs 2 and 3).[10,11] Although these dynamic mechanical properties are characteristic of polymers at the gel point of chemically cross-linked systems, there is now evidence for their validity in some physically cross-linked systems.[12,26] The percolation theory predicts slightly different Δ value, i.e., 0.67, when a percolation-like cluster structure and screened hydrodynamic interaction are assumed to prevail, and 0.72 on the basis of an analogy between gelation dynamics and electrical quantities in random resistor networks (for review, see ref 28). These predictions have been experimentally confirmed in case of chemical gelation, e.g. $\Delta = 0.70$ for gelation of epoxy resins[24] and $\Delta = 0.69$ for gelation of polyurethanes.[25,27] When physical gelation is concerned, Winter et al. have observed the same behavior at the gel point with $\Delta = 0.125$[12] and 0.11[26] for the crystallization-induced gelation of poly(propylene) and poly(β-hydroxyoctanoate), respectively.

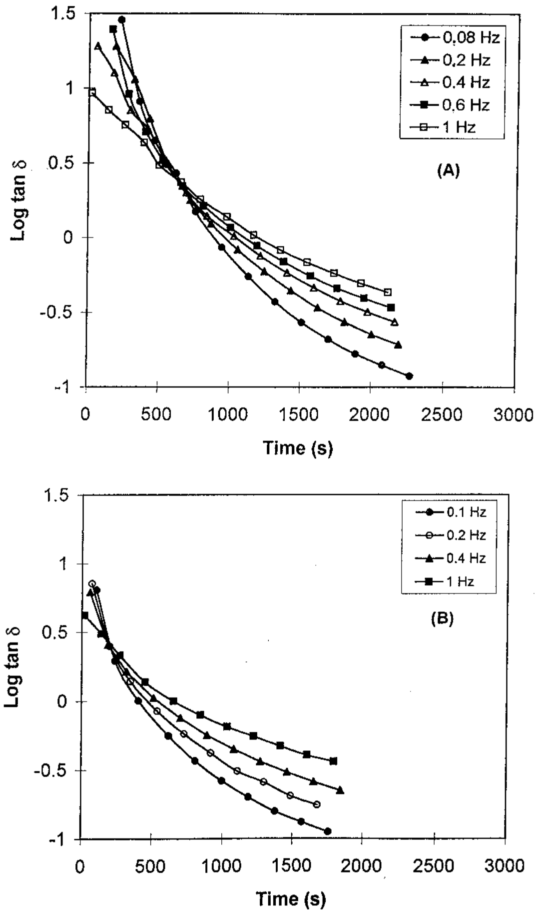

Figure 6. Loss tangent vs time at 24 °C and various frequencies for 7 wt % solutions in *o*-xylene: (A) MBM1/iPMMA (20/1 s/i, wt/wt) mixture; (B) MBM1/iPMMA (15/1 s/i, wt/wt) mixture.

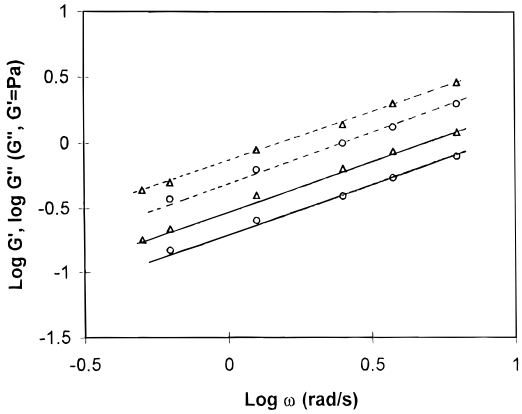

Figure 7. Shear storage (G') and loss (G'') moduli at the gel point vs angular frequency (ω) at 24 °C for 7 wt % solutions in *o*-xylene of MBM1/iPMMA (30/1 s/i, wt/wt) mixture (○: G', —; G'', - - -) and MBM1/iPMMA (20/1 s/i, wt/wt) mixture (Δ: G', —; G'', - - -).

In the previous paper,[16] we have reported that the typical power law $G'(\omega) \sim G''(\omega) \sim \omega^{\Delta}$ is observed for MBM triblock copolymers dissolved in *o*-xylene and that the relaxation exponent Δ is close to 0.7, independent of the copolymer composition, molecular weight, and curing temperature. In order to ascertain that this behavior is maintained in the presence of iPMMA which

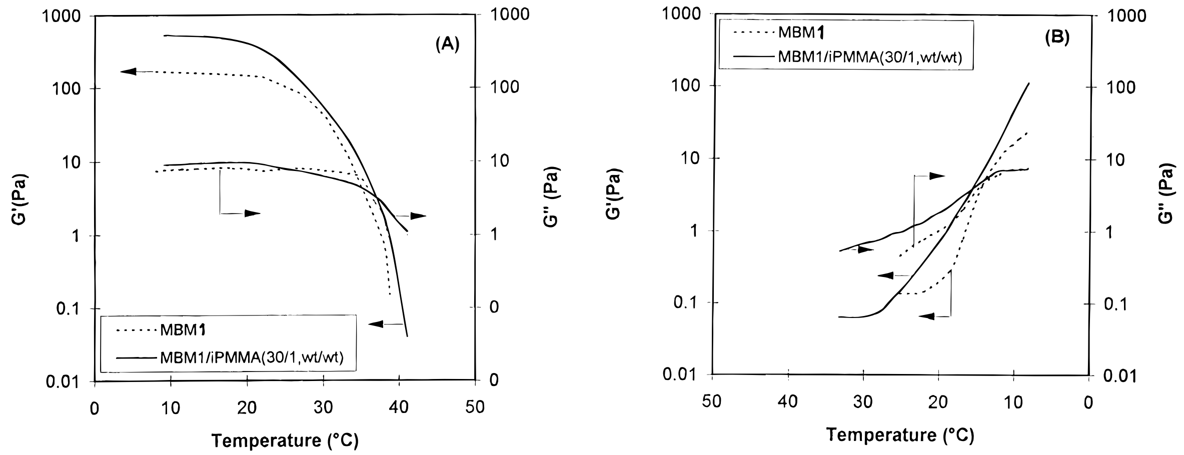

Figure 8. Temperature dependence of shear storage (G') and loss (G'') moduli at 1 Hz for 7 wt % solutions in *o*-xylene of MBM1 (- - -) and MBM1/iPMMA(30/1 s/i, wt/wt) mixture (—) upon heating (A) and cooling (B) at a 1 °C/min rate. The samples were aged for 12 h at 10 °C

decreases the crossing time and increases the thermal stability of the aged gels, tan δ has been plotted against the curing time at 24 °C and at different frequencies for the MBM1 copolymer (B1) and MBM1/iPMMA mixtures of different s/i ratios (B2, B3, and B4 in Table 2). Figures 5 and 6 show that the general behavior is the same for all the samples, i.e., the log(tan δ) vs time dependence for different frequencies intersect at the same time which is the gel time as stated in the introduction. For times shorter than t_g, tan δ decreases as the frequency is increased, which is typical for a viscoelastic liquid. At the gel point, the sample changes from a viscoelastic liquid to a viscoelastic solid, since beyond that point, tan δ increases with frequency. This observation indicates that the scaling law still holds for the MBM1/iPMMA blends in *o*-xylene. The relaxation exponent Δ at the gel point can be extracted from eq 3 where δ_c is δ at the intersection of all the tan δ vs time curves. The experimental gelation time, t_g, and the calculated relaxation exponent, Δ, are listed in Table 2.

The Δ value can also be calculated by plotting G' and G'' vs ω on a log−log plot since $G'(\omega) \sim G''(\omega) \sim \omega^{\Delta}$. Parallel straight lines can indeed fit the log−log frequency dependence of G' and G'', where Δ is the slope of these linear relationships shown in Figure 7.

As shown in Table 2, the gel point of the MBM1 gel (sample B1) is reached after 4200 s (Figure 5A) and earlier as increasing amounts of iPMMA are added to the triblock. t_g is 1330 s for sample B2 (Figure 5B) and 650 s for sample B3 (Figure 6A). Although stereocomplexation accelerates the gelation process, the scaling exponent Δ, which is characteristic for the critical condition of gelation, is not significantly affected by the addition of iPMMA, since Δ is in the range of 0.70−0.75 while the mixing ratio is changed from 30/1 to 15/1. This observation may be surprising, since two different mechanisms, self-aggregation of sPMMA and stereocomplexation, contribute to gelation with quite different kinetics. The Δ values observed for the physical gels of MBM and mixtures with iPMMA are thus in good agreement with Δ reported for chemical gels.[8] It is worth noting that, although the main theories (Rouse approximation and electrical analogy) predict a similar Δ value for the power-law gel point behavior, they predict radically different exponents for the modulus or viscosity increase with reaction. This additional information, which will be the topic of a forthcoming paper, is required to understand the physics behind the gelation dynamics.

Thermal Hysteresis. Whereas the equilibrium modulus, G_e, increases with temperature for chemically cross-linked gels, G_e decreases upon increasing temperature for physical gels. This is the direct consequence of the thermal dissociation of the physical cross-links, i.e., semicrystalline aggregates of the sPMMA blocks of MBM and/or semicrystalline stereocomplexes of sPMMA/iPMMA in MBM/iPMMA blends. Thermoreversibility is one characteristic of physical cross-linking, i.e.; thermally dissociated physical cross-links can re-form upon cooling the system. Nevertheless, hysteresis can be observed, since the re-formation of semicrystalline aggregates is a time-dependent process. The thermal hysteresis for gels aged at 10 °C for 12 h was investigated. Figure 8 shows the temperature dependence of G' and G'' at 1 Hz for the B1 and B2 gels (Table 2) heated from 5 to 40 °C (Figure 8A) and then cooled from 40 °C down to ca. 10 °C (Figure 8B). Originally, sample B2 has a higher storage modulus than sample B1, which is in line with a higher cross-linking density as result of stereocomplexation. On heating, the MBM1 gel (B1) persists up to 35 °C, while it re-forms on cooling at a much lower temperature(15 °C) ($G' = G''$). There is thus a large hysteresis for the melting and re-formation of the MBM gel in o-xylene when the temperature is scanned at a rate of 1 °C/min. The addition of small amounts of iPMMA slightly improves the thermal stability, since the MBM1/iPMMA gel (B2) persists up to 38 °C and it re-forms on cooling at 18 °C, so that the hysteresis is not significantly affected. Therefore, although very small amounts of iPMMA significantly accelerate the gelation, it does not contribute very much to the thermal stability of the gel due to a limited cross-linking density by stereocomplexation. In case of sample B4 (Table 2) containing a larger amount of iPMMA, the thermal stability of the gel is further increased up to 45 °C (Figure 9A) and it re-forms at 21 °C (Figure 9B): self-aggregation of sPMMA blocks still dominates the gelation mechanism. Although the storage modulus, G', of sample B5 (Table 2) decreases by ca. one decade from 20 to 50 °C (Figure 9A) as a consequence of the dissociation of the sPMMA blocks, it remains higher than G'' even at 70 °C, which indicates that the gel, thus a three-dimensional chain network, is maintained by stereocomplexation beyond the thermal dissociation of the sPMMA blocks. Above 50 °C, only a very slow

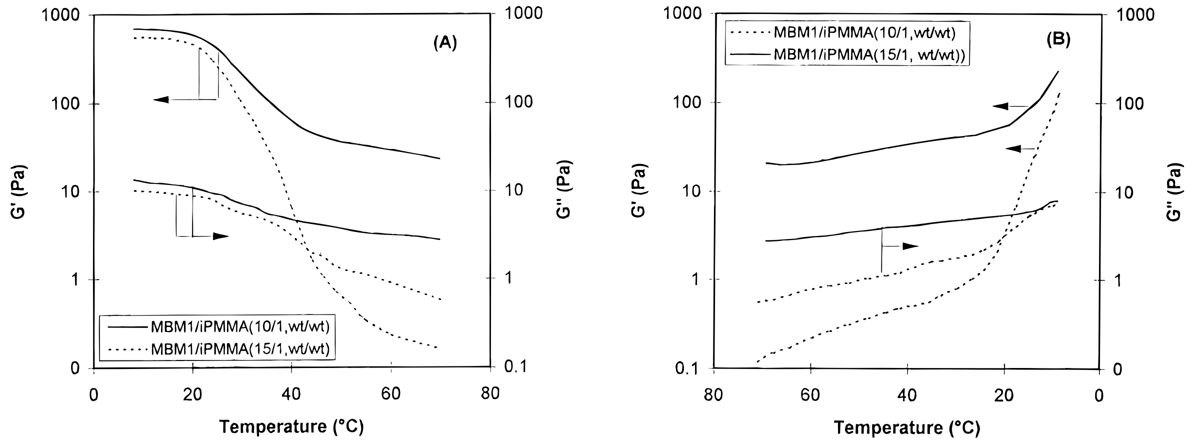

Figure 9. Temperature dependence of shear storage (G') and loss (G'') moduli at 1 Hz for 7 wt % solutions in *o*-xylene of MBM1/iPMMA (15/1 s/i, wt/wt) mixture (- - -) and MBM1/iPMMA (10/1 s/i, wt/wt) mixture (—) upon heating (A) and cooling (B) at a 1 °C/min rate. The samples were aged for 12 h at 10 °C.

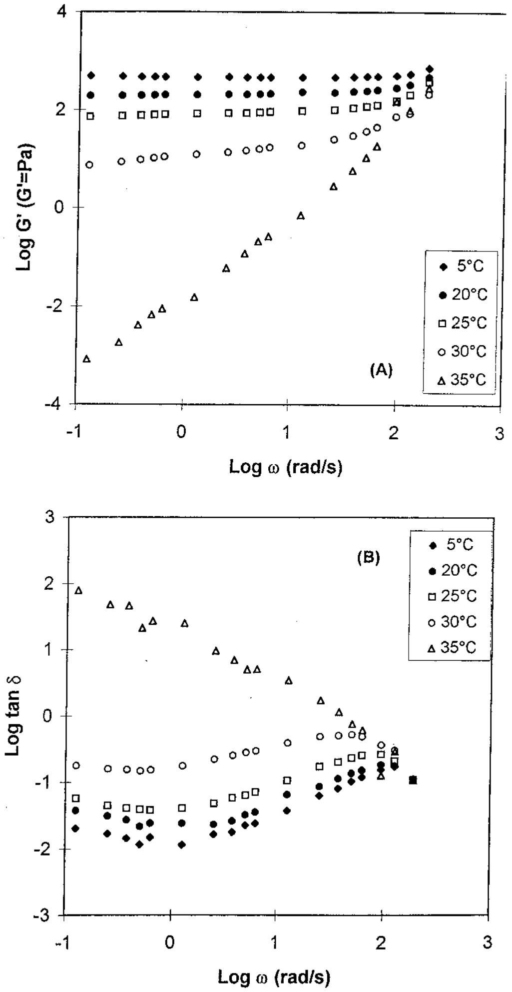

Figure 10. Frequency sweep of shear storage modulus G' (A) and tan δ (B) at various temperatures for the 7 wt % MBM1 solution in *o*-xylene. The sample was aged for 24 h at 10 °C

decrease in G′ is observed in agreement with the thermal stability of the stereocomplexes ($T_m = 113$ °C), as observed by DSC. When the sample B5 is cooled from 70 °C, G′ first increases slowly down to 25 °C and then a sharp increase is observed at lower temperatures as result of the self-aggregation of the sPMMA outer blocks.

Isothermal Frequency Sweep. Figure 10 shows the frequency dependence of G' and tan δ ($=G''/G'$) at different temperatures for the MBM1 gel (B1, Table 2) aged at 10 °C for 24 h. At low temperature (<25 °C), tan δ shows a faint minimum at ca. 1 rad/s (Figure 10B), whereas G' is essentially independent of frequency (Figure 10A), which is a behavior characteristic of an elastic material. At 25 °C, a maximum is clearly observed at an angular frequency of 100 rad/s which is thought to originate from the relaxation of the sPMMA blocks aggregates. The same phenomenon has been reported by Winter et al. for the physical gelation of poly(propylene).[12] The maximum is shifted to a lower frequency at 30 °C in agreement with a loss in stability for these aggregates. At 35 °C, i.e., at the gel melting temperature (DSC), G' rapidly increases with ω ($G' \sim \omega^n$), so that n changes from 0.02 at 25 °C to 1.7 at 35 °C. In parallel, tan δ decreases rapidly upon increasing frequency, and the loss modulus, G'' (not shown here), closely matches the anticipated $G'' \sim \omega$ law for a viscoelastic liquid.

Figure 11 shows the frequency dependence of G' and tan δ at different temperatures for the B4 gel. Although this dependence is essentially similar to B1 at low temperatures (<25 °C), a significant difference is observed at higher temperatures (>30 °C), where the sPMMA aggregates start to melt, as observed by DSC. The slope of the ω dependence of G' ($G' \sim \omega^n$) slowly increases with temperature (Figure 11A), so that n changes from 0.02 at 25 °C to 0.63 at 60 °C, compared to 1.7 in case of B1 at 35 °C. This difference is indicative of a stabilization mechanism still operative at temperatures higher than the melting temperature of the sPMMA aggregates. Clearly, the sPMMA/iPMMA stereocomplexation is efficient in restricting the terminal flow of the soft butadiene segments in *o*-xylene. It is worth recalling that sample B4 contains only a small amount of iPMMA(s/i = 15/1) much smaller than the optimum mixing ratio (s/i = 2/1) for stereocomplexation. The frequency dependence of tan δ is shown in Figure 11B. At low temperatures (<35 °C), after passing a faint minimum at the lowest frequencies, tan δ increases with frequency. In the melting region (40 °C) of the sPMMA blocks aggregates, tan δ increases quasi-linearly with frequency. At high temperatures (>45 °C), tan δ shows a maximum around 10 rad/s which might correspond to the relaxation of the PMMA chains in the stereocomplexes.

When the amount of iPMMA is further increased (B5: s/i = 10/1), with a s/i mixing ratio of 10/1, G' decreases upon increasing temperature as result of partial thermal dissociation of the physical cross-links,

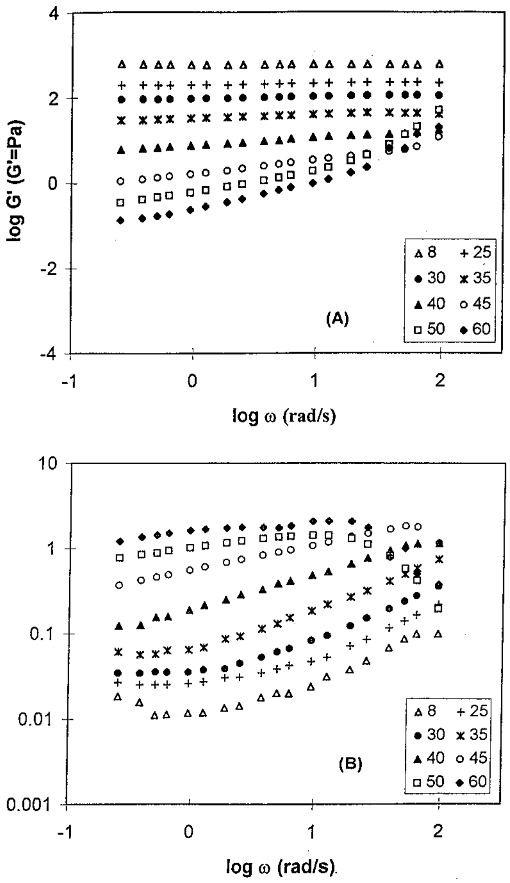

Figure 11. Frequency sweep of shear storage modulus *G'* (A) and tan δ (B) at various temperatures for the 7 wt % MBM1/iPMMA (15/1 s/i, wt/wt) solution in *o*-xylene. The sample was aged for 24 h at 10 °C

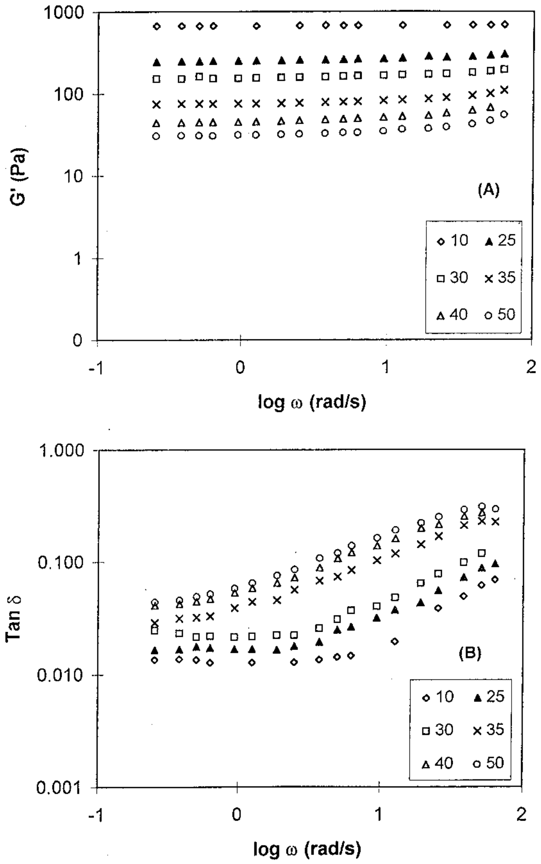

Figure 12. Frequency sweep of shear storage modulus *G'* (A) and tan δ (B) at various temperatures for the 7 wt % MBM1/iPMMA (10/1 s/i, wt/wt) solution in *o*-xylene. The sample was aged for 24 h at 10 °C

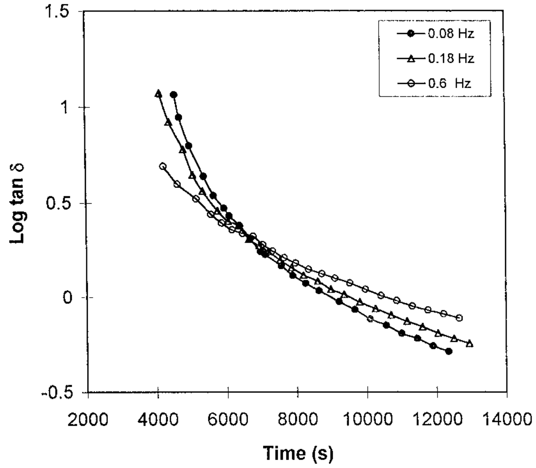

Figure 13. Loss tangent vs time at 24 °C and various frequencies for the 7 wt % solution of MBM1/sPMMA (2/1 s/i, wt/wt) mixture in *o*-xylene.

whereas it is independent of frequency even at 50 °C (Figure 12A), which indicates that no flow occurs beyond the melting temperature of the sPMMA aggregates and that the sample retains its solid consistency. This effect is consistent with a microphase separation between solvated PBD inner blocks of MBM and the sPMMA/iPMMA stereocomplexes which are stable up to 113 °C as shown by DSC analysis. In parallel, tan δ increases with increasing frequency (Figure 12B) at constant temperature up to 50 °C. A sharp difference in tan δ is observed between 30 and 35 °C, in the melting range of the aggregates of the sPMMA outer blocks.

Effect of sPMMA. The effect of the addition of sPMMA homopolymer to MBM on gelation in *o*-xylene has also been studied. Figure 13 shows the time dependence of log tan δ at 24 °C for a 7 wt % solution of MBM1/sPMMA (sample B7, Table 2) in *o*-xylene. A well-defined gelation time is observed at the considered frequencies. While the Δ value is not significantly different compared to the MBM1 gel (B1), the gelation time is higher, 6440 s against 4200 s for B1, which more likely results from the weakening of the three-dimensional chain network by the homo sPMMA chains.

Effect of the PBD Microstructure. In order to know whether the microstructure of the PBD midblock has an effect on gelation in *o*-xylene, two additional MBM samples (MBM2 and MBM3, Table 1) have been synthesized, in which the 1,2-units content of the PBD midblock is smaller and higher than in MBM1, respectively. A MSBSM pentablock copolymer has also been prepared for sake of comparison. Concentration of the copolymer solutions in *o*-xylene was fitted to the copolymer molecular weight, i.e., 12 wt % for MBM2 and 10 wt % for MBM3 (samples B8 and B9, in Table 2). Although the 1,2-units content is lying in a large range from 15 to 68% for the three triblock copolymers, the same scaling exponent ($\Delta = 0.7$) is observed. In case of the MSBSM pentablock copolymer, the scaling exponent is 0.72 (sample B10 in Table 2), i.e., in the 0.65−0.75 range usually observed for gelation of the MBM triblock copolymers in *o*-xylene.

Conclusion

Thermoreversible gelation in o-xylene has been studied for syndiotactic poly(methyl methacrylate) (sPMMA)−

polybutadiene (PBD)−sPMMA triblock copolymers in the presence of isotactic PMMA (iPMMA). Two mechanisms contribute to the gelation process, i.e., self-aggregation of the sPMMA outer blocks of the copolymer and stereocomplexation of these blocks with iPMMA. While the sPMMA aggregates melt at 35 °C, the stereocomplex is thermally more stable with a melting temperature of 113 °C. The relative importance of these two mechanisms depends on the sPMMA/iPMMA (s/i) ratio.

Stereocomplexation of MBM with iPMMA in *o*-xylene is already observed at a very low iPMMA content that corresponds to a 30/1 s/i mixing ratio for 7 wt % polymer solution at 24 °C. For a s/i mixing ratio of 2/1, which is the optimum ratio for stereocomplexation, gelation is instantaneous even for much lower polymer concentration (1 wt %) at 10 °C. A thermal hysteresis is observed when the gel is melted and then re-formed upon cooling at a 1 °C/min rate. Stereocomplexation has no significant effect on this hysteresis loop.

Although stereocomplexation greatly accelerates the gelation process, as assessed by a gelation time which decreases from 4200 s for a MBM gel to 180 s for a MBM/iPMMA gel of the same concentration (s/i mixing ratio = 15/1), the scaling exponent Δ typical of the gel structure at the gel point remains in the range of 0.70−0.75, which is commonly reported for chemical gelation.

In contrast to iPMMA, addition of sPMMA to solutions of MBM triblock copolymer in *o*-xylene delays the gelation process without any effect on the scaling exponent Δ.

This experiment is also independent of the microstructure of the PBD midblock, the 1,2-units content of which has been changed from 15 to 68%. Insertion of a polystyrene block in between the sPMMA and the PBD blocks of MBM, thus resulting in MSBSM pentablock copolymer, does not change the Δ value, so that this scaling exponent is systematically in the range of 0.65−0.75 for the gelation of sPMMA based triblock copolymers of MBM type in *o*-xylene.

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References and Notes

(1) Spevacek, J.; Schneider, B. *Adv. Colloid. Interface Sci.* **1987**, *27*, 81.
(2) Schomaker, F.; Challa, G. *Macromolecules* **1988**, *21*, 3506.
(3) de Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(4) Flory, P. J. *J. Am. Chem. Soc.* **1941**, *63*, 3083.
(5) Stauffer, D.; Coniglio, A.; Adam, M. *Adv. Polym. Sci.* **1982**, *44*, 103.
(6) Stauffer, D. *Introduction to Percolation Theory*; Taylor & Francis: London, 1985.
(7) Hess, W.; Vilgis, T. A.; Winter, H. H. *Macromolecules* **1988**, *21*, 2356.
(8) Martin, J. E.; Adolf, D.; Wilcox, J. P. *Phys. Rev. A* **1989**, *39*, 1325.
(9) Rubinstein, M.; Colby, R. H.; Gillmor, J. R. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1989**, *30* (1), 81.
(10) Chambon, F.; Winter, H. H. *J. Rheol.* **1987**, *31*, 683.
(11) Winter, H.; Chambon, F. *J. Rheol.* **1986**, *30*, 367.
(12) Lin, Y. G.; Mallin, D. T.; Chien, J. C. W.; Winter, H. H. *Macromolecules* **1991**, *24*, 850.
(13) Cuvelier, G.; Launay, B. *Macromol. Chem., Macromol. Symp.* **1990**, *40*, 23.
(14) Te Nijenhuis, F.; Winter, H. H. *Macromolecules* **1989**, *22*, 411.
(15) Yu, J. M.; Teyssié, Ph.; Jérome, R. *Polymer*, in press.
(16) Yu, J. M.; Dubois, Ph.; Teyssié, Ph.; Jérôme, R.; Blacher, S.; Brouers, F.; L'Homme, G. *Macromolecules* **1996**, *29*, 5384.
(17) Yu, J. M.; Yu, Y.; Dubois, Ph.; Teyssié, Ph.; Jérôme, R. *Polymer*, in press.
(18) Yu, J. M.; Dubois, Ph.; Teyssié, Ph.; Jérome, R. *Macromolecules* **1996**, *29*, 6090.
(19) Hatada, K.; Ute, K.; Tanaka, K.; Kitayama, T.; Okamoto, Y. *Polym. J.* **1985**, *17*(8), 977.
(20) Berghmans, H.; Donkas, A.; Frenay, L.; Stoks, W.; De Schryver, F. E.; Moldenaers, P.; Mewis, J. *Polymer* **1987**, *28*, 97.
(21) Tung, C. Y. M.; Dynes, P. J. *J. Appl. Polym. Sci.* **1982**, *27*, 569.
(22) Djabourov, M.; Leblond, J.; Papon, P. *J. Phys. Fr.* **1988**, *49*, 333.
(23) Izuka, A.; Winter, H. H.; Hashimoto, T. *Macromolecules* **1992**, *25*, 2422.
(24) Adolf, D.; Martin, J. E.; Wilcoxon, J. P. *Macromolecules* **1990**, *23*, 527.
(25) Durand, D.; Delsanti, M.; Adam, M.; Luck, J. M. *Europhys. Lett.* **1987**, *3*, 297.
(26) Richtering, H. W.; Gagnon, K. D.; Lenz, R. W.; Fuller, R. C.; Winter, H. H. *Macromolecules* **1992**, *25*, 2429.
(27) Prochazka, F.; Nicolai, T.; Durand, D. *Macromolecules* **1996**, *29*, 2260
(28) Adam, M.; Lairez, D. In *The Physical Properties of Polymeric Gels*; Cohen Addad, J. P. Ed.; John Wiley & Sons Ltd.: New York, 1996; p 87.

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