

Thermoreversible Gelation of Triblock Copolymers in *o*-Xylene

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Introduction

It is well-known that syndiotactic poly(methyl methacrylate) (sPMMA) could crystallize in the presence of some solvents^{1,2}. Supercooled solutions of sPMMA, e.g., in *o*-xylene show a liquid (sol) to solid (gel) transition when the chain cross-linking (ρ) reaches a critical value, which is known as the gel point (GP). Recently, the mechanism for the thermoreversible gelation of homo-sPMMA solutions in *o*-xylene³ and in toluene⁴ has been investigated by Berghmans et al. A two-step mechanism has been proposed, the first step of which is a fast intra-molecular conformational change, followed by an intermolecular association into a tridimensional network. This mechanism was extended to sPMMA - polybutadiene (PBD) - sPMMA triblock copolymers, or MBM triblock copolymers.^{5,6} It has been shown that the dynamic mechanical behaviour at the GP may be described by a scaling relationship between the dynamic moduli (G' and G'') and the angular frequency (ω)^{7,8}

$$G'(\omega) \sim G''(\omega) \sim \omega \quad (1)$$
$$\omega = 2\pi f$$

where f is the frequency and Δ 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 frequencies⁹

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

This paper aims at studying the self-association of sPMMA outer blocks in MBM copolymers in *o*-xylene. The dynamic properties of binary MBM/*o*-xylene system have been studied as a function of temperature, concentration and molecular weight of triblock copolymers.

Experimental

MBM triblock copolymers were prepared by using the diadduct of *tert*-BuLi onto *m*-disopropenylbenzene as a difunctional initiator. The detailed synthesis was described elsewhere⁹. Chemical composition and molecular weight of these materials are listed in Table 1.

Thermal analysis (DSC) was carried out on a aged gel with a Dupont 910 calorimeter in sealed pans at a heating rate of 20° C/min. The dynamic mechanical measurements were performed with a Bohlin CS apparatus equipped with coaxial cylinders ($d = 25$ mm). The polymer solution in *o*-xylene, preheated at 80°C, was rapidly added between the coaxial cylinders thermostated at the requested temperature. The cooling of the solution from 80°C down to the measurement temperature needed ca. 1 minute (as measured with a thermocouple) and the measurements were then immediately started.

Results and Discussion

A transparent gel is formed on cooling a solution of MBM prepared at 80°C in *o*-xylene. Subsequent heating of this gel results in the formation of a transparent solution. This sol-gel transition is quite reversible.

DSC study. Figure 1 shows that an endotherm is observed upon heating a MBM gel in *o*-xylene (10 wt %), which is resulted from the melting of soft-aggregates of sPMMA blocks in the MBM gel. The melting region extends over ca. 20°C from 35°C up to 55°C and shows a maximum at 39°C.

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Frequency measurements. Figure 2 shows the storage (G') and loss (G'') moduli for the sample P6f (Tab. 2) as a function of time at frequencies 0.1, 0.2, 0.6 and 1 Hz, respectively. The transition from a viscoelastic liquid to a viscoelastic solid at $G'=G''$ which is the crossover point strongly depends on frequency. Indeed, the crossover time and the modulus at the crossover point increase with increasing frequency.

Scaling properties. It is known that the dynamic mechanical behavior of polymers at the gel point fits a power law for the frequency dependency of the moduli (eq. 1). According to eq.2, the loss angle [$\tan \delta = G''(\omega)/G'(\omega)$] is independent of frequency at GP. Indeed, Figure 3 shows that the gel point for the P6f sample (Tab. 2) occurs at $t_g = 2300$ 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. The relaxation exponent Δ at the GP is determined from eq. 2 where δ_c is the δ value at the time at which all the $\tan \delta$ vs. time curves intersect whatever the frequency. A scaling exponent $\Delta = 0.7$ is accordingly calculated.

A series of experiments have been 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 2. The effect of the copolymer composition and molecular weight has also been investigated, gelation of MBM copolymers (P3, P4, P5 and P6) of various sPMMA contents (38% to 72%) and block molecular weights: $36000 < M_n(\text{PBD}) < 100000$, $25000 < M_n(\text{sPMMA}) < 51000$, has been studied at different concentrations (2 wt% to 7wt%) (Tab. 2). 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 $M_n(\text{sPMMA})$ and increases upon decreasing concentration at constant temperature and upon increasing temperature at constant concentration (Tab. 2).

As shown in Table 1, the scaling exponent $\Delta = 0.7 \pm 0.02$ is in good agreement with experimental values previously reported for chemical gels such as tetraethoxysilane gel¹⁰, epoxy resins¹¹, polyurethanes¹². Conversely, it disagrees with the behaviour of some physical gels, such as polypropylene¹³, PVC¹⁴.

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 behaviour 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.

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Tab. 1. Characteristics of sPMMA-PBD-sPMMA (M-B-M) triblock copolymers used in gelation studies

sample	M-B-M ($M_n \times 10^{-3}$) ^a	PBD 1,2 % ^b	sPMMA ^b		M_w/M_n
			content(%)	syndio(%)	
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	25-80-75	41	38	78	1.10

^a SEC of PBD with a polystyrene calibration and ¹H NMR analysis of the block copolymer, ^b ¹H NMR

Tab. 2. Critical exponents and gelation time for MBM triblock copolymer solutions in *o*-xylene at different temperatures and concentrations

sample	copolymer	wt %	T(°C)	tg(s)	Δ
P1a	P1	7	10	-	-
P2a	P2	7	10	-	-
P2b	P2	7	15	2930	0.70
P3a	P3	7	10	-	-
P3b	P3	7	15	400	0.69
P3c	P3	7	17	640	0.69
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
P6b	P6	5	15	1360	0.69
P6d	P6	7	17	350	0.68
P6e	P6	7	20	1100	0.69
P6f	P6	7	22	2300	0.70
P6g	P6	7	24	4200	0.70

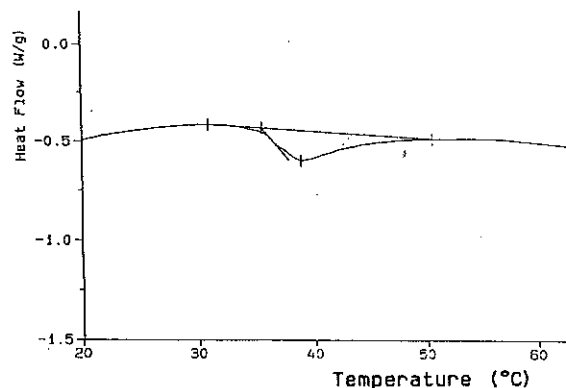


Figure 1. DSC Curve for a 10 wt% solution of the P6 MBM copolymer (Tab. 1) in *o*-xylene

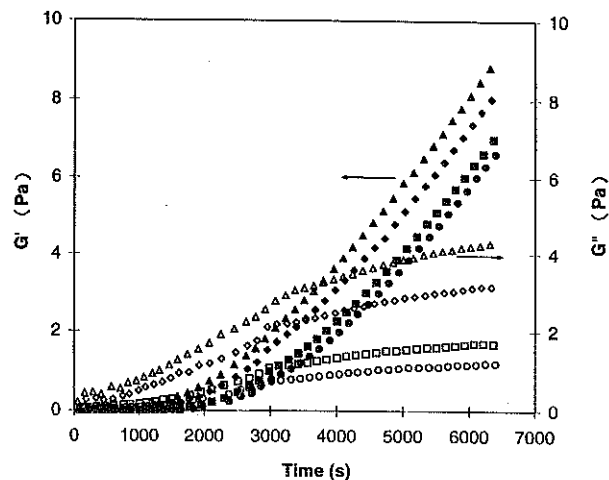


Figure 2. Time dependence of G' and G'' at 22°C for the P6 MBM copolymer in *o*-xylene (7wt%) ((Δ , \blacktriangle) 1, (\diamond , \blacklozenge) 0.6, (\square , \blacksquare) 0.2, and (\circ , \bullet) 0.1 Hz)

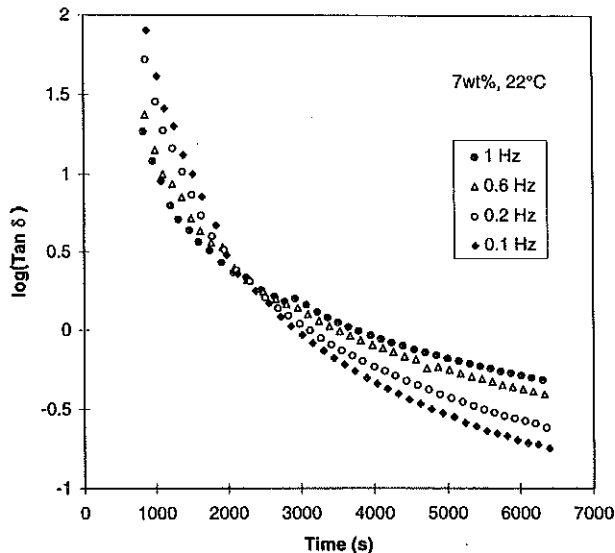


Figure 3. $\tan \delta$ vs. time at 22°C for the P6 MBM copolymer in *o*-xylene (7wt%)