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Triblock Copolymer Based Thermoreversible Gels. 2. Analysis of the Sol−Gel Transition

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ABSTRACT: Syndiotactic poly(methyl methacrylate) (sPMMA)−polybutadiene (PBD)−sPMMA triblock copolymers of various chemical compositions and different molecular weights have been studied in the presence of *o*-xylene, which is a selective solvent for the central PBD block. Thermoreversible gels can be formed in a suitable curing temperature range (<35 °C) and at a high enough concentration (>1 wt %). The time dependence of the storage (G') and the loss (G'') moduli has been measured in a frequency range of 0.08−1 Hz. The static and dynamic properties of the gels have been discussed on the basis of the scaling theory. At the gel point, where the loss angle ($\tan \delta_c = G''/G'$) is independent of frequency, typical power laws $G'(\omega) \sim G''(\omega) \sim \omega^{\Delta}$ have been observed. The scaling exponent Δ has been found equal to 0.70 ± 0.02 independently of the PBD and PMMA molecular weight, i.e., $36\,000 < \bar{M}_n$ (PBD) $< 100\,000$ and $20\,000 < \bar{M}_n$ (PMMA) $< 51\,000$. This exponent is also independent of the copolymer concentration and temperature in the investigated range, i.e., 2−7 wt % and 8−24 °C, respectively. This value of Δ agrees with theoretical predictions as well as with experimental values reported for some chemical gels; it is however different from the experimental values published for most physical gels. A PBD−PMMA diblock copolymer also forms a gel in *o*-xylene, although at higher concentration and lower temperature compared to the parent triblock copolymer. The scaling exponent Δ is then somewhat smaller, i.e., 0.61.

Introduction

In the last decade, much attention has been paid to modifications in the structure and viscoelastic properties of systems going through a sol−gel transition. According to de Gennes,[1] the percolation theory is suitable to account for these modifications near to the gel point.[2,3] A large number of experiments have been performed on very different systems in order to know whether the static properties of the gelation process are analogous to a second-order transition. Would it be so, the transition would be a critical phenomenon with a threshold at which an infinite three-dimensional cluster is formed in solution and triggers important modifications in the rheological properties. If p is the number of bonds in the system, p_c the value at the gel point, and $\epsilon = (|p - p_c|)/p_c$, then a divergence in the static viscosity at $p < p_c$

$$\eta \sim \epsilon^{-s} \tag{1}$$

and in the static elastic modulus at $p_c < p$

$$G_0 \sim \epsilon^{-t} \tag{2}$$

is expected to occur when $\epsilon \rightarrow 0$. The critical exponents s and t are assumed to be independent of the structural details for a gel formed in a random way.

The gelation mechanism has been discussed on the basis of several models that provide power laws for the divergence of the static viscosity and the elastic modulus. In addition to the classical or mean field theory of Flory[4] and Stockmayer,[5] various percolation models have been proposed, such as the model of percolating clusters that obey a Rouse-like dynamics,[6] the percolation model of elastic network,[7] the percolation model of a superconductor-resistor-like network,[1,8,9] and a vector percolation model which takes into account the angular forces between bonds.[10] Values for the s and t exponents as predicted by these theories are summarized in Table 1.

Dynamic rheological measurements give access to kinetics and structural modifications during the gelation process. A complex shear modulus $G^*(\omega,\epsilon) = G'(\omega) + iG''(\omega)$ is measured, where the real part, G', is the storage modulus and the imaginary part, G'', the loss modulus. The general scaling form proposed for G^* [11−13] is as follows:

$$G^*(\epsilon,\omega) = G_0(\epsilon)\, \phi^{\pm}(i\omega/\omega_0) \tag{3}$$

where ϕ^- and ϕ^+ are the scaling functions at $p < p_c$ and $p > p_c$, respectively. Close to the gel point, G_0 diverges as shown by eq 2, ω_0 is the microscopic inverse time scale at which single monomers have an elastic modulus approximated to G_0, and eq 4 is valid

$$G' \sim G'' \sim \omega^{\Delta} \tag{4}$$

At low frequencies $\omega \ll \omega_0$, the function ϕ can be expressed as shown by eqs 5 and 6

$$\phi^-(i\omega/\omega_0) = B^-(i\omega/\omega_0) + C^-(i\omega/\omega_0)^2 + \ldots \quad \text{for} \quad p < p_c \tag{5}$$

$$\phi^+(i\omega/\omega_0) = A^+ + B^+(i\omega/\omega_0) + \ldots \quad \text{for} \quad p > p_c \tag{6}$$

When $\omega \rightarrow 0$, the classical dependence, $G'' \sim \omega$ and $G' \sim \omega^2$, is predicted below the gel point, whereas this dependence is $G'' \sim \omega$ and $G' \sim$ const above the gel

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Table 1. Predicted and Experimental Exponents for the Change in Structure and Viscoelasticity near the Gel Point

	t	s	Δ	ref
theories				
mean field	3		1	2, 4, 5
electrical analogy	1.94	0.75	0.72	25
percolation Rouse approx	2.67	1.33	0.67	6, 12
experimental				
chemical gels				
tetraethoxysilane	2.2−2.6	0.79−0.99	0.70−0.72	24
epoxy		1.4		25
polyurethane			0.69	26
polyester			0.69	12
polysaccharide			0.70	35
physical gels				
10% PVC			0.80	29
crystallizing polypropylene			0.13	28
bacterial elastomer			0.11	20
gelatin	1.82	1.48		23
gelatin, ι-carrugeenan, xanthan-carob			0.50−0.65	27
pectin	1.93	0.82	0.71	32

point. At high frequencies $\omega_0 \ll \omega$, eq 7 is valid

$$\phi^{\pm}(i\omega/\omega_0) \sim (i\omega/\omega_0)^{\Delta} \quad \text{with} \quad \Delta = t/(t+s) \tag{7}$$

The scaling hypothesis (3) has two important consequences. The loss angle, i.e., the phase difference between G' and G'' ($G''/G' = \tan\delta_c$), has an universal value when $\epsilon \rightarrow 0$, thus independently of frequency in the low-frequency range ($\omega \ll \omega_0$):[14]

$$\delta_c = \Delta(\pi/2) \tag{8}$$

Moreover, at the gel point, eq 4 predicts parallel straight lines for the log−log frequency dependence of G' and G''. This characteristic feature has been used to determine the gel point and the scaling exponents.[11,16−18] Predictions for the scaling exponent Δ are summarized in Table 1.

Dynamic properties depend on the gelation mechanism and the power laws may change with the type of bonding molecules or particles.[1,19] Two types of gels are usually distinguished, i.e., the physical or weakly bonded gels and the chemical or strongly bonded gels, which differ from each other by the structure of the cross-linking units. In physical gels, the cross-linking entities can be large and of a high although uneven functionality. In chemical gels, the branching points are well-defined and dictated by the functionality of the cross-linking molecules. In physical gels, cross-links are reversible, whereas they are permanent covalent bonds in chemical gels.

Chemical gelation has been extensively investigated (Table 1), and the scaling exponents have been found in a good agreement with the theoretical predictions. Scaling exponents reported for some chemical gels are listed in Table 1.

Understanding of physical gelation is not as good as chemical gelation. The transient nature of the physical network junctions makes it difficult to study physical gels near the gel point. According to de Gennes,[1] the physical gelation can either obey the universal law for "strong gelation" or be compared to a "glass transition" in the case of "weak gelation". The experimental scaling exponents for some physical gels are shown in Table 1. Although a value of $\Delta = 0.7$ is currently observed for chemical gels, different values can be reported for physical gels.

Table 2. Molecular Characteristics of the sPMMA−PBD−sPMMA (MBM) Triblock Copolymers and MB Diblock under Consideration

samples	$(\bar{M}_n \times 10^{-3})^a$ M−B−M	1.2%^{b} in PBD	sPMMA content (%)^b	syndio %^{b} in sPMMA	$\overline{M_w}/\overline{M_n}^{\,c}$
P1	20-36-20	44	53	77	1.10
P2	35-36-35	47	66	77	1.10
P3	46-36-46	43	72	77	1.10
P4	51-77-51	46	57	79	1.10
P5	51-100-51	45	50	80	1.10
P6	25-80-25	41	38	78	1.10
P7	80-40^d	44	33	78	1.10

[a] Size exclusion chromatography of PBD with a polystyrene calibration and ^{1}H NMR analysis of the block copolymer. [b] Calculated by ^{1}H NMR. [c] Size exclusion chromatography of block copolymers. [d] Diblock M−B.

Recently, we reported on a preliminary study of the viscoelastic behavior of syndiotactic poly(methyl methacrylate) (sPMMA)−polybutadiene (PBD)−sPMMA) triblock copolymer gels in *o*-xylene.[21] This paper deals with a more detailed analysis of the viscoelastic properties of these physical gels in relation to the chemical composition and molecular weight of the triblock copolymers. A diblock copolymer has also been studied near the gel point for the sake of comparison.

Experimental Section

A PBD-sPMMA diblock copolymer was prepared by using the reaction product of *s*-BuLi with 1 equiv of 1,1-diphenylethylene (DPE) as the initiator. sPMMA−PBD−sPMMA triblock copolymers (MBM) were prepared by using the diadduct of *t*-BuLi onto *m*-diisopropenylbenzene (*m*-DIB) as a difunctional initiator. The details of synthesis were reported elsewhere.[21] Chemical composition and molecular weight of these copolymers are listed in Table 2. Solutions in *o*-xylene were prepared at 80 °C.

The dynamic mechanical measurements were performed with a Bohlin apparatus equipped with coaxial cylinders (d = 25 mm). The polymer solution, preheated at 80 °C, was rapidly added between the coaxial cylinders previously thermostated at the requested temperature. Solutions were rapidly cooled from 80 °C down to the desired temperature (ca. 1 min, as measured with a thermocouple), at which the measurements were immediately started.

Results and Discussion

As discussed in the previous paper,[21] the sPMMA outer blocks of sPMMA−PBD−sPMMA triblock copolymers associate in *o*-xylene with formation of thermally reversible gels. The rate of gelation depends on the copolymer concentration and the curing temperature. In this paper, special attention is paid to the possible effect of the relative length of the two constitutive blocks on the gelation process.

Effect of $\bar{M}_n$ (PMMA) and $\bar{M}_n$ (PBD). Figure 1 shows the time dependence of the storage (G') and loss (G'') moduli at 10 °C and 1 Hz for solutions of three triblock copolymers in *o*-xylene (7 wt %). These copolymers (P1−P3 in Table 2) have the same $\bar{M}_n$ (PBD) = 36 000 but contain sPMMA blocks of a different $\bar{M}_n$ = 20 000, 35 000, and 40 000, respectively. Only the most representative part of the curves is shown since the complete leveling off of the storage modulus required more than 24 h.

For the three solutions, G' is originally smaller than G'', which is typical of the dynamic mechanical behavior of liquids. The two moduli increase with increasing time as the result of a more extensive aggregation. Beyond the crossing point where $G' = G''$, G'' rapidly reaches an equilibrium value, while G' goes on increasing. From

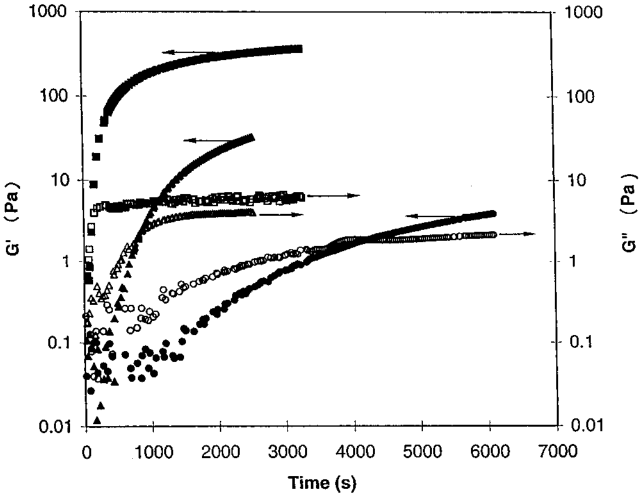

Figure 1. Shear storage (G') and loss (G'') moduli vs time at 10 °C and 1 Hz, for solutions of various MBM copolymers: P1 (○, ●), P2 (△, ▲) and P3 (□, ■) in *o*-xylene (7 wt %).

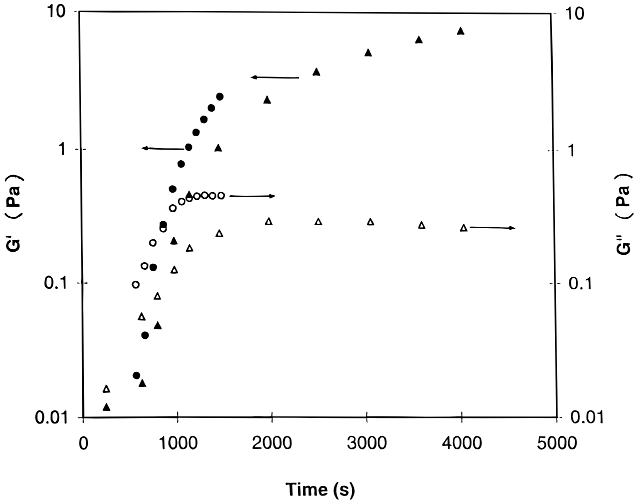

Figure 2. Shear storage (G') and loss (G'') moduli vs time at 8 °C and 0.4 Hz, for solutions of different MBM copolymers: P4 (△, ▲) and P5 (○, ●) in *o*-xylene (2 wt %).

the comparison of the curves in Figure 1, it appears that the moduli at the crossing point, $G' = G''$, are not deeply different for the three copolymers. The time at which the crossing point is reached decreases with the increasing length ($\bar{M}_n$) of the sPMMA blocks. Finally, the storage modulus, G', at the end of the gelation process rapidly increases with $\bar{M}_n$ of the aggregated sPMMA sequences.

Figure 2 shows the time dependence of G' and G'' for the two P4 and P5 triblock copolymers containing the same sPMMA block ($\bar{M}_n = 51\,000$) and a central (PBD) block of a different $\bar{M}_n$, i.e., 77 000 and 100 000, respectively. The copolymer concentration in *o*-xylene is 2 wt %, and the measurements are carried out at 8 °C and 0.4 Hz. It is clear that the difference in $\bar{M}_n$ (PBD) has only a minor effect on the moduli and time at which the crossing point, $G' = G''$, is observed.

As stated in the previous paper, only the sPMMA sequence is responsible for the network formation, whereas the PBD sequence is soluble in *o*-xylene and does not contribute to the network construction. The network then results from the self-association of the sPMMA outer blocks, the length of which controls the gelation rate and the cross-linking density, in agreement with a higher ultimate storage modulus G' when $\bar{M}_n$ (sPMMA) is increased. In contrast, at least in the investigated range, $\bar{M}_n$ (PBD) does not affect the cross-linking density or the entanglement density of the PBD midblock more likely due to the low solution concentration (7 wt %).

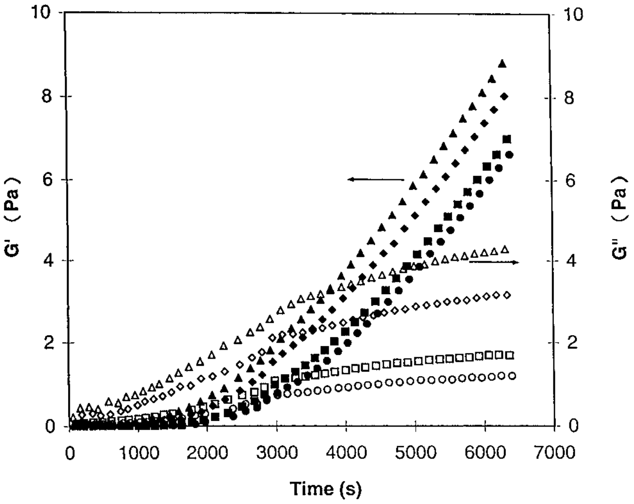

Figure 3. Time dependence of G' and G'' at 22 °C and four frequencies ((△, ▲) 1, (◇, ◆) 0.6, (□, ■) 0.2, and (○, ●) 0.1 Hz) for the P6 MBM copolymer in *o*-xylene (7 wt %).

Frequency Measurements. The effect of frequency on the time dependence of G' and G'' is shown in Figure 3, for the P6 triblock copolymer in *o*-xylene (7 wt %) at 22 °C. Although the general shape of the curves is maintained, the crossing point $G' = G''$ is observed at a decreasing time as the frequency is decreased.

Figure 4 illustrates on a log–log plot the frequency dependence of G' (A) and G'' (B) at different gelation times. At short aging times and low frequencies ($\omega \ll \omega_0$), the copolymer solution behaves as predicted by theory (see eqs 5 and 6) for a Newtonian liquid:

$$G'(\omega) \propto \omega^2 \tag{9}$$

$$G''/\omega = \eta, \quad \omega = 2\pi f \tag{10}$$

where η is the solution static viscosity. This means that the characteristic relaxation time τ is much smaller than the reciprocal frequency.

As the gelation time increases, the slope of the log–log curves decreases, the relaxation spectrum is shifted toward longer times, and the medium changes into a viscoelastic solid. After a sufficiently long time, the storage modulus agrees with eq 11, indicating that the medium becomes solid.

$$G'(\omega) \propto \omega^{cte} \quad \text{with} \quad cte \rightarrow 0 \quad \text{as} \quad t \rightarrow \infty \tag{11}$$

Scaling Properties of the sPMMA–PBD–sPMMA Triblock Copolymers. The question of whether the above data suggest an intermediate point that is governed by the scaling law (eq 4) is addressed. This point should be referred to as the gel point (GP) and the related curing time as the gel time (t_g). According to eq 8, the loss angle [$\tan \delta = G''(\omega)/G'(\omega)$] is independent of frequency at GP. Indeed, Figure 5 shows that the gel point for the P6 sample occurs at $t_g = 2200$ s and that the sample changes from a viscoelastic liquid for which $\tan \delta$ decreases with increasing frequency to a viscoelastic solid for which $\tan \delta$ increases with frequency.

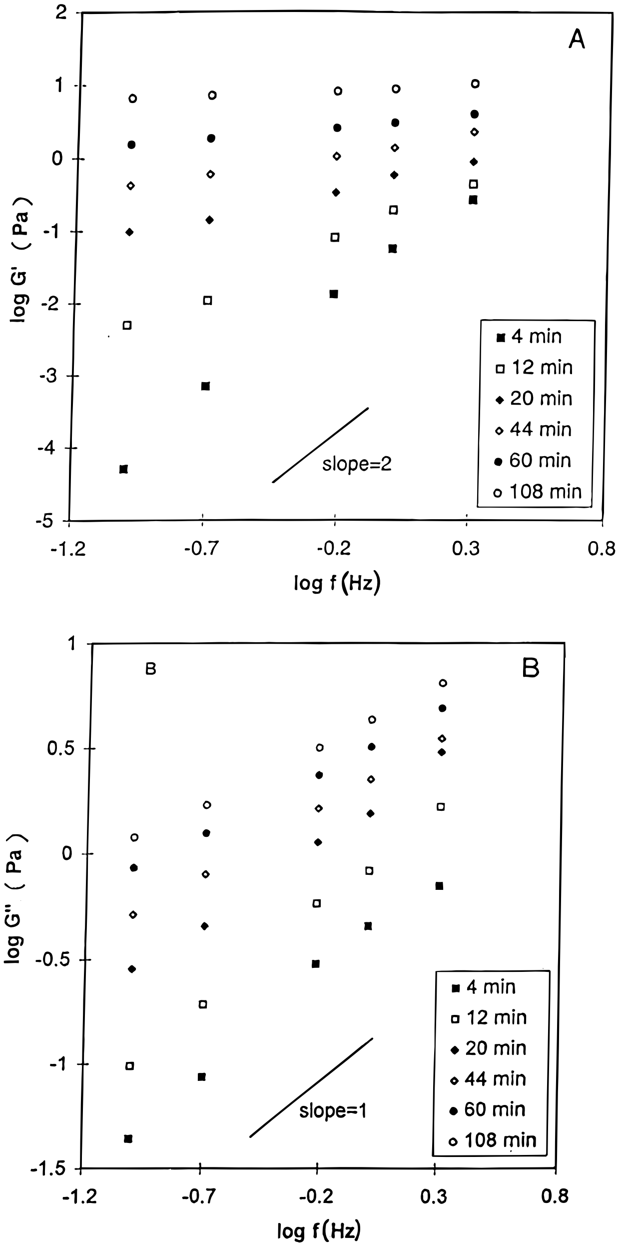

Figure 4. Frequency sweep of storage (A) and loss (B) moduli for the P6 copolymer at various curing times.

The relaxation exponent Δ at the GP is determined from eq 8, where δ_c is the δ value at the time at which all the tan δ vs time curves intersect whatever the frequency. A scaling exponent $\Delta = 0.7$ is accordingly calculated. Although Winter et al. expected a universal value for the scaling exponent, they[15−17] found that Δ was changing with the structure and chemical composition of PDMS chemical gels.[30] In the case of polycaprolactone critical gels,[31] Δ was found to decrease with increasing concentration and increasing molecular weight. Physical gelation of bacterial elastomers[20] resulted in a strong dependence of viscoelasticity on temperature. An exponent $\Delta = 0.11$ was found at 15 and 20 °C, and no gel was formed at 30 °C.

In order to know whether or not Δ for MBM gels in *o*-xylene has a unique value, a series of experiments were carried out at different temperatures and copolymer concentrations for copolymers containing blocks of various lengths. The experimental gelation time, t_g, and the calculated scaling exponent, Δ, are listed in Table 3.

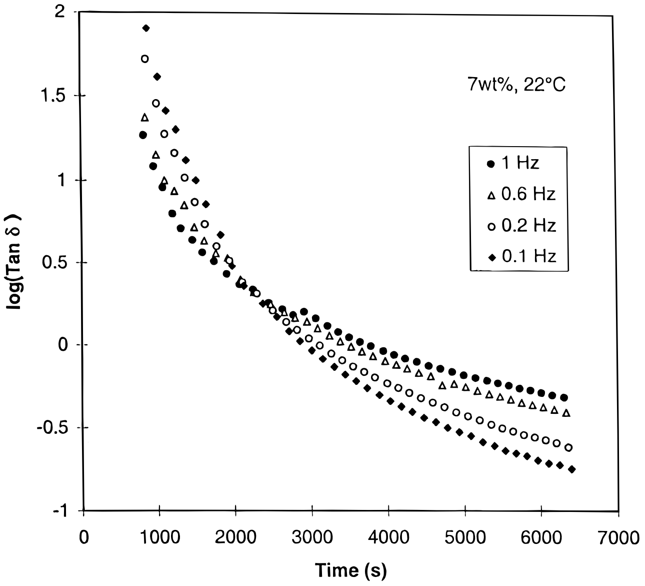

Figure 5. Tan δ vs time at four frequencies ((●) 1, (△) 0.6, (○) 0.2, and (◆) 0.1 Hz)) for the P6 copolymer at 22 °C.

Table 3. Critical Exponents and Gelation Time for Solutions of Block Copolymers in *o*-Xylene at Different Temperatures and Concentrations

sample	copolymer	wt %	T (°C)	t_g (s)	Δ	Δ′
P1a	P1	7	10			
P2a	P2	7	10			
P2b	P2	7	15	2930	0.70	0.70
P3a	P3	7	10			
P3b	P3	7	15	400	0.69	0.70
P3c	P3	7	17	640	0.69	0.67
P4a	P4	2	8	820	0.70	
P4b	P4	2	15	6370	0.70	
P4c	P4	7	24	740	0.72	
P5a	P5	2	8	700	0.72	
P6a	P6	2	8	10800	0.70	0.75
P6b	P6	5	15	1360	0.69	
P6d	P6	7	17	350	0.68	0.67
P6e	P6	7	20	1100	0.69	0.75
P6f	P6	7	22	2300	0.70	0.72
P6g	P6	7	24	4200	0.70	0.67
P7a	P7	10	8	17400	0.61	

Figure 6 shows the time dependence of tan δ at frequencies ranging from 0.08 to 2 Hz for 7 wt % solutions and three different temperatures: 17 (A), 20 (B), and 24 °C (C). It is clearly observed that the tan δ curves for different frequencies intersect at the same point which is the gel point for the systems under consideration (B, C). In the case of Figure 6A, the transition is so fast that the determination of the gel point is not very accurate. t_g increases with increasing temperatures from 1100 s at 20 °C to 4200 s at 24 °C, whereas the scaling exponent Δ is kept unchanged. The same conclusion holds for lower concentrations as shown in Figure 6D for a 5 wt % concentration at 15 °C; Δ is again 0.69.

In order to investigate the effect of the copolymer composition and molecular weight, gelation of MBM copolymers (P3−P6) of various sPMMA contents (38−72%) and block molecular weights (36 000 < $\bar{M}_n$ (PBD) < 100 000, 25 000 < $\bar{M}_n$ (sPMMA) < 51 000), has been studied at different concentrations (2−7 wt %). Figures 7 and 8 show typical tan δ vs time curves at different frequencies. In spite of large differences in $\bar{M}_n$ (PBD) and $\bar{M}_n$ (PMMA) and in copolymer concentrations, the scaling exponent does not change significantly, 0.69 <

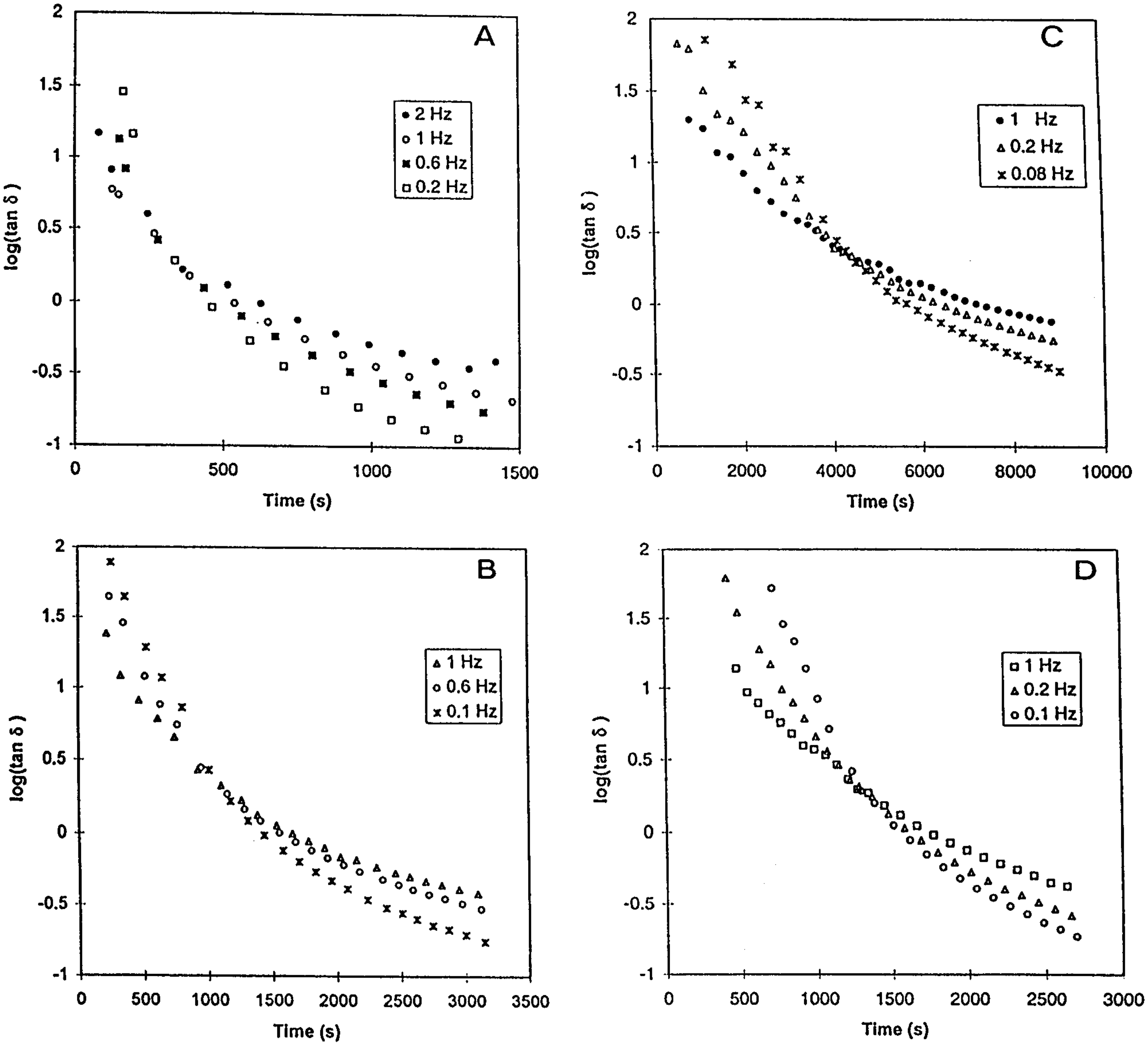

Figure 6. Tan δ vs time at various frequencies for the P6d (A), P6e (B), P6g (C), and P6b (D) copolymers (Table 3) at different temperatures and concentrations.

$\Delta < 0.72$ (Table 3). Moreover, no significant influence on Δ is observed when temperature is changed from 8 to 24 °C.

In contrast to the scaling exponent Δ, which appears to be independent of all the previously discussed experimental variables, the gelation time, t_g, decreases with increasing $\bar{M}_n$ (sPMMA) and increases upon decreasing concentration at constant temperature and upon increasing temperature at constant concentration.

Equation 8 allows the gelation time and the scaling exponent to be calculated for each sample. Δ can also be calculated by eq 4, from the frequency dependence of the storage and the loss moduli. Figure 9 shows typical log−log G' and G'' vs frequency plots for the P6a and P6g samples (Table 2) at 8 and 24 °C, respectively. Two parallel straight lines are observed for G' and G'', which provides a scaling exponent Δ of exactly the same value as calculated from eq 8.

The experimental value of Δ thus agrees with the predictions of the scaling theory for percolating clusters that obey a Rouse-like dynamics[6] ($\Delta = 2/3$) and for the percolation model for superconductor-resistor-like network[1,8,9] ($\Delta = 0.73$). It is inconsistent with predictions by the mean field theory ($\Delta = 1$)[4,5] and the vector percolation model.[10] As shown in Table 1, the scaling exponent $\Delta = 0.7$ is in good agreement with experimental values previously reported for chemical gels such as tetraethoxysilane gel,[24] epoxy resins,[25] polyurethanes,[26] and polyesters.[12] Conversely, it disagrees with the behavior of physical gels, such as polypropylene,[28] PVC,[29] and bacterial elastomers.[20]

Scaling Properties of a PBD−SPMMA Diblock Copolymer. It is worthwhile to investigate whether a change in the molecular architecture of sPMMA- and PBD-containing block copolymers, e.g., a MB diblock compared to a MBM triblock, can have an effect on the scaling properties.

We previously reported[21] that the association of sPMMA is less favorable in a diblock compared to a triblock copolymer. Moreover, an MB diblock structure is less prone to form a gel than an MBM triblock. It is the reason why the gelation process for MB diblocks in *o*-xylene has been studied at a higher concentration and a lower temperature compared to triblocks. Panels A and B of Figure 10 show the tan δ vs time curves and the log−log plot of G' and G'' vs frequency, respectively, for the P7 diblock (Table 2). From these curves, $\Delta =$

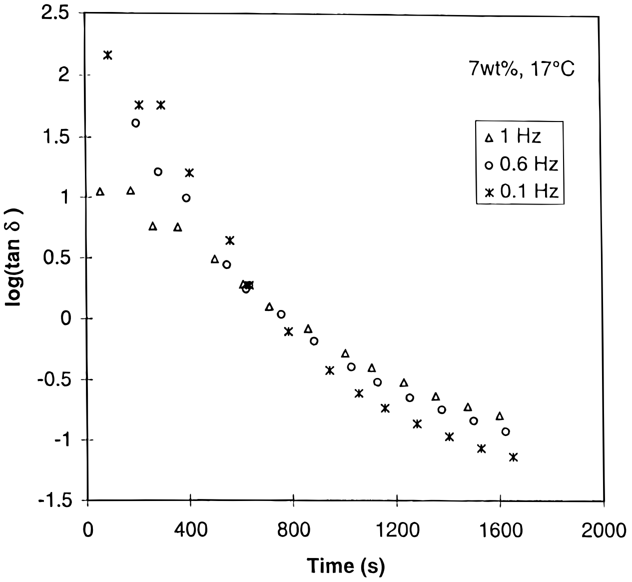

Figure 7. Tan δ vs time at various frequencies for the P3c sample (Table 3).

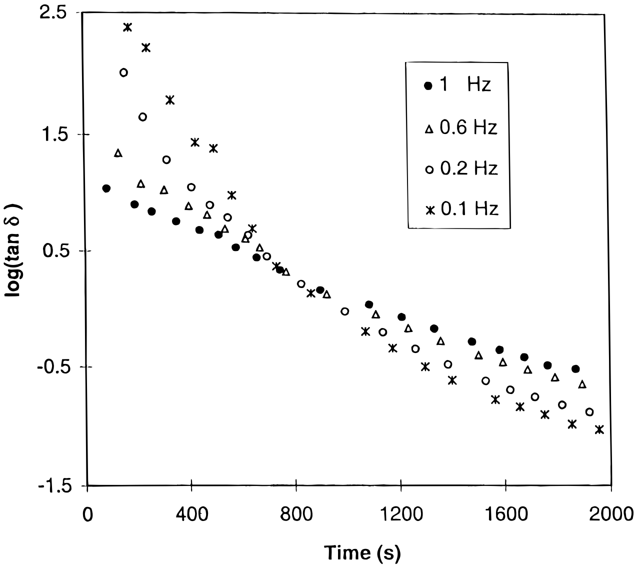

Figure 8. Tan δ vs time at various frequencies for the P4c sample (Table 3).

0.61 has been calculated, which is somewhat smaller than the value observed for gelation of the triblock copolymers.

Temperature Dependence of the Gelation Time. As shown in Table 3, t_g is strongly dependent on temperature. For instance, t_g increases from 350 to 4200 s when the temperature of a 7 wt % solution of P6 is increased from 17 to 24 °C. In order to know whether t_g obeys the Arrhenius equation

$$t_g = A e^{-E/kT} \tag{12}$$

ln t_g has been plotted vs $1/T$ for the P6d−g samples (Table 3). Figure 11 is actually a straight line, which indicates that gelation of MBM solutions in *o*-xylene is a thermoactivated process.

Dependence of the Crossing Point $G' = G''$ on Frequency. In some instances of chemical gelation,[15−17,22] the crossing point $G' = G''$ and the gel point merge together. This point is frequency dependent in physical gels as was reported for the physical gelation of gelatin,[23] for which the gel point at the lowest frequency used was identified with the crossing point (G_c). In this study, a power law of the same type as eq 4 has been used to express the frequency dependence of the crossing point.

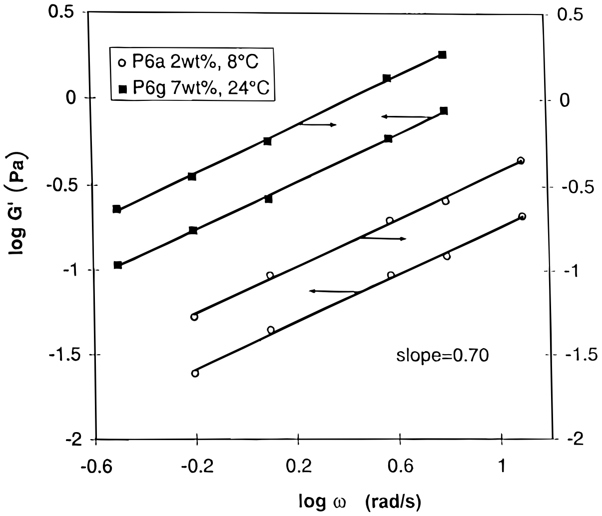

Figure 9. Log−log plot of G' and G'' vs frequencies at the gel point for the P6a and P6g copolymers. The slope is 0.70 in the two graphs.

$$G' \sim G'' \sim \omega^{\Delta'} \tag{13}$$

Δ' is thus supposed to be different from the scaling exponent Δ at gel point. Figure 12 shows a linear dependence for log G_c vs log ω for the P6 copolymer at a 7 wt % concentration and various temperatures (17, 20, 22, and 24 °C). The exponent Δ' calculated from the slope of the straight lines is reported in Table 3. Δ' lies between 0.67 and 0.75, which is close to the scaling exponent Δ calculated at the gel point.

Conclusion

Aggregation of the sPMMA block of MBM triblock copolymers dissolved in *o*-xylene is responsible for the formation of a three-dimensional structure, in such a way that a scaling law behavior is observed at the gel point. The scaling exponent Δ is in good agreement with the predictions of the scalar percolation theory and with experimental measurements for chemical gelation, although functionality and size of the cross-linking entities are quite different in chemical and physical gels.

It is remarkable that the exponent Δ has been found to be independent of molecular weight and composition of the MBM copolymers, and the experimental conditions such as concentration and temperature. This is a valuable demonstration of universality in the vicinity of the critical point. The MBM triblock copolymers seem to be a particular class of physical gels, in which the interactions are stronger than in most physical gels.

The gelation time strongly depends on molecular weight of the sPMMA block in triblock copolymers, on polymer concentration, and temperature. The thermal dependence of t_g fits an Arrhenius equation.

The crossing point of the storage and loss moduli is found to depend on frequency, and this dependence obeys a power law with an exponent that is quite comparable to the scaling exponent found at the gel point.

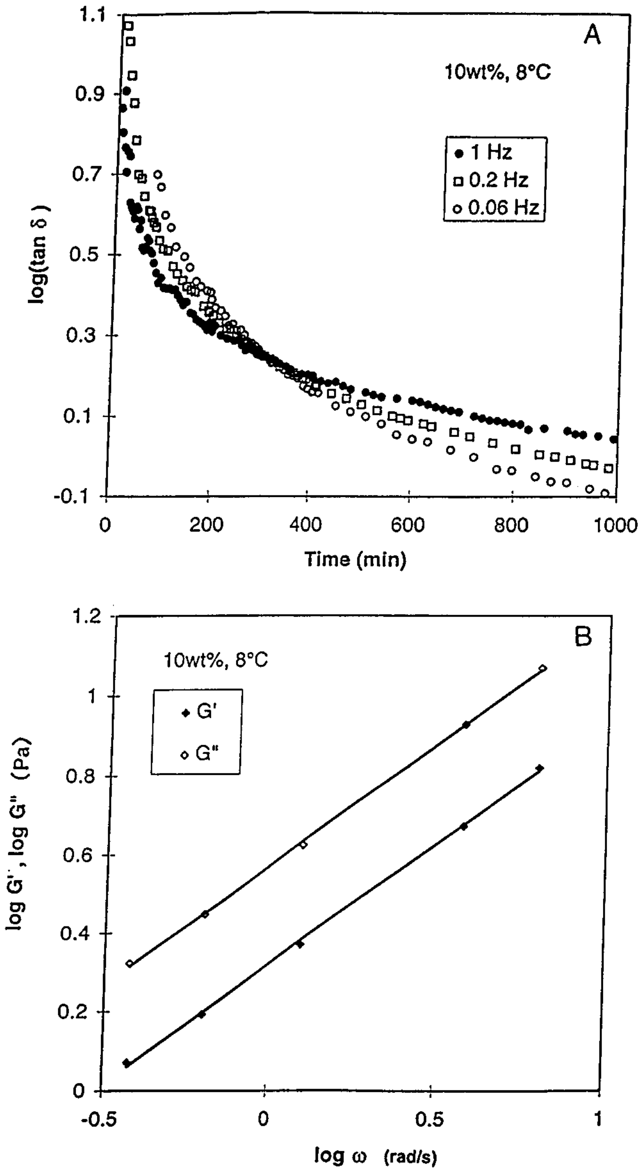

Figure 10. Tan δ vs time at three frequencies and 8 °C for the P7 diblock (A). Log−log plot of G' and G'' vs frequency at the gel point for the same sample (B).

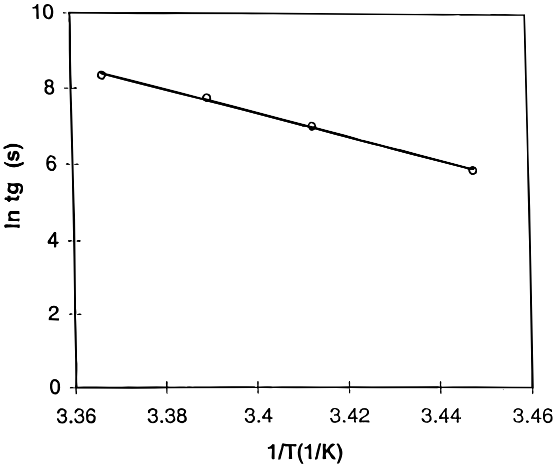

Figure 11. Gelation time t_g vs reciprocal temperature and fitting by the Arrhenius equation for the P6 copolymer in *o*-xylene (7 wt %).

A PBD−sPMMA diblock copolymer agrees with the scaling law at the gel point with a somewhat smaller exponent than for the parent triblock copolymers.

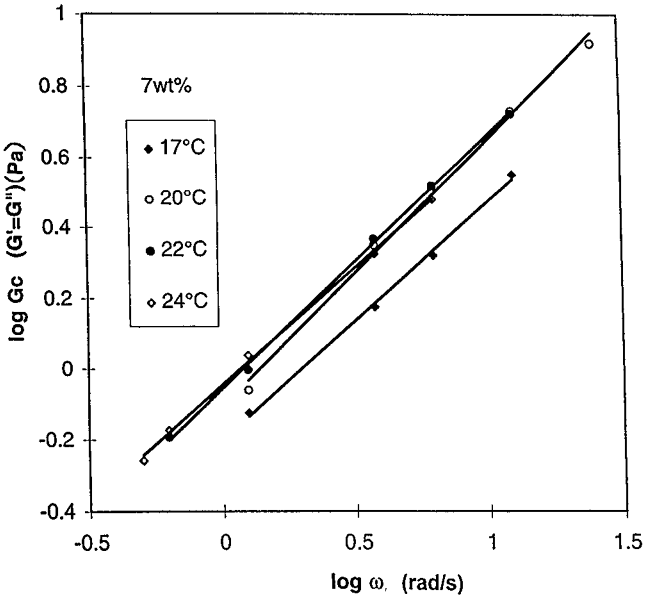

Figure 12. Log−log plot of G_c vs frequency at various temperatures for the P6 copolymer in *o*-xylene (7 wt %).

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