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Radical copolymerization reactivity of binary macromonomers

Koji Ishizu* and Kenro Sunahara
Department of Polymer Science, Tokyo Institute of Technology 2-12, Ookayama, Meguro-ku, Tokyo 152, Japan

Vinylbenzyl-terminated polystyrene (PS) and polyisoprene (PI) macromonomers were synthesized by the coupling reaction of corresponding living anions with *p*-chloromethylstyrene. Free-radical copolymerizations of binary PS and PI macromonomers were carried out in benzene, varying the molecular weight of macromonomers. The reactivity ratios of these systems were close to an azeotropic copolymerization, in the case of the same degree of polymerization of binary macromonomers.

(Keywords: macromonomer; radical copolymerization; reactivity ratio)

Introduction

The particular chemical structure of block copolymers is reflected in the most fundamental and interesting ways by incompatibility effects. Leibler[1] was the first to make clear theoretically the order–disorder transition of diblock copolymers. Subsequently, de la Cruz and Sanchez[2] calculated, from mean-field theory, the phase stability criteria and static structure factors for a simple AB graft copolymer, for star copolymers with equal number of A and B arms (A_nB_n star: heteroarm star), and for *n*-arm star diblock copolymers. They predicted that it is easier to phase-separate star copolymers than the corresponding graft and block copolymers.

There have been reports of attempts to prepare A_nB_n stars via radical[3], anionic[4–10] and cationic[11] polymerizations. We have suggested a novel architecture for A_nB_n stars by means of the organized polymerization of a microphase-separated structure formed by diblock macromonomers possessing central polymerizable groups[12–14]. In this environment, the polymerizable groups at the position of the block junction should be oriented regularly at the domain interfaces.

In previous work[15], vinylbenzyl-terminated polystyrene (PS) and polyisoprene (PI) macromonomers were synthesized by the coupling reaction of corresponding living anions with *p*-chloromethylstyrene (CMS). The reactivity ratios of anionic copolymerizations of binary PS and PI macromonomers were close to an azeotropic copolymerization.

In this article, free-radical copolymerizations of binary PS and PI macromonomers were carried out in benzene, varying the molecular weight of macromonomers. The copolymerization reactivity was estimated from the distribution functions by gel permeation chromatography (g.p.c.) of the comb-shaped copolymers produced.

Experimental

Synthesis and characterization of macromonomers. Vinylbenzyl-terminated PS macromonomers were synthesized by the coupling reaction of polystyryl lithium living anion with an excess amount of CMS in a benzene–tetrahydrofuran (THF) mixed solvent. Details concerning the synthesis and characterization have been given elsewhere[15,16].

Vinylbenzyl-terminated PI macromonomers were also synthesized by the coupling reaction between polyisoprenium lithium end-capped with α-methylstyrene (MS) and CMS in a benzene–THF mixture[15]. Details concerning the synthesis and characterization have also been given elsewhere[15]. The characteristics of the PS and PI macromonomers (SM and IM) used are listed in *Table 1*.

Free-radical copolymerization of binary macromonomers. Free-radical copolymerization of binary macromonomers was carried out in benzene at 60°C using 2,2′-azobisisobutyronitrile (AIBN) as an initiator in a sealed glass apparatus under high vacuum. After polymerization, the copolymerization solution was poured into a large excess of methanol. Next, the copolymerization product was extracted by n-hexane to remove PI homopolymer.

Free-radical copolymerization of binary macromonomers will form copolymers with comb-shaped structure. However, although the primary structure in the copolymers is the comb-shape, the solution and solid properties will be similar to those of heteroarm star copolymers. In the preparation process, the relevant copolymerization parameters are very important in determining the arm distribution in the resulting comb-shaped copolymers, regardless of the same terminal end group (vinylbenzyl).

In this copolymerization, kinetic equations are expressed with four propagation steps, as developed by Mayo and Lewis[17]. Two monomers, M_1 and M_2, are defined as the vinylbenzyl-terminated PS and PI macromonomers, respectively. Each propagation reaction has a characteristic rate constant, k_{ab}, where the first

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* To whom correspondence should be addressed

Table 1 Characteristics of PS and PI macromonomers

Code[a]	M_n[b] × 10^{-4}	M_w/M_n[b]	Vinylbenzyl group (number/1-polymer)
SM1	1.35	1.05	0.89
IM1	1.02	1.06	0.97
IM2	1.67	1.01	1.02

[a] SM, PS macromonomer; IM PI macromonomer
[b] Determined by g.p.c.
[c] Determined by g.p.c. with r.i. and u.v. double detectors

Table 2 Copolymerization conditions and composition of heteroarm copolymers[a]

No.	Feed macromonomer M_1[b]	M_2[c]	F_1[d]	Heteroarm copolymer f_1[e]
RC1-1	SM1	IM1	0.274	0.204
RC1-2			0.350	0.411
RC1-3			0.694	0.704
RC1-4			0.791	0.752
RC2-1	SM1	IM2	0.236	0.179
RC2-2			0.382	0.302
RC2-3			0.520	0.496
RC2-4			0.773	0.706
RC2-5			0.889	0.783

[a] Polymerized in benzene initiated by AIBN (0.049 mol l^{-1}) at 60°C (macromonomer concentration ~0.01 mol l^{-1})
[b] SM1, $\overline{DP} = 130$
[c] IM1, $\overline{DP} = 150$; IM2, $\overline{DP} = 246$
[d] M_1 mole fraction in feed macromonomers
[e] M_1 mole fraction in heteroarm copolymers: determined by g.p.c. with r.i. and u.v. double detectors

subscript refers to the active centre and the second refers to the monomer. Defining the propagation rate constant ratio k_{11}/k_{12} and k_{22}/k_{21} as r_1 and r_2, respectively, one finally obtains:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]}\,\frac{r_1[M_1]+[M_2]}{r_2[M_2]+[M_1]} \qquad (1)$$

The reactivity ratios r_1 and r_2 can be estimated by the curve-fitting procedure[18]. The conversion was controlled at less than 15 wt% in order to estimate the copolymerization reactivities. The mole fraction of the monomer M_1 in the copolymer (f_1) was determined by the area ratio of refractive index (r.i.) and u.v. (252 nm) intensities on a g.p.c. chart (using a calibration curve constructed from a mixture of PS and PI homopolymers[15]). The g.p.c. measurements were performed on a Tosoh high-speed liquid chromatograph (HLC-8020) with THF as eluent at 38°C, a TSK gel GMH$_{XL}$ column and a flow rate of 1.0 ml min^{-1}.

Results and discussion

Table 1 lists characteristics of vinylbenzyl-terminated PS and PI macromonomers. The conversion was almost 100%, within experimental error, in SM and IM macromonomers. The g.p.c. profiles showed that SM and IM macromonomers had a single and narrow molecular weight distribution. The direct coupling of polystyryl or polyisoprenium (capped with MS units) anions with CMS formed the SM or IM macromonomer, respectively, possessing one vinylbenzyl group at the terminal end.

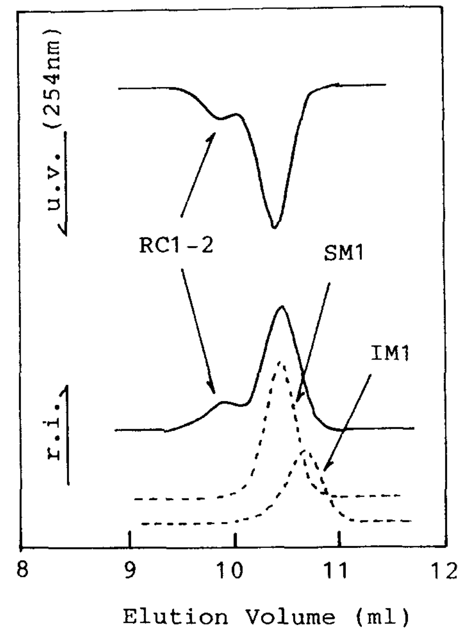

Figure 1 G.p.c. profiles of RC1-2 and macromonomers

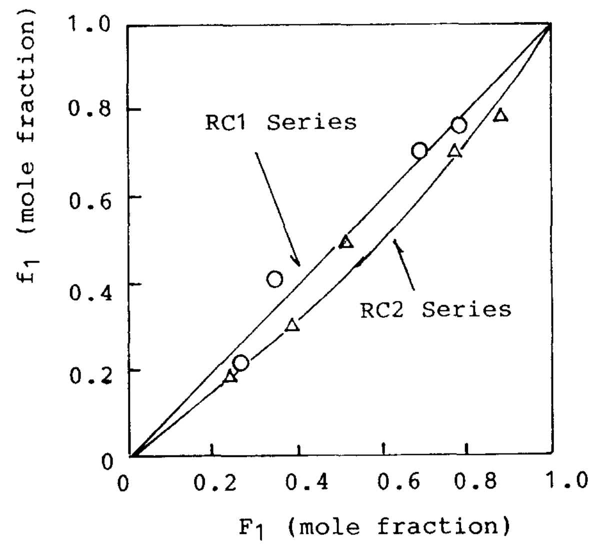

Figure 2 Instantaneous composition (mole fraction f_1) as a function of macromonomer composition (mole fraction F_1) for RC1 and RC2 copolymerization series

Free-radical copolymerizations of binary SM and IM macromonomers were carried out in benzene, varying the feed molar ratio of SM (M_1) to IM (M_2) macromonomers (macromonomer concentration ~0.01 mol l^{-1}). *Table 2* lists the copolymerization conditions (F_1 and f_1 indicate the M_1 fraction of feed macromonomer concentration and the M_1 fraction of the heteroarm copolymer, respectively). Typical g.p.c. profiles of RC1-2, SM1 and IM1 macromonomers are shown in *Figure 1*. In both copolymerization series, new peaks appear at the high-molecular-weight side compared to SM and IM macromonomers. These peaks correspond to heteroarm copolymers. After separation of the distribution of heteroarm copolymer by simulation, using a personal computer, f_1 was determined from the calibration curve.

Figure 2 shows the instantaneous composition (mole fraction f_1) as a function of macromonomer composition (mole fraction F_1) for the RC1 and RC2 copolymerization series. It is found from these curves that the RC1 series ($r_1 = \sim 1.0$ and $r_2 = \sim 1.0$) proceeds with azeotropic copolymerization. So, when $r_1 = r_2 = 1$, the macromonomers show equal reactivity towards both propagating species, and the copolymer composition is the same as the comacromonomer composition. In this copolymerization system, the degree of polymerization (DP) of both macromonomers was almost the same (for SM1 $\overline{DP} = 130$, for IM1 $\overline{DP} = 150$).

However, in the case of RC2, where the two reactivities are different ($r_1 = 0.65$ and $r_2 = 1.39$), the IM macromonomer is more reactive and the heteroarm copolymer contains a large proportion of the more reactive monomer in random placement. In the RC2 system, the DP of the IM macromonomer was larger than that of SM (for SM1 $\overline{DP} = 130$, for IM2 $\overline{DP} = 246$).

There have been many reports on the copolymerization reactivity of macromonomer with comonomer having low molecular weight. In some cases, the copolymerization reactivity of a macromonomer is nearly identical to that of the small monomer corresponding to the polymerizable end group. However, the low copolymerization reactivity of the macromonomer in suspension polymerization in aqueous media was also shown to be due to the phase separation during the copolymerization[19]. Ito *et al.*[20,21] have studied the effect of the molecular weight of the macromonomers on the copolymerization reactivity. They found that the relative reactivities were reduced with an increase in molecular weight of the macromonomers. Such reduction of the relative reactivity was discussed in terms of the thermodynamic repulsive interaction between unlike polymers or the aggregation. The observed reactivity involves the effects of various kinds of interactions between polymer segments or between polymer segment and solvent. These interactions cause the aggregation (micelle formation) or segregation (phase separation) of the particular reaction species. When the polymerization solvent is a good solvent for the macromonomer and comonomer chain, homogeneous distribution of the macromolecular species is expected. However, a small difference between solvent quality for the macromonomer and the comonomer chain can cause inhomogeneous distribution of the reaction species in the reaction mixture in contrast to the case of the corresponding small monomer pairs.

For a series of experiments (RC1) involving macromonomers with a similar $\overline{DP}$, it was found that $r_1 = r_2 = 1$. However, for a series of experiments (RC2) involving a longer PI macromonomer, the PI macromonomer was found to be more reactive. We would have expected benzene at 60°C to be a good solvent for both types of PI and PS polymers. Then, we would not expect micellization to occur. One possible explanation for these results seems to be the compatibility effect between the macromonomers and the propagating copolymer chains. The copolymerization mechanism is explained as follows.

(1) In the RC1 system, the propagating copolymers with equal volume fraction for PS and PI components seem to be produced at the initial reaction stage. So, the compatibility between the propagating copolymer chain and PS or PI macromonomers is similar. Binary macromonomers can interpenetrate with equal probability into the propagating copolymer chains to bring their end groups near the radical sites.

(2) In the RC2 system, the propagating copolymers produced at the initial stage have a high content of the PI component. These propagating copolymer chains are more compatible with the PI macromonomer than with the PS macromonomer, because the propagating copolymer has a high PI component. As a result, PI macromonomer can interpenetrate sufficiently into propagating copolymer chains that have radical sites. Thus, the copolymerization reactivity seems to depend strongly on the molecular weights, even in the copolymerization systems of binary macromonomers composed of the same functional group.

We are investigating another architecture of A_nB_n heteroarm copolymers by means of radical alternating copolymerization of binary vinylbenzyl-terminated A and maleimide-terminated B macromonomers. These results will be reported in the near future.

References

1 Leibler, L. *Macromolecules* 1980, **13**, 1602

2 de la Cruz, M. O. and Sanchez, I. C. *Macromolecules* 1986, **19**, 2501

3 Berlinova, I. V. and Panayotov, I. M. *Makromol. Chem.* 1989, **190**, 1515

4 Tsitsilianis, C., Chaumont, P. and Rempp, P. *Makromol. Chem.* 1990, **191**, 2319

5 Tsitsilianis, C., Graff, S. and Rempp, P. *Eur. Polym. J.* 1991, **27**, 243

6 Penisi, R. W. and Fetters, L. J. *Macromolecules* 1988, **31**, 1094

7 Quirk, R. P., Lee, B. and Schock, L. *Makromol. Chem. Macromol. Symp.* 1992, **53**, 201

8 Quirk, R. P. and Ingatz-Hoover, F. in 'Recent Advances in Anionic Polymerization' (Eds T. E. Hogen-Esch and J. Smid), Elsevier, New York, 1987, p. 393

9 Einert, G. and Herz, J. *Makromol. Chem.* 1980, **181**, 59

10 Eshwey, H. and Burchard, W. *Polymer* 1975, **16**, 180

11 Kanaoka, S., Omura, T., Sawamoto, M. and Higashimura, T. *Macromolecules* 1992, **25**, 6407

12 Ishizu, K., Yukimasa, S. and Saito, R. *Polymer* 1992, **33**, 1982

13 Ishizu, K., Yukimasa, S. and Saito, R. *Polym. Commun.* 1991, **32**, 386

14 Ishizu, K. and Kuwahara, K. *J. Polym. Sci., Polym. Chem. Edn* 1993, **31**, 661

15 Ishizu, K. and Kuwahara, K. *Polymer* 1994, **35**, 4907

16 Ishizu, K., Shimomura, K. and Fukutomi, T. *J. Polym. Sci., Polym. Chem. Edn* 1991, **29**, 923

17 Mayo, F. R. and Lewis, F. M. *J. Am. Chem. Soc.* 1944, **66**, 1594

18 Tidwell, P. W. and Mortimer, G. A. *J. Polym. Sci., Part A* 1965, **3**, 369

19 Schulz, G. O. and Milkovich, R. J. *J. Polym. Sci., Polym. Chem. Edn* 1984, **22**, 1633

20 Ito, K., Tsuchida, H., Hayashi, A., Kitano, T., Yamada, E. and Matsumoto, T. *Polym. J.* 1985, **17**, 827

21 Ito, K., Yokoyama, S., Arakawa, F., Yukawa, Y., Iwashita, T. and Yamasaki, Y. *Polym. Bull.* 1986, **16**, 337