Triblock Copolymer Based Thermoreversible Gels. 4. Effect of the Midblock and Characterization of the Sol−Gel Transition

J. M. Yu,[†] S. Blacher,[‡] F. Brouers,[‡] G. L'Homme,[‡] and R. Jérôme*,[†]

Center for Education and Research on Macromolecules and Génie Chimique et Physique des Matériaux, University of Liège, B6 Sart-Tilman, 4000 Liège, Belgium

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ABSTRACT: Thermoreversible gelation has been studied in *o*-xylene for poly(methyl methacrylate) containing 80% syndiotactic triads (*s*PMMA) and block copolymers of the MXM type, where M is *s*PMMA and X is either polybutadiene (PBD), hydrogenated PBD (PEB), poly(styrene-*b*-butadiene-*b*-styrene) (SBS) triblock, or the hydrogenated version of this triblock (SEBS). In *o*-xylene, which is a selective solvent for the central X block, *s*PMMA forms thermoreversible gels provided that the molecular weight is high enough. When *s*PMMA is the outer block of MXM triblock copolymers, the midblock X appears to favor the gelation and it considerably improves the thermal stability of the matured gels. This thermal stability is, however, largely independent of the actual nature of the midblock. The dynamic properties of solutions and gels have been analyzed and discussed on the basis of scaling assumptions. At the gel point, where the loss angle tan $\delta_c = G''/G'$ is independent of the probing frequency, the sample obeys the typical power law $G'(\omega) \sim G''(\omega) \sim \omega^{\Delta}$. The scaling exponent Δ is found in the 0.65−0.75 range for both *s*PMMA and MXM block copolymers, independent of the nature of the midblock. Modulus−frequency master curves have been built by using appropriate reaction time dependent renormalization factors for the individual frequency and modulus data. The scaling of these factors with reaction time has allowed us to calculate the static scaling exponents for the increase observed in both modulus and viscosity. The accordingly calculated values agree with the scalar elasticity percolation model.

Introduction

Syndiotactic poly(methyl methacrylate) (*s*PMMA) is known for self-aggregation in suitable solvents, such as *o*-dichlorobenzene, butyl acetate, and *o*-xylene,[1] which manifests itself as a liquid to solid transition provided that the chain cross-linking exceeds a critical value.[2] As a rule, gelation may be physical or chemical, 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., that of the cross-linker. The thermoreversibility of the *s*PMMA gels is a clear indication of physical cross-linking.

Recently, increasing attention has been paid to the mechanism that sustains the sol−gel transition.[3−16] Chemical gelation has indeed been extensively investigated and particularly the viscoelastic behavior of near-critical gels.[3−8] Analysis of the dynamics near the critical gelation point has led to predictions for the frequency dependence of the shear storage modulus ($G'(\omega)$) and the shear loss modulus ($G''(\omega)$), where ω is the angular frequency. At the gel point, these moduli are predicted and observed to scale with frequency (*f*) according to eq 1,[3−7] where $\omega = 2\pi f$ and Δ is the scaling exponent.

$$G'(\omega) \sim G''(\omega) \sim \omega^{\Delta} \qquad (1)$$

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 a universal value at least at low frequencies (eq 2)[6,7]

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

In contrast to chemical gelation, only a few studies have focused on physical gelation.[9−14] The transient nature of the physical network junctions makes it difficult to study these systems near the gel point. Very recently, we have reported on physical gels formed by *s*PMMA−PBD−*s*PMMA, or MBM, copolymers in *o*-xylene, which is a selective solvent of the central block. The intermolecular association of the *s*PMMA outer blocks is at the origin of this phenomenon.[12,13] At the gel point, where the loss angle, tan δ_c, is independent of frequency, these samples fit the power law expressed by eq 1, with the scaling exponent Δ in the 0.65−0.75 range, whatever the PBD and *s*PMMA molecular weight, the copolymer concentration (2−7 wt %) and the temperature (8−24 °C).[13] The effect of the addition of isotactic PMMA (*i*PMMA) to MBM solutions in *o*-xylene has also been studied.[14] In this system, two mechanisms contribute to gelation: self-aggregation of *s*PMMA and stereocomplexation of *s*PMMA/*i*PMMA, which greatly accelerates the gelation process and increases the thermal stability of the gels, while keeping the range of the scaling exponent Δ unchanged.

In this paper, the midblock X of triblock copolymers of the MXM type has been changed, in order to know whether the gelation in *o*-xylene is perturbed and the Δ value as well. The dynamic scaling theory of viscoelasticity for near-critical gels[4,15,16] provides a method to determine accurately the dynamic scaling exponent Δ. Indeed, scaling arguments allow us to show that the viscoelastic functions, G' and G'', at different stages of the network formation, can be superimposed into a master curve, provided that frequency and complex modulus are renormalized by appropriate reaction time (t_r) dependent factors. The theory shows that the renormalization factors for the frequency and the complex modulus are the longest relaxation time (τ_z) and the steady-state creep compliance (J_e^0),[17] respectively,

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[†] Center for Education and Research on Macromolecules.

[‡] Génie Chimique et Physique des Matériaux.

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Table 1. Characteristics of the MXM Block Copolymers (M Being Syndiotactic PMMA)

samples	midblock[a] (X)	$10^{-3}M_n$[b] (MXM)	M_w/M_n	syndio (%)[c] in PMMA	1,2-units (%)[c] in PBD
M1		30	1.15	80	
M2		78	1.10	80	
MBM1	B	25-80-25	1.10	80	41
MEBM1	EB	25-80-25	1.10	80	
MBM2	B	13-61-13	1.10	77	68
MSBSM	SBS	19-18-79-18-19	1.10	79	44
MSEBSM	SEBS	19-18-79-18-19	1.15	79	

[a] B = polybutadiene, EB = hydrogenated polybutadiene, SBS = poly(styrene-*b*-butadiene-*b*-styrene), SEBS = hydrogenated SBS, I = isoprene. [b] Measured by SEC and ^{1}H NMR. [c] Content of syndiotactic triads measured by ^{1}H NMR.

which at the gel point scale with $\epsilon = (|t_r - t_g|)/t_g$, according to eqs 3 and 4.

$$\tau_z \sim \epsilon^{s-t} \qquad (3)$$

$$J_e^{\,0} \sim \epsilon^{-t} \qquad (4)$$

In these expressions, t_g is the reaction time at the gel point and s and t are the static scaling exponents that describe the divergence of the static viscosity, $\eta_0 \sim \epsilon^{-s}$, at $t_r < t_g$ and the static elastic modulus $G_0 \sim \epsilon^{-t}$ at $t_g < t_r$. The gelation mechanism has been discussed on the basis of several models based on the percolation theory (for review, see ref 18) that provide power laws for the divergence of the static viscosity and the elastic moduli. Characteristic values for the s, t, and Δ exponents are predicted by each of these models.

The thermal stability of the matured gels formed by the MXM copolymers has also been studied. Rheological measurements have proved to be a sensitive tool for detecting the order−disorder transition as a discontinuity in the low-frequency rheological properties.[19−22] This approach will be used in this study and superposition of the reduced dynamic mechanical data and frequencies will be investigated, particularly at the gel-sol transition, in relation to the midblock X.

Experimental Section

The MXM block copolymers were prepared by sequential anionic polymerization of butadiene, styrene and methyl methacrylate with the diadduct of *t*BuLi onto *m*-diisopropenylbenzene (*m*-DIB) as a difunctional initiator. Details on the synthesis and subsequent hydrogenation of the polybutadiene blocks were reported elsewhere.[23] Chemical composition, molecular weight, and chain microstructure of the MXM copolymers are listed in Table 1. Tacticity of the *s*PMMA block was quite comparable for all the samples, in contrast to the PBD microstructure, which was in the range from 41 to 68% 1,2-units. All these triblock copolymers were of a very narrow molecular weight distribution.

*s*PMMA was prepared by anionic polymerization of MMA initiated by the reaction product of *s*-BuLi with 1 equiv of 1,1-diphenylethylene (DPE) in THF at −78 °C.[24] The molecular characteristics of *s*PMMA are also reported in Table 1. The molecular weight of M1 is rather close to the outer *s*PMMA block in the MBM copolymers and the tacticity is the same (80% syndiotactic triads).

Homogeneous solutions of *s*PMMA and block copolymers in *o*-xylene were prepared at 80 °C, which is higher than the melting temperature (<40 °C) of *s*PMMA aggregates,[12] in view of dynamic mechanical measurements with a Bohlin CS apparatus equipped with coaxial cylinders (d = 25 mm). The polymer solution, preheated at 80 °C, was rapidly added between the coaxial cylinders thermostated at the requested temperature. Solutions were cooled from 80 °C to the desired temperature within ca. 1 min (as measured with a thermocouple), and the measurements were then immediately started.

Table 2. Gelation time (t_g) and Scaling Exponents for Solutions of *s*PMMA and MXM Triblocks in *o*-Xylene

sample	polymer	wt %	T (°C)	t_g (s)[a]	Δ[b]	t[c]	s[c]
G1	M1	30	8				
G2	M2	17	8	1180	0.67		
G3	MBM1	7	17	350	0.67		
G4	MEBM1	7	17	800	0.70		
G5	MSBSM	7	15	2000	0.72	1.84	0.67
G6	MSEBSM	7	15	28000	0.75	2.05	0.69
G7	MBM1	7	22	2300	0.70	1.84	0.67
G8	MBM1	7	24	4200	0.72	1.95	0.69
G9	MBM2	10	10	3660	0.72	1.96	0.67

[a] Time required for tan δ to be independent of frequency. [b] Scaling exponent defined by eqs 1 and 2. [c] t and s are the static scaling exponents that describe the divergence of the static elastic modulus and the static viscosity, respectively, in the gelation process.

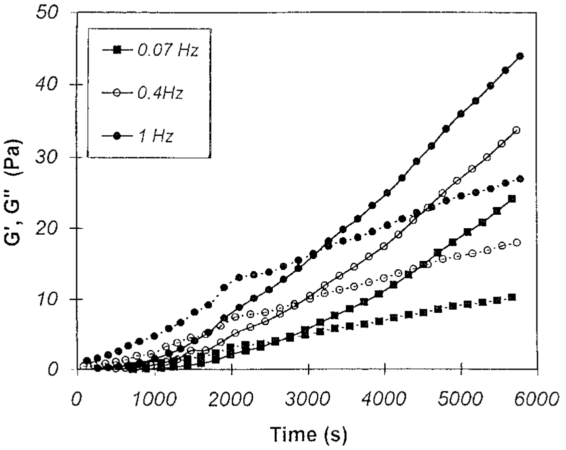

Figure 1. Time dependence of the shear storage (G') and loss (G'') moduli at 8 °C and various frequencies for the 17 wt % solution of sPMMA (sample M2 in Table 1) in *o*-xylene.

Results and Discussion

Gelation and Scaling Law. *s*PMMA Homopolymer. In the first paper of this series,[12] the IR spectra of 10 wt % solutions in *o*-xylene of *s*PMMA (M1, Table 1) and an MBM triblock copolymer (MBM1, Table 1) were compared. It was reported that the regular all-trans conformation did not dominate in the case of *s*PMMA, whereas the all-trans conformation was considerably more important when *s*PMMA was part of a triblock copolymer. As a consequence, the gelation of the MBM1 solution occurred rapidly at room temperature, whereas the *s*PMMA solution formed no gel, even at 0 °C for 1 week. Note that this 10 wt % *s*PMMA solution was optically transparent. In order to know whether *s*PMMA is able to form a gel in *o*-xylene, the solution concentration has been increased to 30 wt %, at which the solution is slightly opaque. This solution has been aged at 0 °C for 24 h, and the storage (G') and loss (G'') moduli have then been measured at 8 °C (G1, Table 2) as a function of frequency. The frequency dependence of G' and G'' fits the $G' \sim \omega^2$ and $G'' \sim \omega$ relationships in the frequency range of 0.06−30 Hz, which are characteristic of a viscoelastic liquid. Thus, gelation does not occur under these conditions.

In a second approach, a sample of 80% syndiotactic triads containing *s*PMMA of a much higher molecular weight (M2, Table 1) has been studied. Figure 1 shows how G' (full curve) and the G'' (dotted curve) depend on time at three frequencies: 0.07, 0.4, and 1 Hz for a

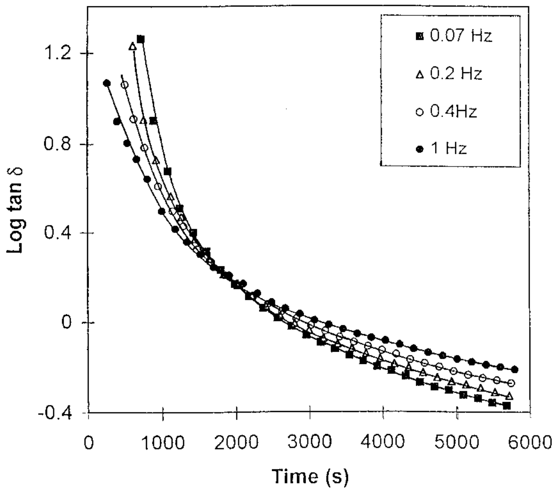

Figure 2. Loss tangent vs time at 8 °C and various frequencies for the 17 wt % solution of sPMMA (sample M2 in Table 1) in *o*-xylene.

17 wt % solution (G2, 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 a result of the progress of the *s*PMMA 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.[7] Figure 1 shows that the crossing time is frequency-dependent. Actually, it increases from 2600 s at 0.07 Hz to 3100 s at 1Hz, while the apparent modulus changes from 4.2 to 16.0 Pa.

It is known that the dynamic mechanical behavior of polymer solutions at the gel point fits a power law for the frequency dependence of the moduli (eqs 1 and 2). In previous papers,[12−14] we reported that the typical power law $G'(\omega) \sim G''(\omega) \sim \omega^{\Delta}$ was observed for MBM triblock copolymers dissolved in *o*-xylene, and that the relaxation exponent Δ was in the 0.65−0.75 range, independent of the copolymer composition and molecular weight and the curing temperature. In order to ascertain that this behavior persists in the case of *s*PMMA, i.e., in the absence of the midblock, tan δ has been plotted against the curing time. Figure 2 shows that the log(tan δ) vs time dependences at different frequencies (from 0.07 to 1 Hz) intersect at the same time, which is the gel time (t_g), as stated in the Introduction. For times shorter than t_g, tan δ decreases as the frequency is increased, which is typical of 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 homo *s*PMMA in *o*-xylene. The relaxation exponent Δ at the gel point can be extracted from eq 2 where δ_c is δ at the intersection of all the tan δ vs time curves. The value of Δ (0.67, Table 2) is found in the same range as for MBM triblock copolymers.

Block Copolymers Containing Different Midblocks. In order to check whether the Δ value found for MXM triblock copolymer gels is dependent on the chemical nature of the midblock, additional experiments have been carried out for a series of block copolymers of the MXM type, where X is hydrogenated polybutadiene (PEB), poly(styrene-*b*-butadiene-*b*-styrene) (SBS), and hydrogenated poly(styrene-*b*-butadiene-*b*-styrene) (SEBS), respectively (Table 1). Solutions in *o*-xylene of all these copolymers have been observed to gel at suitable concentrations and temperatures, and the gelation process fits the scaling law at the gel point. The experimental gelation time, t_g, and the calculated scaling exponent, Δ, are reported in Table 2.

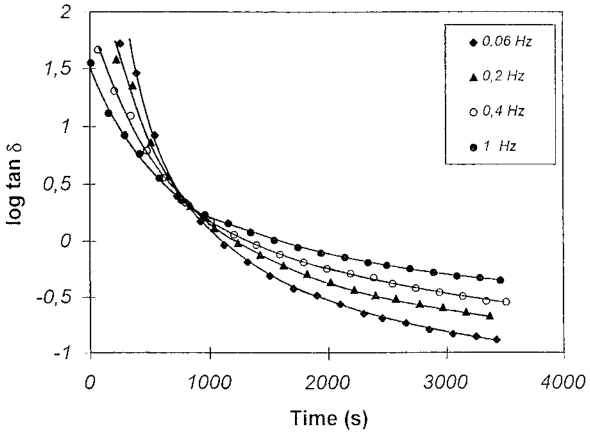

Figure 3. Loss tangent vs time at various frequencies for the G4 sample (Table 2).

A typical example for the tan δ vs time curves at different frequencies is shown in Figure 3 for the gel sample G4 (Table 2). In spite of differences in the nature of the midblock, the copolymer molecular weight, and the experimental conditions, the value of Δ is quite similar for all gel samples in Table 2. In contrast, the gelation time is quite different, which proves it to be dependent on the polymer concentration, molecular weight, and curing temperature.

Comparison of the G3/G4 and G5/G6 copolymer pairs shows that the gelation time of a hydrogenated block copolymer is much longer compared to the original copolymer under the same experimental conditions. Indeed, the gelation time for the hydrogenated sample G4 is more than 2 times higher than the parent triblock copolymer G3, whereas a 10-fold increase is observed as a result of hydrogenation of the pentablock copolymer G5. Nevertheless, the scaling exponent Δ for all these samples remains in the 0.65−0.75 range, as was previously observed for the MBM triblock copolymers in *o*-xylene. So, the scaling exponent Δ for MXM triblock copolymer gels appears to be essentially independent of the chemical nature of the midblock.

Characterization of the Sol-Gel Transition. Scaling predictions for static and dynamic moduli are quite general and assign different sets of scaling exponents to different gelation mechanisms. Two main percolation models have been proposed to describe the dynamics of polymers near the gel point.[18] One is the percolation model of the elastic network, which was first proposed by de Gennes and is often referred to as the electrical analogy. The second model is based on the Rouse approximation, which assumes the absence of any hydrodynamic interaction between the polymers. Static exponents have been accurately calculated by numerical methods for the two models: $t = 1.94$, $s = 0.75$, and $\Delta = 0.72$ for the electrical analogy and $t = 2.67$, $s = 1.33$, and $\Delta = 0.72$ for the Rouse model.

The experimental determination of the exponents s and t from the divergence of the static viscosity η_0 and the static elastic modulus G_0 near the gel point is not very accurate because the measurements are carried out at low but not at zero shear rates. Furthermore, in the

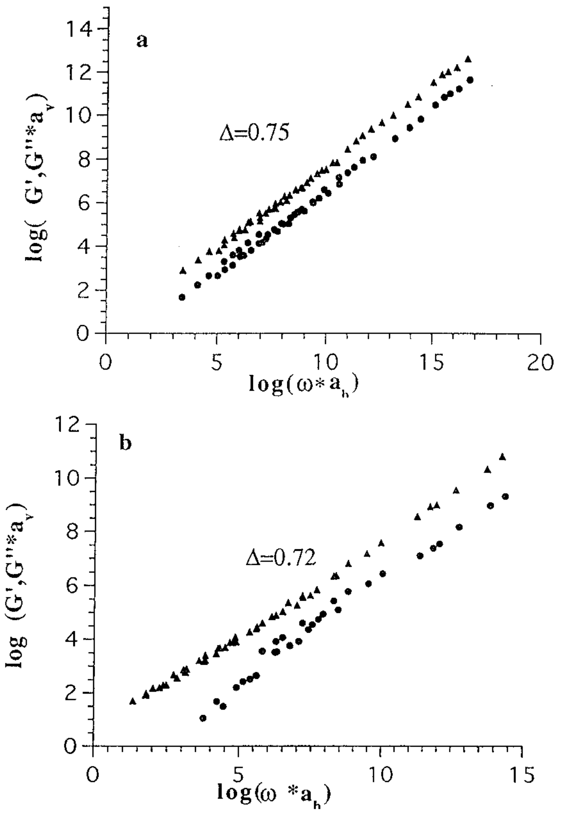

Figure 4. Plots of log G' (●) and log G'' (▲) versus log(reduced frequency) constructed from data available near the gel threshold for the G6 (a) and G8 (b) samples (Table 2).

case of physical gelation, the noncovalent nature of the cross-links prevents the gelation reaction from being stopped in order to characterize the static properties at various gelation times. Static exponents can also be determined from eqs 3 and 4. In this case, τ_z and J_e^0 can be determined experimentally[25] or numerically by building up a unique master curve as a result of the vertical and horizontal shifts of the individual frequency-dependent data.[26] This second approach has been used in this work. Figure 4 shows the collapsed curves for the copolymer G6 (Table 2) at $t_g = 28\,000$ s and for the copolymer G8 (Table 2) at $t_g = 4200$ s, where the empirical horizontal and vertical shift factors are abbreviated as a_h and a_v, respectively. Figure 4 shows that the renormalized G' and G'' moduli scale with the renormalized frequencies when Δ is ca. 0.70, in good agreement with the value obtained from eq 2. This value for the exponent Δ is consistent with the theoretical predictions by both the electrical and the Rouse models.

The renormalized horizontal and vertical factors used to build up the master curve follow the longest relaxation time τ_z and the steady-state creep compliance J_e^0, respectively.[4,15,16] Therefore, the scaling relationships expressed by eqs 3 and 4 can be used to calculate the static exponents s and t. Figure 5 shows the log–log plot of a_h and a_v versus log ϵ, in case of sample G8, for which $t = 1.95$ and $s = 0.69$. The values of s, t, and Δ are listed in Table 2 not for all the samples, but only when enough experimental data were available in the sol–gel transition so as to construct accurately the master curves.

Comparison of the critical exponents reported in Table 2 and in previous papers for MXM triblocks shows a good agreement with the predictions by the electrical analogy model. The observations of static and dynamic exponents quite comparable for all the samples suggest that a unique gelation mechanism is operative, i.e., that the midblok of the MXM triblock does not interfere in the percolation process. According to the electrical analogy, near the percolation threshold, gels formed by the triblock copolymers would consist of *s*PMMA outer blocks, randomly connected and weakly entangled, with an elasticity of a scalar nature. This indicates that chains between cross-links are very flexible and provide no mechanical contribution to the elasticity. This picture is in agreement with the gelation mechanism for the MBM triblock that was emerging from the infrared analysis.[2,12] In this case, gelation is a two-step mechanism in which an intramolecular change from a coil to a helix conformation of the *s*PMMA outer blocks is followed by an intermolecular association. In this process, the flexible PBD midblock does not hinder the gel formation. Then, the helix junction zones play the

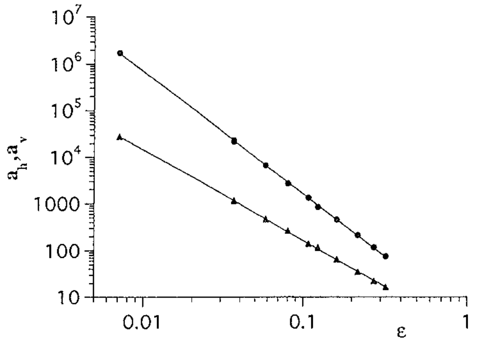

Figure 5. Log–log scaling plot of the horizontal shift a_h (●) and vertical shift a_v (▲) in Figure 4 versus the reduced extent of reaction, ϵ, in the region near the gel point for the G8 sample.

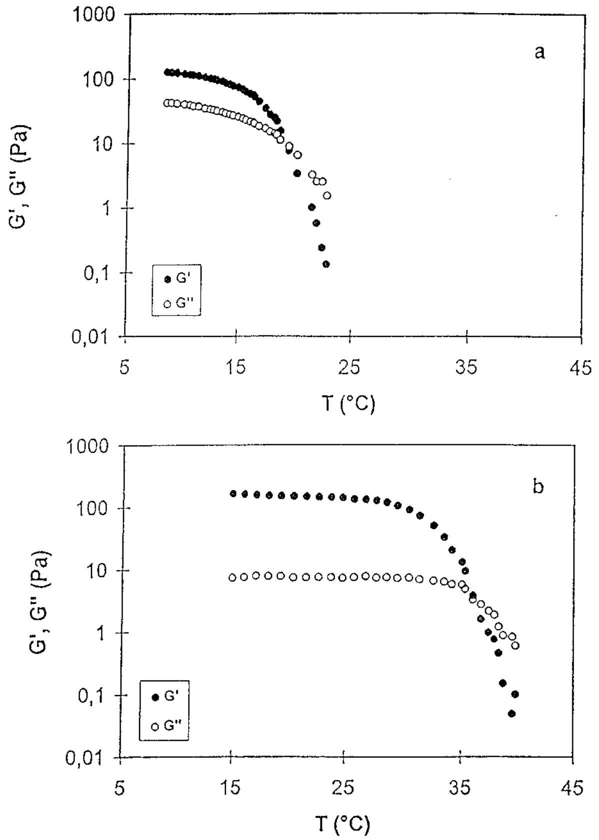

Figure 6. Temperature dependence of the shear storage (G') and loss (G'') moduli (1 Hz) for the 17 wt % M2 solution in *o*-xylene (a) (Table 2) and the 7 wt % MBM1 in *o*-xylene (b) (Table 2). Heating rate = 1 °C/min.

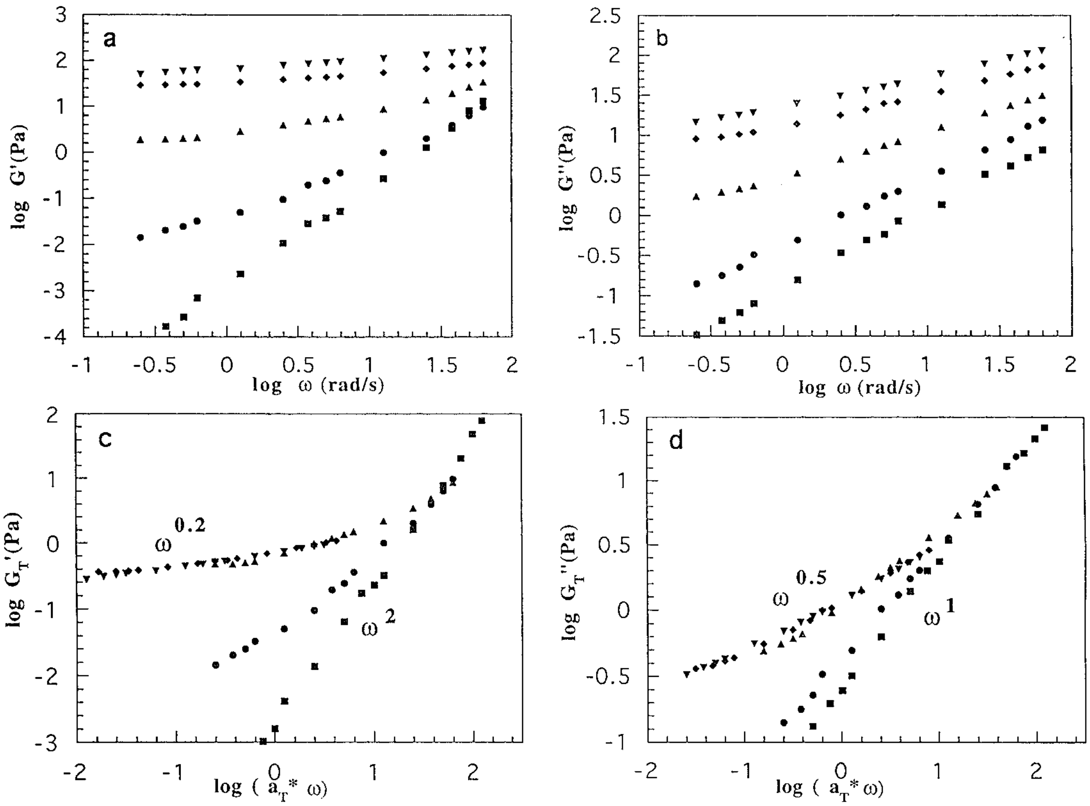

Figure 7. Frequency sweep of the shear storage G' (a) and loss G'' (b) moduli at various temperatures for the 17 wt % M2 solution in *o*-xylene (G2, Table 2) and the isotherm superposition (c, d): (▼) 8 °C; (◆) 12 °C; (▲) 16 °C; (●) 20 °C; (■) 24 °C.

role of the cross-linking points in the traditional picture of the percolation model applied to the sol–gel transition. Moreover, the scalar nature of the elasticity observed near the percolation threshold relies upon the low polymer concentration used in this study, so that a dense cross-linking is not favored. It is worth noting that similar conclusions have been drawn for physical gels based on Pectin biopolymers (s = 0.82, t = 1.93, Δ = 0.70),[27] for semidilute solutions of polydiacetylene in the red phase (s = 1.0, t = 1.9),[28] and for semidilute solutions of polyacrylamide cross-linked by Cr(III) complexation (s = 0.9, t = 1.9).[29]

Analysis of the Gel–Sol Transition. In contrast to chemical cross-linking for which the equilibrium modulus (G_e) increases with temperature, G_e of physical gels decreases upon increasing temperature. This behavior is the straightforward consequence of the thermal dissociation of the physical cross-links formed as result of the *s*PMMA aggregation. The thermal stability of the gels depends on the aggregates stability, in a possible dependence on the presence of a soft midblock. Figure 6 compares the thermal dependence of the storage (G') and loss (G'') moduli, particularly when the gel is heated throughout the melting range of the *s*PMMA aggregates in the case of the homopolymer (sample G2, Table 2) (Figure 6a) and triblock MBM copolymer (sample G3, Table 2) (Figure 6b). The *s*PMMA gel persists up to 18 °C (with $G' > G''$), in contrast to the MBM gel, which is stable up to a much higher temperature (35 °C), indicating an improved thermal stability for the triblock copolymer.

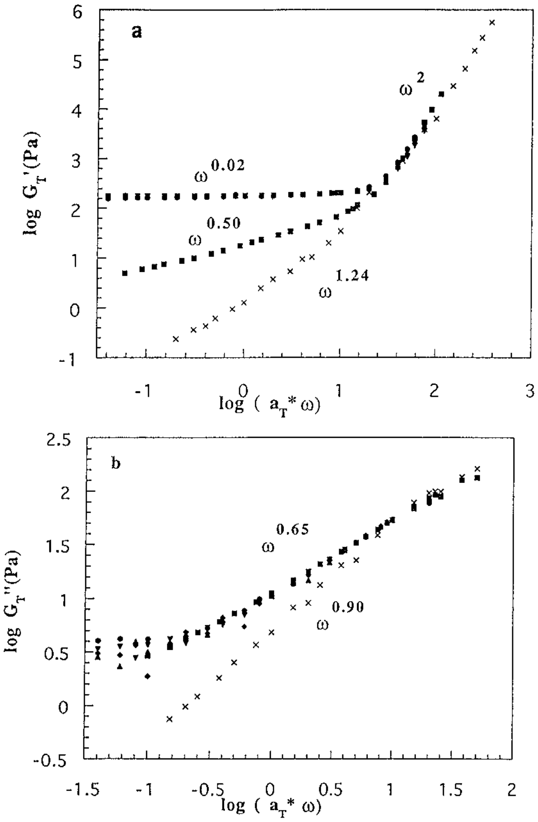

Figure 8. Superposition of isothermal frequency sweeps of the shear storage G' (a) and loss G'' (b) moduli for the 7 wt % MEBM1 solution in *o*-xylene (G4, Table 2): (▼) 5 °C; (◆) 11 °C; (▲) 15 °C; (●) 20 °C; (■) 30 °C; (×) 35 °C.

Parts a and b of Figure 7 show the isothermal frequency sweep of G' and G'' in the 8–25 °C range for the same *s*PMMA gel (G2, Table 2). Parts c and d of Figure 7 show the reduced frequency plots constructed from Figure 7a,b according to the time–temperature superposition principle[17] at a reference temperature T_0 of 20 °C. The original data were shifted both vertically and horizontally so as to reach the best fit of the data recorded at different temperatures. A lack of super-

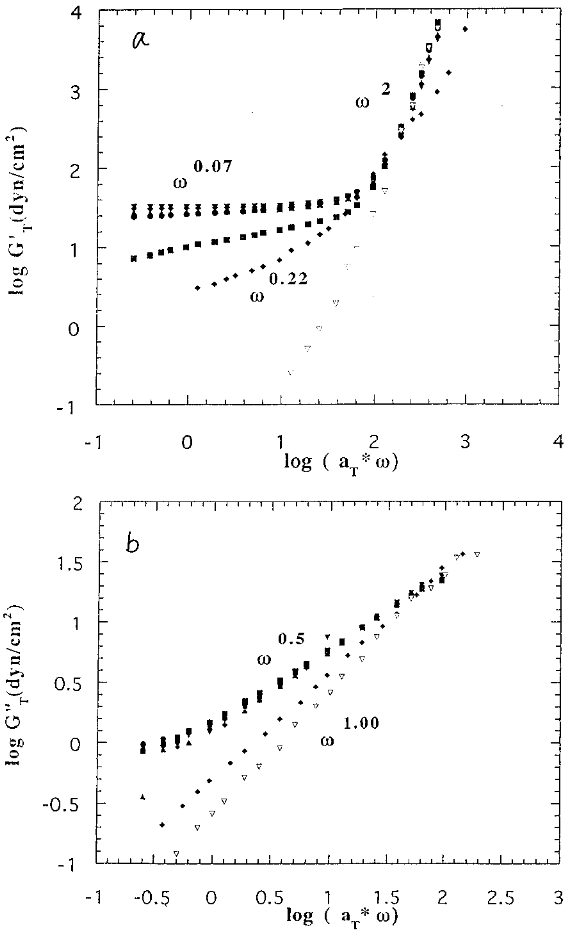

Figure 9. Superposition of isothermal frequency sweeps of the shear storage G' (a) and loss G'' (b) moduli for the 7 wt % MEBM1 solution in *o*-xylene (G5, Table 2): (▼) 5 °C; (◆) 11 °C; (▲) 15 °C; (●) 20 °C; (■) 25 °C; (◆) 30 °C; (▽) 35 °C.

posability is observed at $T > 20$ °C for reduced frequencies ($a_T{}^*\omega$) smaller than $10^{1.6}$ rad/s. At $T < 20$ °C, $G' \sim \omega^{0.2}$ and $G'' \sim \omega^{0.5}$ consistently with a near solid-like state and a high concentration of cross-links. At $T = 24$ °C, $G' \sim \omega^2$ and $G'' \sim \omega^1$, which is the characteristic frequency dependence of moduli for a viscoelastic liquid. At this temperature, the gel has completely melted. At $T = 20$ °C, an intermediate situation is observed with $G' \sim \omega^{0.54}$ and $G'' \sim \omega^{0.8}$. It thus appears that the transition from the gel to the liquid-like behavior is not sharp at all, but rather occurs over a finite temperature range (i.e., 16 °C $< T <$ 24 °C), where concentration fluctuations take place as result of the partial dissociation of the physical cross-links.

Since the MBM triblock copolymer gel has a higher thermal stability than the *s*PMMA gel, the question may be addressed whether the chemical nature of the midblock has some effect on the thermal stability of the gels. Figures 8 and 9 show reduced frequency plots at the reference temperature of 30 °C constructed from isotherms in the 5−35 °C range for gels of block copolymers containing different midblocks (samples MEBM1 and MSBSM, Table 1). The midblock of the sample MEBM1 is a hydrogenated PBD block, whereas a SBS triblock copolymer is the midblock of the MSBSM sample. In the two cases, the reduced frequency dependence of G' and G'' is quite comparable. As shown in Figures 8 and 9, the isotherm superposition works well at $T < 20$ °C. At higher temperatures, the superposition works only in the reduced frequency range higher than $a_T{}^*\omega \sim 20$ rad/s for the MEBM1 gel and than $a_T{}^*\omega \sim 100$ rad/s for the MSBSM gel. At $T < 20$ °C in low frequencies, G' is essentially independent of frequency, whereas $G'' \sim \omega^{0.65}$ and $G'' \sim \omega^{0.50}$ for MEBM1(Figure 8) and MSBSM (Figure 9) gels, respectively. At $T \geq 30$ °C for MEBM1 and $T \geq 25$ °C for MSBSM gels, an abrupt drop of G' is observed as a consequence of the increased mobility of the physical cross-linkers with temperature. At 35 °C, the MSBSM gel becomes a liquid (Figure 9) with $G' \sim \omega^{2.0}$ and $G'' \sim \omega^{1.0}$, whereas some elasticity still persists in the MEBM1 gel, since $G' \sim \omega^{1.24}$ and $G'' \sim \omega^{0.9}$. At higher reduced frequency, the viscosity response of a typical liquid-like system is observed at all investigated temperatures. In parallel, G'' changes quite moderately with temperature, since the frequency dependence of G'' varies from $G'' \sim \omega^{0.65}$ at 5 °C to $G'' \sim \omega^{0.90}$ at 35 °C for the MEBM1 gel (Figure 8b), and from $G'' \sim \omega^{0.50}$ to $G'' \sim \omega^{1.0}$ for the MSBSM gel (Figure 9b). It appears that the thermal stability of triblock copolymer gels is not deeply affected by the nature of the midblock, the MEBM1 gel being, however, somewhat more stable than the MSBSM gel.

Conclusion

This paper has shown that PMMA containing 80% syndiotactic triads forms thermoreversible gels in *o*-xylene provided that the molecular weight is high enough ($M_n = 78\,000$). At the gel point, where the loss angle ($\tan \delta = G''/G'$) is independent of the probing frequency, the sample obeys a typical power law $G' \sim G'' \sim \omega^{\Delta}$, with a dynamic scaling exponent $\Delta = 0.70$, as previously observed for MBM triblock copolymers where *s*PMMA is the outer block and polybutadiene the midblock.

The gelation of block copolymers of the MXM type in *o*-xylene has also been studied in relation to the X midblock, i.e., polybutadiene (PBD), hydrogenated PBD (*h*PBD), poly(styrene-*b*-butadiene-*b*-styrene) (SBS), and hydrogenated poly(styrene-*b*-butadiene-*b*-styrene) (SEBS), respectively. The scaling law previously observed for gels of the MBM triblock copolymer is not perturbed when different rubbery polymers are substituted for PBD, since the dynamic scaling exponent remains in the 0.65−0.75 range. In contrast, the gelation time changes with the midblock; e.g., it is increased as result of hydrogenation of the PBD midblock.

Modulus−frequency master curves have been constructed by applying appropriate time-dependent renormalization factors to the frequency and modulus individual data. From the scaling of these factors with reaction time, the static scaling exponents t and s have been calculated and observed to be independent of the chemical nature of the midblock, suggesting a unique gelation mechanism. For all the samples, $1.84 < t < 2.01$ and $0.65 < s < 0.70$ have been observed in good agreement with the scalar elasticity percolation model.

The thermal stability of the gels has also been studied. The *s*PMMA gel that melts at ca. 20 °C is less thermostable than the gels formed by the MBM triblock copolymers, all the other conditions being the same (melting at ca. 30 °C). The thermal stability of the MXM gels is only slightly dependent on the chemical nature of the midblock.

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