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Bulk properties of multibranched polystyrenes from polystyrene macromonomers: rheological behavior I

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Abstract

Dynamic shear moduli of multibranched polystyrenes were measured as functions of frequency and temperature using a parallel-plate rheometer. The multibranched polystyrenes are poly(macromonomer)s of ω-methacryloyloxyethyl polystyrene macromonomers (MA-PSt)s and statistical copolymers of the MA-PSt with methyl methacrylate (MMA) monomer. The master curve of the storage dynamic shear modulus G' for the poly(macromonomer)s did not show the so-called plateau region and the G' gradually decreased from the edge of the glass transition region to the terminal zone and the loss modulus G'' was always larger than G'. The plateau region became clear in the copolymers with less branch density. These results indicate that the intermolecular chain entanglement might be strongly restricted in the poly(macromonomer) systems due to the multibranched structure of high branch density, which also explains the brittle property of the poly(macromonomer) films. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Macromonomer; Poly(macromonomer); Branched polymer

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1. Introduction

Rheological properties of branched polymers, such as star polymers, comb-shape polymers, and H-shape polymers, have been investigated to understand the effect of branching structure on the molecular motion and the viscoelastic properties [1–6]. However, the effect of branched structure on the rheological properties is still not well understood. Chain polymerizations of vinyl-terminated macromonomers produce multibranched polymers of extremely high branch density [7–12]. The branch density can be varied by copolymerizations with the comonomers corresponding to the polymerizable end group of the macromonomer [10]. Recently, it has been revealed that poly(macromonomer)s show very unique and interesting molecular and bulk properties associated with the tethered branch chains around the backbone chain [13–23]. However, there is so far no report on the rheological properties of the poly(macromonomer)s.

We have investigated the rheological properties of poly(macromonomer)s in order to understand how the specific multibranched structure influences the condensed state of polymer molecules and how it affects the rheological properties. In this paper, we report some characteristic features in the rheological properties of poly(macromonomer)s and a copolymer prepared from ω-methacryloyloxyethyl polystyrene macromonomer (MA-PSt). The results are compared with those of a linear polystyrene under the same measuring conditions.

2. Experimental

2.1. Materials

ω-Methacryloyloxyethyl polystyrene macromonomer MA-PSt2740 ($M_w = 3450$, $M_n = 2740$, and $M_w/M_n = 1.26$) was synthesized by living anionic polymerization of styrene with *s*-BuLi followed by addition of ethylene oxide and termination with methacryloyl chloride [7–9]. The macromonomer was polymerized or copolymerized with methyl methacrylate (MMA) using azobisisobutyronitrile (AIBN) initiator in benzene. Polymerization conditions are shown in Table 1. Polymerization products were purified by precipitation–extraction procedures with cyclohexane–petroleum ether mixed solvents to remove unreacted macromonomer and comonomer. The purification was repeated several times until the sharp peak in the gel permeation chromatograph (GPC), corresponding to the unreacted macromonomer, completely disappeared.

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Table 1
Preparation conditions for multibranched polystyrenes

Sample code	MA-PSt (mmol)	MMA (mmol)	Benzene (ml)	$[M]_{total}$ (mol/l)	AIBN	
					(mmol/l)	(mg)
Poly(MA-PSt)-1	3.65	0	6.67	0.219	15.0	41.1
Poly(MA-PSt)-2	2.19	0	2.40	0.256	28.6	39.4
Poly(MMA-*co*-(MA-PSt)	0.73	20.0	4.00	2.55	25.0	33.0

Polymerizations were carried out in glass ampoules under vacuum at 50–60°C for 24–48 h.

The weight-average molecular weight, M_w, and the polydispersity index, M_w/M_n, of the macromonomer were determined by GPC (Tosoh HLC802A/LS-8) with a calibration curve constructed using polystyrene (PSt) standards, and those of poly(macromonomer)s, poly(MA-PSt2740)s, were determined by the GPC with a low-angle laser light scattering (LALLS) detector and a refractive index (RI) detector [7]. The GPC was operated with Tosoh G5000H-G3000H columns on chloroform at 35°C. M_n of poly[MMA-*co*-(MA-PSt2740)] was determined by a membrane osmometer (Jupiter model 230) in toluene at 35°C. A linear polystyrene, LPSt ($M_w = 382 \times 10^3$, $M_w/M_n = 1.20$), was used for comparison which was synthesized by living anionic polymerization of styrene with *s*-BuLi in toluene/THF mixed solvent at −78°C under vacuum. The molecular characteristics of these polymer samples are shown in Table 2.

2.2. Measurement of rheological property and other bulk properties

Rheological property of the polymer samples was measured by a Bohlin CSM Rheometer with a parallel plate geometry under nitrogen atmosphere. Disk samples of 24 mm diameter were prepared for the rheological measurements by hot press at 160°C, using polymer powder samples obtained by freeze-drying with benzene. The rheological measurements were carried out in the angular frequency range of 0.1–100 s^{-1} and the temperature range 120–220°C. The film forming property was investigated in connection with the rheological data. The film specimens were prepared by solvent casting of toluene solution of each sample onto slide glasses at room temperature (20°C).

3. Results and discussion

Fig. 1 shows the schematic representation of the multibranched polymers in this study. The poly(macromonomer)s, poly(MA-PSt)-1 and poly(MA-PSt)-2, have a polymethacrylate backbone of different chain lengths as the result of the chain polymerization of methacryloyl end group of the macromonomer, the degree of polymerization, DP, of which are 397 and 2545, respectively. The weight-average molecular weight, M_w, of polystyrene branches is 3450, which is much lower than the critical molecular weight of the chain entanglement for linear polystyrene. The weight fraction of the central backbone chain in the poly(macromonomer) is 3.3% and the rest is polystyrene branches. Thus, the poly(macromonomer)s are approximately considered as multibranched polystyrenes. The fraction of the central polymethacrylate backbone depends on the molecular weight of the macromonomer but does not depend on the DP of the poly(macromonomer)s. The weight fraction of the backbone chain of poly[MMA-*co*-(MA-PSt)] is 55.6%. From our recent investigation of the chain tacticity of poly(MA-PSt)s prepared under similar polymerization conditions, the central backbone chain of the poly(macromonomer)s and also poly[MMA-*co*-(MA-PSt)] in this study have similar tactic structure to that of

Table 2
Characteristics of multibranched and linear polystyrenes

Sample code	Total			Backbone		Wt% of backbone chain	Branch	
	M_w[a] ($\times 10^{-6}$)	M_n[a] ($\times 10^{-6}$)	M_w/M_n	M_w ($\times 10^{-3}$)	DP[b]		M_n ($\times 10^{-3}$)	M_w/M_n
Poly(MA-PSt)-1	1.372	0.759	1.81	39.7	397	3.3	3.45	1.26
Poly(MA-PSt)-2	8.780	5.624	1.56	255	2545	3.3	3.45	1.26
Poly[MMA-*co*-(MA-PSt)]	1.183	0.735	1.61[c]	658	6577	55.6[d]	3.45	1.26
LPSt	0.382	0.317	1.20	382	3673	–	–	–

[a] Molecular weights of poly(macromonomer)s were determined using GPC equipped with a low-angle laser light scattering detector. M_n for poly[MMA-*co*-(MA-PSt)] was determined by membrane osmometry. Standard PSt calibration curve was used for the LPSt.

[b] DP is based on the weight-average molecular weight.

[c] Estimated from GPC curve.

[d] Determined by ^1H NMR.

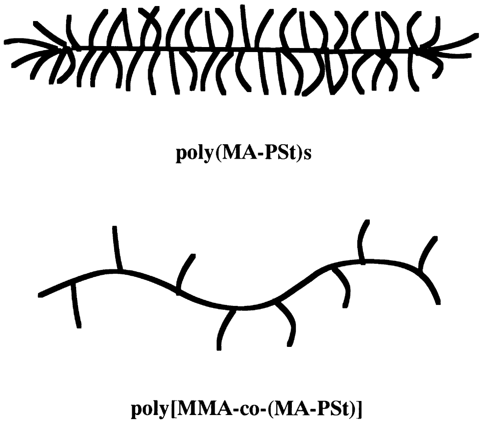

Fig. 1. Schematic representation of poly(MA-PSt)s and poly[MMA-*co*-(MA-PSt)].

poly(methyl methacrylate) (PMMA) prepared by conventional free radical polymerizations [24].

Fig. 2 shows the dynamic shear moduli: (a) G'; and (b) G'' measured for the poly(MA-PSt)-1 possessing polystyrene 397 branches in the temperature range from 120 to 200°C. Each curve of G' and G'' in Fig. 2(a) and (b) was shifted onto the curve at a reference temperature, $T_r = 160^\circ C$, assuming the time–temperature superposition principle to construct the master curves. The master curves are shown in Fig. 3 together with those of G' and G'' for a LPSt for comparison, at the same T_r measured under the same condition. In Figs. 4 and 5, the master curves of G' and G'' for the data of poly(MA-PSt)-2 and poly[MMA-*co*-(MA-PSt)] are shown. The shift factors plotted against $T - T_r$ are shown in Fig. 6.

It is seen in Fig. 3 that there is a clear plateau region in G' curve for the LPSt which is associated with the intermolecular chain entanglement network commonly observed for high molecular weight linear flexible polymers [25]. If we take 5.3 from Fig. 3 as the value of the plateau modulus, $\log (G_N^0/\mathrm{Pa})$, the molecular weight between the two entanglement coupling loci, M_e, is estimated as 18 000 from the relation $M_e = \rho RT/G_N^0$. This value is very close to the M_e values for LPSts in literature [25,26].

On the other hand, the G' master curve for the multi-branched polystyrene, poly(MA-PSt)-1, shows no rubbery plateau region. The G' as well as G'' monotonically decrease from the edge of the glass transition zone and directly go to the terminal zone with decrease in the frequency. In the edge of the glass transition zone, the value of G' is almost the same as that of G'' and these overlap each other. In the other regions, the value of G' is always lower than that of G''. Similar tendency is observed for the master curve of poly(MA-PSt)-2 in Fig. 4, where G' and G'' become closer and a weak shoulder is seen at the low frequency region. These results suggest that the chain entanglement coupling is suppressed in the poly(macromonomer) systems.

The weight-average DP of the backbone chain of poly(MA-PSt)-1 and poly(MA-PSt)-2 is 397 and 2545, respectively. Therefore, the backbone chain length of poly(MA-PSt)-1 is roughly twice the critical molecular

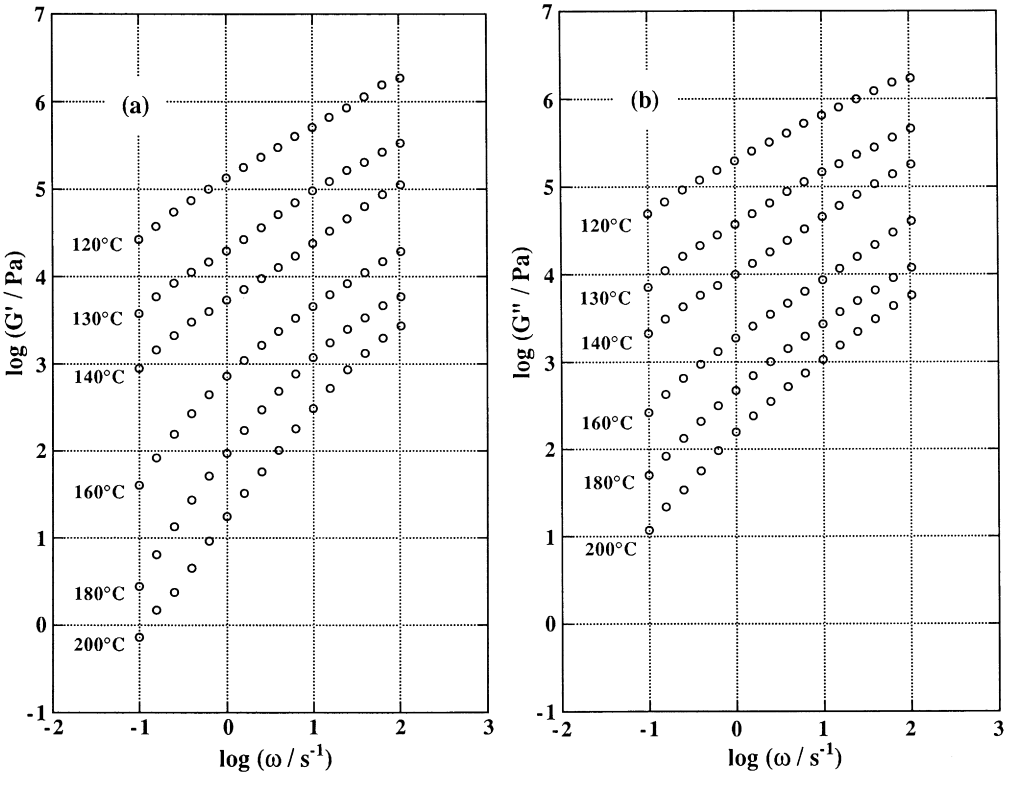

Fig. 2. Frequency dependence of G' and G'' for poly(MA-PSt)-1 measured at different temperatures.

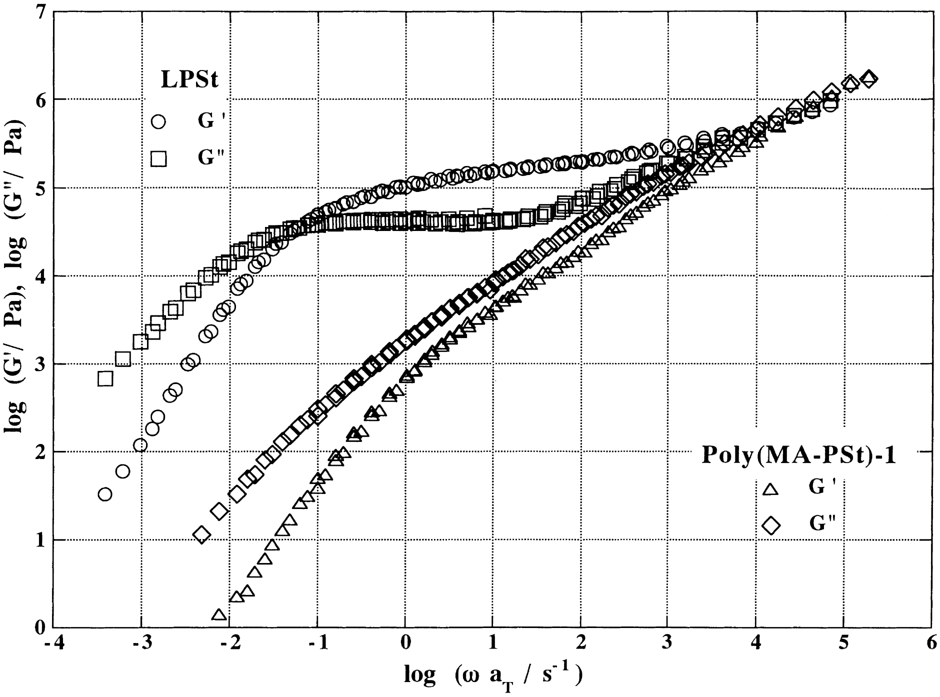

Fig. 3. Master curves of G' and G'' of poly(MA-PSt)-1 and LPSt at $T_r = 160$°C.

weight of chain entanglement, M_c, for linear atactic PMMA ($M_c = 2M_e = 2 \times 10^4$) [25], while the chain length of poly(MA-PSt)-2 is about 10 times longer than the M_c. Therefore, the absence of the plateau region in these multibranched polystyrenes is not ascribed to the low molecular weight of the central backbone, but may be ascribed to the tethered PSt branches of high density around the backbone chain [27].

M_e of amorphous flexible polymers is related to the polymer molecular structure. For example, M_e of methacrylate polymers increases with increase in the size of the ester group [25]. M_e of poly(n-octyl methacrylate) is much larger

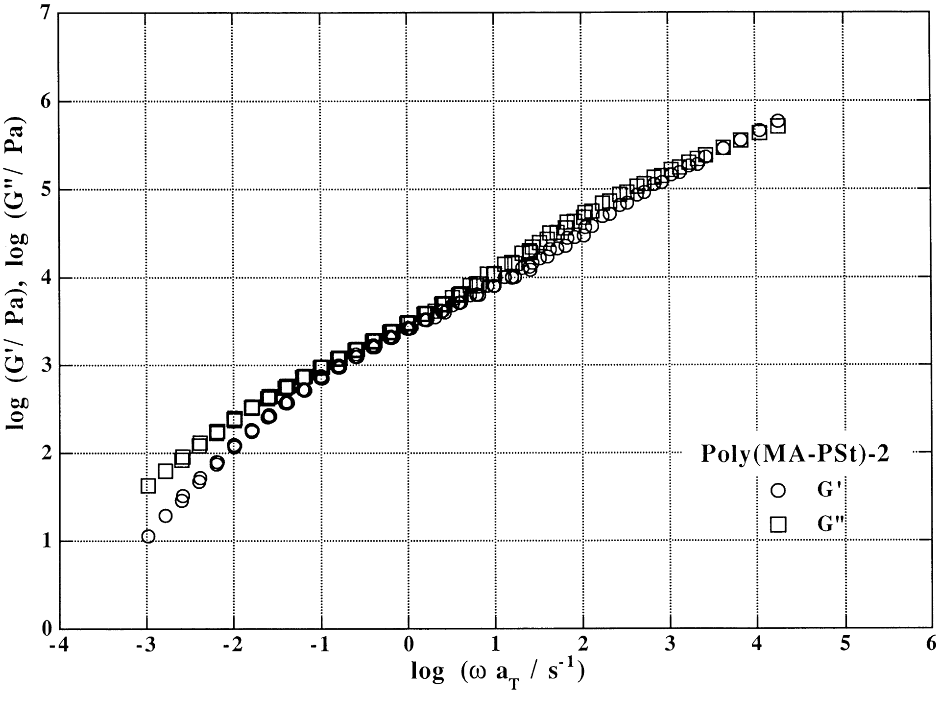

Fig. 4. Master curves of G′ and G″ of poly(MA-PSt)-2 at $T_r = 160$°C.

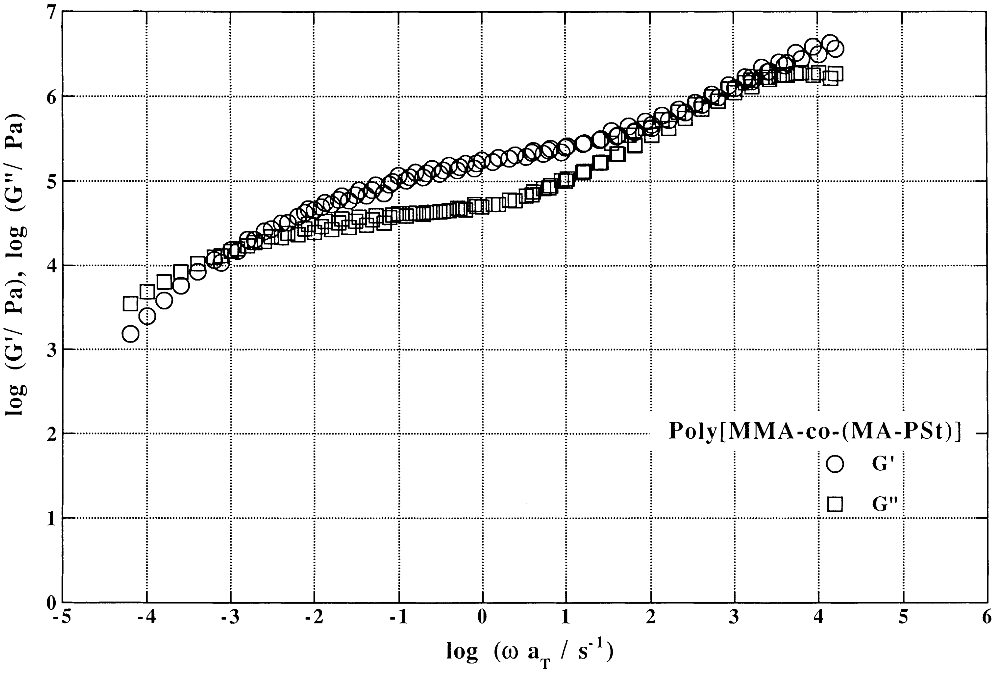

Fig. 5. Master curves of G' and G'' of poly[MMA-*co*-(MA-PSt)] at $T_r = 160°C$.

than that of PMMA [28]. We consider that M_c ($= 2M_e$) is related to the molecular cross sectional area of the polymer molecules. The increase in the molecular cross sectional area may increase M_c of polymers of the same chain length, because the increase in the cross sectional area tends to exclude other molecules in a unit volume. The specific multibranched structure of the poly(macromonomer)s may increase the molecular cross sectional area. Recently, it was found that the multibranched structure of very high branch density gave marked repulsive interaction between PSt branch chains in the poly(macromonomer)s which strongly affects the chain stiffness of the backbone chain and the molecular conformation in solution [17–22]. This repulsive interaction between the PSt branches may also prevent the interpenetration of the PSt branches of other molecules. Therefore, the absence of the plateau region can be ascribed to the suppression of the formation of intermolecular chain entanglement network in bulk.

On the other hand, the master curve of poly[MMA-*co*-(MA-PSt)] in Fig. 5 shows a clear plateau region, where G' is larger than G'' and frequency dependence of G' is weak in this region. The mole fraction of the incorporated polystyrene

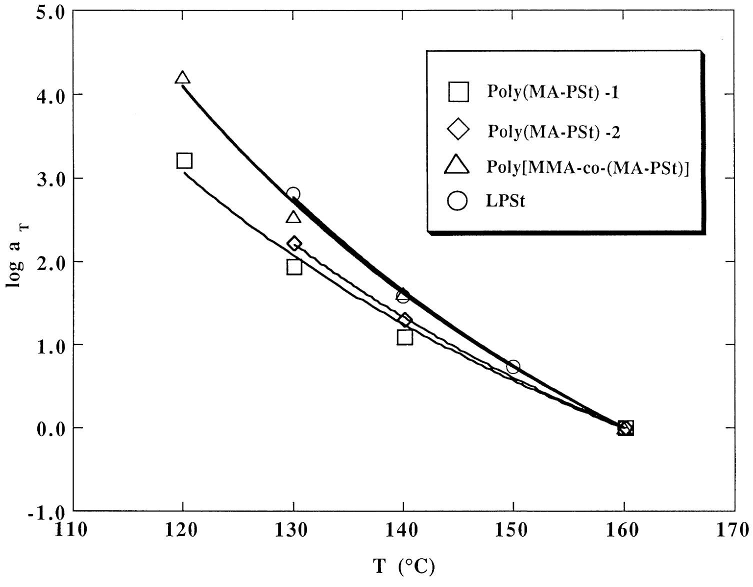

Fig. 6. Temperature dependence of the shift factor a_T for all polymers. $T_r = 160°C$.

Table 3
WLF parameters (reference temperature $T_r = 160$°C) and film forming properties

Sample code	C_1^r	C_2^r	f_r	$\alpha_f \times 10^4$	Film forming properties
Poly(MA-PSt)-1	6.91	130.3	0.0628	4.82	Brittle
Poly(MA-PSt)-2	6.30	142.8	0.0689	4.83	Brittle
Poly[MMA-*co*-(MA-PSt)]	7.77	115.8	0.0559	4.83	Good
LPSt	7.68	117.2	0.0565	4.82	Good

macromonomer in poly[MMA-*co*-(MA-PSt)] is 2.9% which means there are nearly three branches per 100 repeating units in the backbone chain. Thus, the branch density of poly[MMA-*co*-(MA-PSt)] is much less than those of the poly(macromonomer)s poly(MA-PSt)-1 and poly(MA-PSt)-2. The DP of the backbone chain of the copolymers is 6577 which is much larger than the M_c of PMMA. Therefore, the appearance of the plateau region in the poly[MMA-*co*-(MA-PSt)] is considered as the molecular chain entanglement. It should be considered here that the effect of phase separated structure in the copolymer samples can also affect the rheological properties. Temperature dependences of the shift factors for all of the polymers including poly[MMA-*co*-(MA-PSt)] are shown in Fig. 6. The temperature dependence of all the shift factors is represented by the WLF equation with different C_1 and C_2 parameters as shown in Table 3.

From C_1 and C_2, the volume fraction of free volume at the reference temperature, f_r, and the thermal expansion of free volume relative to total volume, α_f, can be calculated by the following relations [25]:

$$C_1 = \frac{B}{2.303 f_r} \tag{1}$$

$$C_2 = \frac{f_r}{\alpha_f} \tag{2}$$

The calculated values of f_r and α_f are shown in Table 3 assuming the constant B is unity. In Table 3, the value of α_f is almost the same for all polymers, while f_r for the poly(macromonomer)s is larger than those of poly[MMA-*co*-(MA-PSt)] and LPSt. The tendency of f_r is consistent with the fact that T_g of the poly(macromonomer)s is lower than those of poly[MMA-*co*-(MA-PSt)] and linear PSt [15]. The behavior of the copolymer is similar to that of linear polymers probably because the polystyrene branches are too short to cause the clear phase separation effect.

We investigated the film forming property by the solvent casting method. The results are shown in Table 3. When the poly(macromonomer)s, poly(MA-PSt)-1 and poly(MA-PSt)-2, were cast onto glass plates, many cracks were always created by sample contraction during the solvent evaporation and the formed films were too brittle to handle as already reported [14], while no crack was formed in the film specimens of the LPSt and poly[MMA-*co*-(MA-PSt)].

The mechanical strength of the linear amorphous polymers like fracture strength and tensile strength depends on the molecular weight of the polymer molecules which decreases as the molecular weight of the polymer decreases [29–32]. Turner reported that the tensile strength decreases linearly with the inverse molecular weight [30], and becomes zero at a certain critical molecular weight, M_0, where polymer materials become very brittle. Since M_0 is believed to be closely related to M_c, the brittle property of the poly(macromonomer)s in this study is considered to be ascribed to the absence of the chain entanglement. Therefore, both the rheological properties and the film forming property of the poly(macromonomer)s are well explained by the absence of the molecular chain entanglement network.

4. Conclusion

It was shown from the rheological data that the intermolecular chain entanglement couplings are restricted in the poly(macromonomer) systems due to the multibranched structure of high branch density. This is consistent with the poor film forming property of the branched polymers.

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