Miscibility of regular multibranched polystyrene with linear polystyrene

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Differential scanning calorimetry (d.s.c.) measurements on the 50/50 blends of well-defined multibranched polystyrenes and linear polystyrenes were carried out to investigate the miscibility between polymer components having the same constitutional repeating units but different molecular architectures. Multibranched polystyrenes with different branch number and length were prepared by the radical polymerization of polystyrene macromonomers of different molecular weights possessing a different polymerizable end group, i.e. a vinylbenzyl end group and methacryloyl end group. D.s.c. curves showed one or two thermal transitions corresponding to the glass transitions depending on both the branching architecture of the multibranched polystyrene, namely poly(macromonomer)s, and the molecular weight of the linear polystyrenes. The miscibility between the poly(macromonomer) and the linear polystyrenes decreased with increase in both branch number of poly(macromonomer)s and the molecular weight of the linear polystyrene. The miscibility increases with increase in the branch length but was not much influenced by the chemical structure of the central backbone of the poly(macromonomer)s. These results indicate that the miscibility in the athermal binary multibranched–linear polystyrene blends is influenced by the branching architecture, and the blends locate near the miscible/immiscible boundary.

(Keywords: polymer blend; miscibility; polystyrene)

Introduction

Polymer blend systems are one of the major branches of polymer science and technology[1–4], where understanding of the miscibility of the constituent polymers, the phase diagram as well as the morphology, are very important. Miscibility in blends of unlike polymer components has been discussed by Flory–Huggins lattice theory with the χ parameter. There have been many investigations on the limitation and expansion of Flory–Huggins theory to explain the effect of the free volume of mixing and the specific interaction in polymer blends which produce the lower critical solution temperature[5–8].

Recently, the architectural and conformational effects on the miscibility in polymer blends and solutions have been investigated from the theoretical point of view[9–12]. Bates and Fredrickson have proposed a theoretical treatment of such effects on miscibility in athermal binary blends, where each component has similar constitutional repeating units but different polymer architectures[11,12]. However, there are only limited published data on this subject at present.

We have been investigating the properties of poly(macromonomer)s, i.e. polymerization products of macromonomers[13–17]. Poly(macromonomer)s are regular multibranched polymers with very high branch density. For example, poly(macromonomer)s prepared from polystyrene macromonomers are multibranched polystyrenes with (i) regular branch length, (ii) regular branch number, and (iii) regular branching period[17]. Since both the degree of polymerization and the length of branches can be varied, the blends of poly(macromonomer)s with linear polystyrene might be interesting polymer blend systems for the study of the effect of the branching architecture on miscibility. In this paper, we report the preliminary results of differential scanning calorimetry (d.s.c.) measurements on poly(macromonomer)–linear polystyrene blends to discuss the miscibility in athermal binary blends of the multibranched polystyrene and linear polystyrene.

Experimental

ω-Vinylbenzyl and ω-methacryloyloxyethyl polystyrene macromonomers (VB-PSt-sBu and MA-PSt-sBu) of different molecular weights were synthesized by the living anionic polymerization technique[18]. That is, living anionic polymerizations of styrene monomer were carried out in toluene with s-BuLi. Then, after the consumption of the monomer, termination by tetrahydrofuran (THF) solution of vinylbenzyl chloride was carried out at −78°C to produce the macromonomer VB-PSt-sBu, while for MA-PSt-sBu, ethylene oxide was added and terminated by THF solution of methacryloyl chloride at −78°C.

These macromonomers were polymerized using azobisisobutyronitrile as an initiator in benzene at 60°C for 24 h. Polymerization products were purified by precipitation–extraction procedures with cyclohexane–petroleum ether mixed solvents to remove unreacted macromonomers. The purification was repeated several times until the sharp peak in gel permeation chromatography (g.p.c.), corresponding to the unreacted macromonomer, completely disappeared. The poly(macromonomer)s obtained by this method have the chemical structures shown below, with different n and k values which are shown in *Table 1*.

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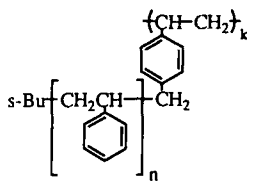
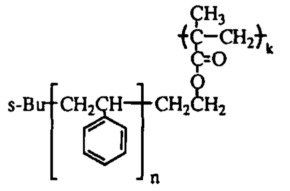
Table 1 Characteristics of multibranched and linear polystyrenes

Sample code	$M_w \times 10^{-4}$ [a]	M_w/M_n	k [b]	n [c]	T_g (°C) Onset	T_g (°C) Midpoint
Multibranched polystyrene[d]						
Poly(VB-PSt-sBu840)-13.8	1.43	1.23	13.8	6.6	69.5	71.7
Poly(VB-PSt-sBu840)-244	25.1	1.06	244	6.6	70.8	73.4
Poly(MA-PSt-sBu800)-12.7	1.13	1.21	12.7	6.1	52.3	54.9
Poly(MA-PSt-sBu800)-549	48.4	2.13	549	6.1	62.9	66.7
Poly(MA-PSt-sBu2900)-20	6.27	1.86	20	26.3	89.6	93.5
Poly(MA-PSt-sBu2900)-171	54.7	2.52	171	26.3	88.5	90.7
Linear polystyrene						
PSt5K	0.52	1.03	-	49.5	84.9	87.6
PSt10K	0.98	1.02	-	93.7	94.7	97.3
PSt100K	10.3	1.02	-	990	103.5	105.5
PSt1260K	126	1.05	-	12 100	102.3	104.1

[a] Determined by g.p.c. using a low angle light scattering detector
[b] Number of branch chains
[c] Number of styrene units per polystyrene branch and linear polystyrene
[d] The number in parentheses in the sample code represents the molecular weight (M_n) of the macromonomer and those following the code represent the degree of polymerization of poly(macromonomer)



Poly(VB-PSt-sBu)



Poly(MA-PSt-sBu)

The M_w and M_w/M_n values of poly(macromonomer)s were determined by g.p.c. (Tosoh HLC802A) equipped with a low angle laser light scattering detector (Tosoh LS-8) and a refractive index detector[15]. G.p.c. was operated with Tosoh G6000H, G4000H and G2000H columns on toluene at 25°C. The weight average molecular weight (M_w), molecular weight distribution (M_w/M_n), the number of branches (k) of poly(macromonomer)s, and the M_w of the macromonomers are summarized in *Table 1*. Linear polystyrenes (PSt) are the polystyrene standards supplied from Tosoh Co. Ltd.

Blend samples as well as poly(macromonomer)s and PSt for thermal analysis were prepared by freeze-drying a benzene solution (10% w/v) of each polymer and the poly(macromonomer)/PSt mixtures (50/50 by weight) and further dried under vacuum for several days.

The glass transition temperatures, T_g, of poly(macromonomer)/PSt blends and each polymer component were determined using a Rigaku-DSC8230. The samples (~6–9 mg) were sealed into Al pans and heated from -20 to 150°C with a heating rate of 10°C min^{-1}, then held at 150°C for 5 min and cooled to room temperature at ~5–10°C min^{-1}. Liquid N_2 was used for cooling from room temperature to -20°C. The second scan was carried out under the same conditions. The third scan curves were taken as the d.s.c. data.

Results and discussion

Poly(VB-PSt-sBu840)s in *Table 1* have short polystyrene branches, with $M_n = 840$, and also have a polystyrene central backbone ($k = 13.8$, 244) as the result of polymerization of the vinylbenzyl end group. D.s.c. curves of these two poly(macromonomer)s are shown as curve a in *Figures 1* and *2*. It is seen that there is a single endothermic transition at 70°C which corresponds to the T_g of the poly(macromonomer)s. This temperature is

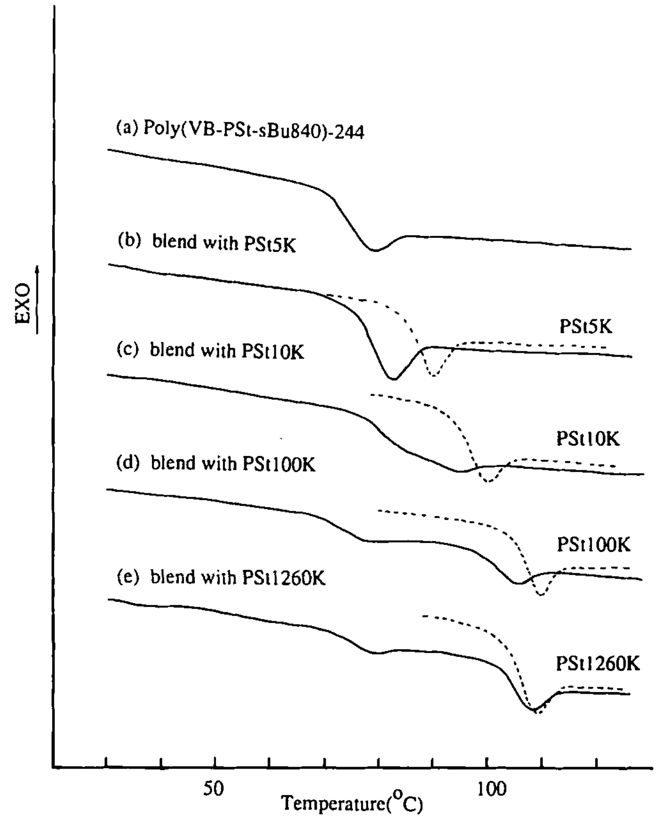


Figure 1 Comparison of d.s.c. curves of multibranched polystyrene/linear polystyrene blends (50/50) with different molecular weight linear polystyrene. The multibranched polystyrene is poly(VB-PSt-sBu840) possessing 244 branches. D.s.c. curves for the linear polystyrenes around their T_g are also shown by dashed lines for comparison. Heating rate was 10°C min^{-1}. The third scan data are shown

much lower than the T_g of PSt of the same molecular weight (102–103°C for onset value). The lowering in T_g of poly(VB-PSt-sBu840)s is ascribed to the excess free volume associated with the many branched chain ends per molecule[13]. The reduction of T_g decreases as the branch length increases and is also affected by the chemical structure of the branching points[19]. The T_g determined by both onset and midpoint of the transition for these poly(macromonomer)s and those of linear polystyrenes are shown in *Table 1*.

D.s.c. curves for the blend samples of poly(VB-PSt-sBu840) having 244 branches with linear polystyrenes (PSt5K, 10K, 100K and 1260K) are shown in *Figure 1*. It is seen that there is only a single transition at ~75°C in curve b for the blend with PSt5K, which is intermediate between those of the poly(VB-PSt-sBu840) and PSt5K alone. This indicates that the poly(VB-PSt-sBu840) with $n = 244$ is miscible with PSt5K. On the other hand, there are two distinct transitions in curves c–e for the blends with PSts 10K, 100K and 1260K, indicating that the poly(VB-PSt-sBu840) is partially miscible (curve c) or immiscible (curves d and e) with the higher molecular weight PSts.

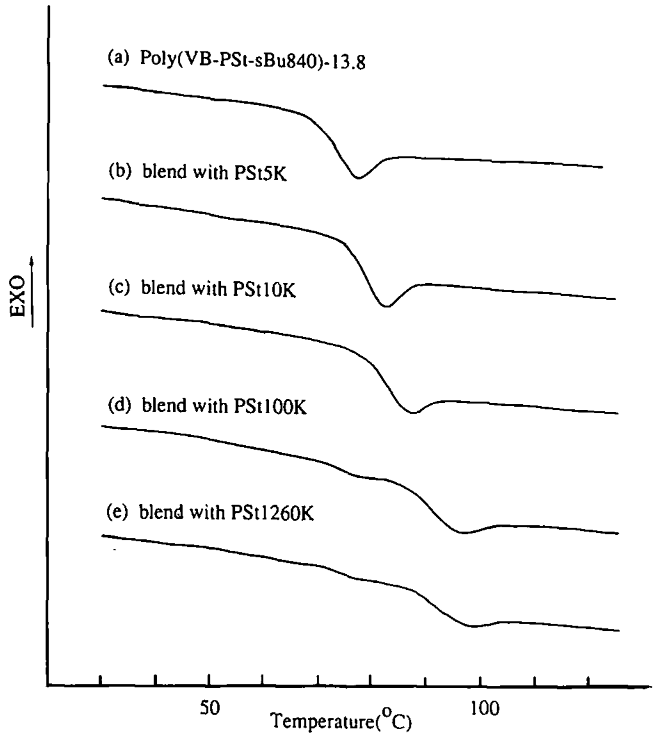


Figure 2 Comparison of d.s.c. curves of multibranched polystyrene/linear polystyrene blends (50/50) with different molecular weight linear polystyrene. The multibranched polystyrene is poly(VB-PSt-sBu840) possessing 13.8 branches. Heating rate was 10°C min^{-1}. The third scan data are shown

D.s.c. curves for the blends of poly(VB-PSt-sBu840) having 13.8 branches with PSts are shown in *Figure 2*. Similarly to *Figure 1*, d.s.c. curves in *Figure 2* indicate the miscibility decrease as the molecular weight of the PSt increases. However, the effect of the number of branches on the miscibility is also seen by comparing *Figures 1* and *2*. That is, in contrast to two transitions in curve c of *Figure 1*, there is only a single transition in curve c of *Figure 2*. Furthermore, in curves d and e for the blends with PSts 100K and 1260K in *Figure 2*, the higher temperature transitions, corresponding to the T_g of PSt, are shifted towards lower temperature and the low temperature transition, corresponding to the T_g of the poly(macromonomer), is unclear. These features are the result of the increased miscibility in *Figure 2*.

Figure 3 shows the comparison of d.s.c. curves of the blends of poly(VB-PSt-sBu)s and poly(MA-PSt-sBu)s with PSt100K to investigate the effect of the central backbone structure and the branch length. Poly(MA-PSt-sBu)s have a polymethacrylate backbone as the result of polymerization of the methacrylate end group of the macromonomers. Thus, precisely speaking, these are a type of graft copolymer with high polystyrene branch density. The weight fraction of the central methacrylate backbone is 0.14 for poly(MA-PSt-sBu800)s and 0.039 for poly(MA-PSt-sBu2900)s, and the values are constant against the change in k, i.e. number of branches, but decrease with increase in M_n of the branch length.

D.s.c. curves c and d for the blends of poly(MA-PSt-sBu800)s with PSt100K in *Figure 3* are similar to curves a and b for blends of poly(VB-PSt-sBu840)s, where the branch lengths of these poly(macromonomer)s are nearly equal. This result indicates that the miscibility between

Table 2 Glass transition temperatures of blends (50/50) of multibranched and linear polystyrenes

Blend sample		T_g (°C)				
		1st peak		2nd peak		
Multibranched polystyrene	Linear polystyrene	Onset	Midpoint	Onset	Midpoint	Remarks
Poly(VB-PSt-sBu840)-13.8	5K	74.9	77.0	–	–	miscible
	10K	77.8	80.9	–	–	miscible
	100K	68.1	72.7	86.1	88.8	partially miscible
	1260K	69.3	73.1	86.9	90.8	partially miscible
Poly(VB-PSt-sBu840)-244	5K	75.2	77.3	–	–	miscible
	10K	75.8	79.1	86.0	87.8	partially miscible
	100K	69.2	72.8	98.4	100.2	immiscible
	1260K	70.9	73.2	100.5	102.6	immiscible
Poly(MA-PSt-sBu800)-12.7	100K	54.5	60.7	79.3	84.3	partially miscible
Poly(MA-PSt-sBu800)-549	100K	62.3	65.1	100.7	102.9	immiscible
Poly(MA-PSt-sBu2900)-20	100K	77.7	86.3	–	–	miscible
Poly(MA-PSt-sBu2900)-171	100K	85.6	89.7	100.8	103.0	immiscible

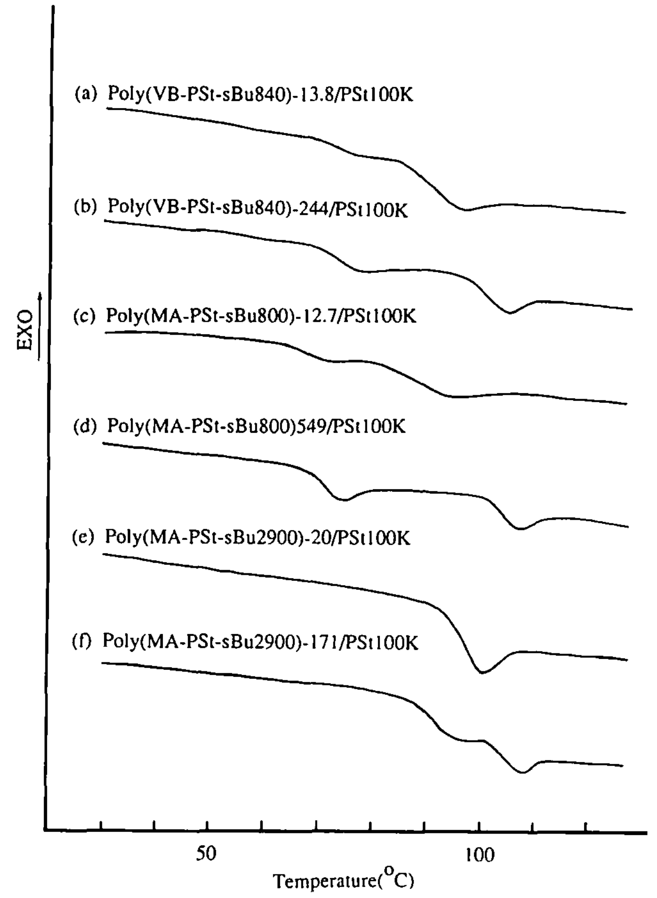


Figure 3 Comparison of d.s.c. curves of multibranched polystyrene/linear polystyrene blends (50/50) with 100K linear polystyrene. The multibranched polystyrenes are poly(VB-PSt-sBu840)s possessing 13.8 and 244 branches, poly(MA-PSt-sBu800)s possessing 12.7 and 549 branches, and poly(MA-PSt-sBu2900)s possessing 34 and 171 branches. The measurement conditions are the same as in *Figure 1*

poly(macromonomer)s and linear polystyrene is little affected by the chemical structure of the central backbone. Furthermore, the d.s.c. curve e in *Figure 3* for poly(MA-PSt-sBu2900)-20/PSt100K blend shows a single transition, while there are two distinct transitions in curve c for poly(MA-PSt-sBu800)-12.7/PSt100K blend. This indicates that increase in branch length increases the miscibility. The T_g values for these blends are summarized in *Table 2*.

Very recently, Fredrickson *et al.* have proposed a theoretical treatment of miscibility in athermal binary blends of chemically identical linear and branched homopolymers with the consideration of the entropic contribution to the excess free energy associated with the non-local liquid structure greater than the size of the monomeric units[12]. They derived a spinodal equation for the linear/branched blend in dimensionless form as:

$$1/\phi + 1/[(V_2/V_1)(1-\phi)] - 2\alpha_\varepsilon V_1 = 0 \qquad (1)$$

under the assumption of the Gaussian statistics in the pure component melt. Here, V_1 is the molecular volume of the linear polymer given by vN_1, and V_2 is that of the branched polymer given by $vQ(L+M)$. L is the statistical length of the backbone chain between the two neighbouring branch chains, M is the branch length, v is the volume of these statistical repeating units, N_1 and Q are their numbers, ϕ is the composition, and α_ε is the interaction energy density in dimensionless form (entropic contribution). Fredrickson *et al.* discuss the critical condition for the miscibility between the components with $V_1 = V_2$ using the parameters L and M as:

$$\sigma = \frac{1}{L+M} \sim \frac{b^2}{V_s^{2/3}} \qquad (2)$$

where b is the statistical segment length and V_s is defined as the minimum of V_1 and V_2.

Although the Gaussian approximation cannot be applicable to the multibranched polymers in this study, it is worth considering with this treatment because the blend systems here can be considered to be athermal and also the branch period and branch length correspond to L and M. For the poly(macromonomer)s, $Q=k$, $L=1$ and $1/(L+M) \approx 1/M$. Thus, the increase in branch length increases the miscibility of the blends, as observed in the data of poly(MA-PSt-sBu2900)/PSt100K blends in *Figure 3*. These multibranched–linear polystyrene blends might locate much closer to the miscible/immiscible boundary than the polyethylene–poly(ethylethylene) blends[12] because of the large M. However, since L and M have the same value for the poly(macromonomer)s in *Figures 1* and *2*, the miscibility between poly(macromonomer)s and linear polystyrenes is also influenced by the branch number, i.e. the central backbone length under the same L and M.

Increase in the branch number at the same L and M increases the molecular volume V_2 in equation (1), which is one reason for the increase in immiscibility. On the other hand, when the branch number increases to a great extent, the chain length ratio of the backbone to the branch becomes large and the molecular shape of the poly(macromonomer)s changes gradually from that of the spherical star-branched polymer to the comb-branched polymer[14]. Recently, we found that the backbone chain of poly(macromonomer)s has a long statistical segment length in the large branch number region because of the high branch density[20]. The poly(macromonomer) can be considered to be a polymer having axisymmetric tethered polystyrene chains around it[21]. Therefore, the enhancement of immiscibility by increase in branch number can also be partially explained by the conformational asymmetry, i.e. by the increase in the asymmetry parameter $(\beta_{PM}/\beta_{PSt})^2$ from unity, which increases α_ε in equation (1); $\beta_i^2 = (b_i^2/6v_i)$ and the subscript PM represents the poly(macromonomer). In addition to this, the effect of the whole molecular shape or anisotropy[22] might also be involved in the immiscibility between the poly(macromonomer)s of large branch number and linear polystyrene. Further study, including phase behaviour, is necessary and is now in progress.

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