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Radical copolymerization reactivity of maleate-terminated poly(ethylene glycol) with vinylbenzyl-terminated polystyrene macromonomers

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Abstract

Free-radical copolymerizations of vinylbenzyl-terminated polystyrene (PS–VM; M_1) and maleate-terminated poly(ethylene glycol methyl ether) PEG–MM; M_2) were carried out in benzene. Mixtures of the PEG–MM and PS–VM showed phase separation during copolymerization. The copolymerization reactivity was estimated from the distribution functions by gel permeation chromatography of the comb-shaped copolymers produced. The reactivity ratios ($r_1 = 0.765$ and $r_2 = 0.064$) obtained for the binary macromonomer system were different from corresponding model systems of styrene and maleic acid ethyl ester ($r_1 = 0.13$ and $r_2 = 0.035$) due to phase separation. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Macromonomer; Reactivity ratio; Comb-shaped copolymer

1. Introduction

Homopolymerization of macromonomers provides regular multi-branched polymers with a branch density. Since both the degree of polymerization (P_w) and the length of branches are varied, poly(macromonomer)s are interesting models for the study of branched polymers [1–4]. Recent structure characterization of such long-chain poly-(macromonomer)s revealed that the main chain exhibits an almost rodlike conformation [5,6]. Investigations on such poly(macromonomer)s by X-ray scattering and polarized light microscopy showed the formation of lyotropic phases [7,8].

Free-radical copolymerization of binary macromonomers will form copolymers with comb-shaped structure. In the preparation process, the relevant copolymerization parameters are very important in determining the branch distribution in the resulting comb-shaped copolymers. In a previous work [9], free-radical copolymerizations of binary vinylbenzyl-terminated polystyrene (PS) and polyisoprene (PI) macromonomers were carried out in benzene, varying the molecular weight of the 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.

In this article, free-radical copolymerizations of maleate-terminated poly(ethylene glycol methylether) (PEG–MM) with vinylbenzyl-terminated PS (PS–VM) macromonomers were carried out in benzene. The copolymerization reactivity was estimated from the distribution functions by gel permeation chromatography (g.p.c.) of the comb-shaped copolymer produced.

2. Experimental

2.1. Synthesis and characterization of macromonomers

Vinylbenzyl-terminated PS macromonomer (PS–VM) was synthesized by the coupling reaction of polystyryl lithium living anion with an excess amount of *p*-chloromethylstyrene (CMS) in a benzene-tetrahydrofuran (THF) mixed solvent. Details concerning the synthesis and characterization have been given elsewhere [10,11].

Maleate-terminated poly(ethylene glycol methylether) macromonomer (PEG–MM) was prepared under nitrogen from commercially available poly(ethylene glycol methylether) (PEG; Aldrich: $\bar{M}_n = 5000$) by alkoxidation with sodium hydride in benzene followed by reaction with maleic anhydride (for 6 h at 25°C). Reaction product was poured by a large excess of diethyl ether. PEG–MM was separated by filtration and purified by column chromatography (silica gel, chloroform as eluent). The content of terminal maleate group was determined by ^{1}H nuclear magnetic resonance

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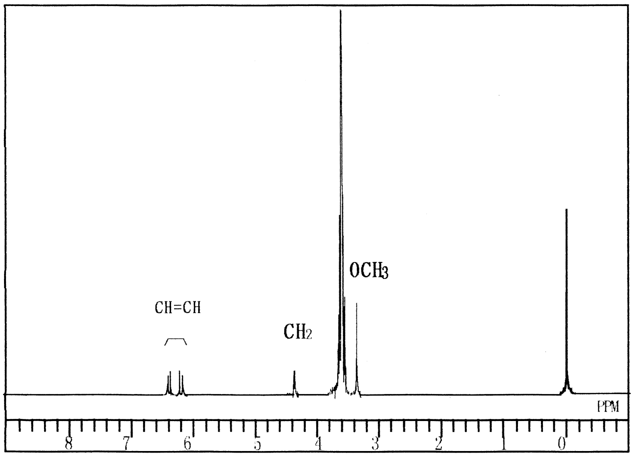

Fig. 1. ^{1}H n.m.r. spectrum of PEG–MM macromonomer.

(n.m.r.; 500 MHz JEOL GSX-500, n.m.r. spectrometer) in $CDCl_3$.

2.2. 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 *n*-heptane. Next, the copolymerization product was extracted by methanol to remove PEG homopolymer. The collected yield of PEG homopolymer was measured to determine the conversion of comb-shaped copolymers.

In this copolymerization, kinetic equations are expressed with four propagation steps, as developed by Mayo and Lewis [12]. Two monomers, M_1 and M_2, are defined as the vinylbenzyl-terminated PS (PS–VM) and maleate-terminated PEG (PEG–MM) macromonomers, respectively. Each propagation reaction has a characteristic rate constant, k_{ab}, where the first 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:

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

The reactivity ratios r_1 and r_2 can be estimated by Kelen and Tüdos procedure [13]. The mole fraction ratio in the copolymer ($d[M_1]/d[M_2] = f$) was determined by the area ratio of refractive index (r.i.) and u.v. (254 nm) intensities on a g.p.c. chart (using a calibration curve constructed from a mixture of PS and PEG homopolymers). We deduced the g.p.c. distribution (r.i. chart) of the homopolymer of PS macromonomer from that of the copolymerization product by using a personal computer, because the g.p.c. distribution of PS macromonomer is the known curve. On the other hand, the conversion was estimated from the relationship between the separated weight ratio of comb-shaped copolymer to homopolymer of PS macromonomer and the collected yield of PEG homopolymer. 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}.

Table 1
Characteristics of vinylbenzyl-terminated PS and maleate-terminated PEG macromonomers

Code	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$ [a]	Functional group (number per molecule)
PS–VM	2300[b]	1.02	1.04[c]
PEG–MM	5000	1.03	1.00[d]

[a] Determined by g.p.c. distributions.
[b] Determined by vapour pressure osmometer in benzene.
[c] Determined by g.p.c. equipped with r.i. and u.v. (254 nm) double detectors using *p*-methylstyrene as model compound.
[d] Determined by ^{1}H n.m.r. in $CDCl_3$.

3. Results and discussion

Lacroix-Desmazes and Guyot reported the synthesis of PEG–MM macromonomers by the reaction of PEG with maleic anhydride (for 4 h at 80°C) [14]. In this work, we performed the synthesis of PEG–MM macromonomer by the reaction of alkoxidated PEG with maleic anhydride. These reaction systems proceeded under mild reaction conditions. Fig. 1 shows the ^{1}H n.m.r. spectrum of PEG–MM macromonomer. In addition to the signals of the methylene protons [3.65 ppm; (4n-2)H, CH_2 (PEG chain except the first methylene group)], the spectrum exhibits absorptions assignable to the methoxy protons (3.38 ppm; 3H, OCH_3), the methylene protons [4.37 ppm; 2H, CH_2 (the first methylene group)] and the double bond protons (6.40 ppm; 1H, =CH and 6.23 ppm; 1H, =CH). From the integrated peak intensities, the PEG–MM macromonomer possessed one maleate group at the terminal end. Table 1 lists the characteristics of PS–VM and PEG–MM macromonomers.

Free-radical copolymerization of binary PS–VM and PEG–MM macromonomers was carried out in benzene, varying the feed molar ratio of PS–VM (M_1) to PEG–MM (M_2) macromonomers (macromonomer concentration ~ 0.1 mol l^{-1}). All of the experimental series showed phase separation, because the reaction mixture indicated turbidity in solution. Table 2 lists the copolymerization conditions and composition of comb-shaped copolymers (F and f indicate the feed ratio of macromonomer concentrations, $[M_1]/[M_2]$ and the copolymer composition, $d[M_1]/d[M_2]$, respectively).

Typical g.p.c. profiles of CP-3 (extracted by methanol to PEG homopolymer), PS–VM and PEG–MM macromonomers are shown in Fig. 2. In these copolymerization series, new peaks appear at the high-molecular-weight side

Table 2
Copolymerization conditions and composition of comb-shaped copolymers[a]

No.	Feed macromonomer			Comb-shaped copolymer (f^c)
	M_1	M_2	F^b	
CP-1			9.0	7.589
CP-2			2.333	3.654
CP-3			1.5	2.056
CP-4	PS–VM	PEG–MM	1.0	1.745
CP-5			0.667	1.450
CP-6			0.429	1.047
CP-7			0.111	0.706

[a] Polymerized in benzene initiated by AIBN (0.01 mol l^{-1}) at 60°C (macromonomer concentration ~ 0.1 mol l^{-1}).

[b] Feed ratio of macromonomers, $[M_1]/[M_2]$.

[c] Copolymer composition, $d[M_1]/d[M_2]$.

compared to PS–VM and PEG–MM macromonomers. PEG has no absorption in the u.v. monitor (254 nm). After separation of the distribution of comb-shaped copolymer by simulation, f was determined from the calibration curve. The values of f are listed in Table 2. The conversion of comb-shaped copolymers was in the range 13–40%.

Fig. 3 shows the Kelen–Tüdos plot for CP series, where α is an arbitrary constant ($\alpha = 0.432$). The problem involves choosing a value of α so as to minimize experimental error. Reactivity ratios ($r_1 = 0.765$ and $r_2 = 0.064$) were derived from this plot. On the other hand, the reactivity ratios for styrene (M_1) and maleic acid ethyl ester (M_2) as a model system were $r_1 = 0.13$ and $r_2 = 0.035$ (60°C) [15]. It is well known that highly alternating copolymers were prepared by copolymerizing strongly electron-accepting monomers such as maleic anhydride with electron-donating monomers such as styrene. It has been suggested that alteration results from the homopolymerization of 1:1 complexes formed between the donor and acceptor monomers [16]. Thus, in the familiar styrene–maleic anhydride system, the double bonds have opposite polarities, being electron-rich and electron-deficient, respectively, and complex formation results.

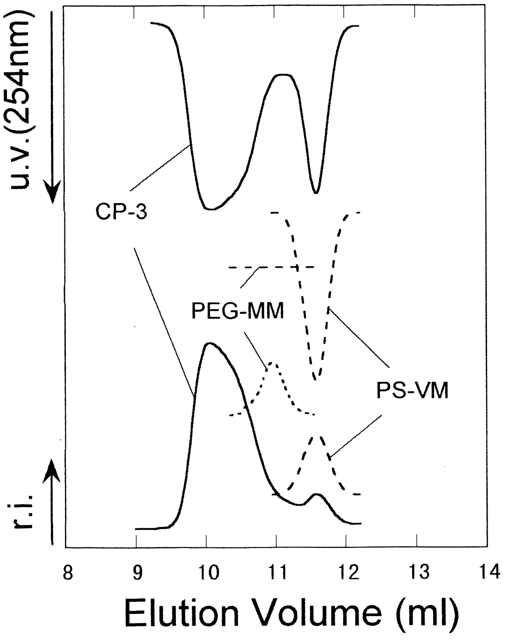

Fig. 2. G.p.c. profiles of CP-3, PS–VM and PEG–MM macromonomers.

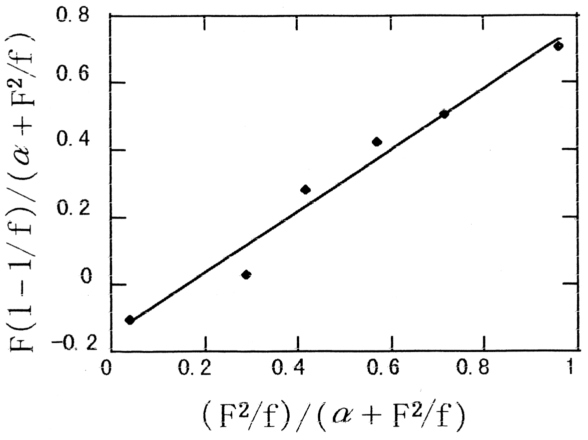

Fig. 3. Kelen–Tüdos plot for copolymerization CP series.

Copolymerization reactivity of the styrene–maleic acid ethyl ester system is also similar to that of the styrene–maleic anhydride system. However, it is found that copolymerization reactivity of binary PS–VM and PEG–MM macromonomers does not show accurate alternation. 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 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 shown to be due to the phase separation during the copolymerization [17]. The observed reactivity involves the effects of various kinds of interaction 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.

It was mentioned earlier that all of the copolymerization systems (CP1–CP7) showed phase separation in solution. In these copolymerization systems, the propagating copolymers produced at the initial stage have a high content of the PS component. These propagating copolymer chains are more compatible with the PS macromonomer than with the PEG macromonomer, because the propagating copolymer has a high PS component. PEG macromonomer cannot interpenetrate sufficiently into propagating copolymer chains that have radical sites due to phase separation. Thus, the copolymerization reactivity seems to depend strongly on the reaction phase. In order to obtain highly alternating comb-shaped copolymers, it is necessary to select the homogeneous reaction system.

It would be interesting to study the dilute solution properties and phase separation behaviour of the comb-shaped copolymers. The results obtained will be reported in the near future.

References

[1] Tsukahara Y, Tsutsumi K, Okamoto Y. Macromol Rapid Commun 1992;13:409.
[2] Tsukahara Y, Mizuno K, Segawa A, Yamashita Y. Macromolecules 1989;22:1546.
[3] Tsukahara Y, Tsutsumi K, Yamashita Y, Shimada S. Macromolecules 1989;22:2869.
[4] Tsukahara Y, Tsutsumi K, Yamashita Y, Shimada S. Macromolecules 1990;23:5201.
[5] Wintermantel M, Schmidt M, Tsukahara Y, Kajiwara K, Kohjiya S. Macromol Rapid Commun 1994;15:279.
[6] Wintermantel M, Gerle M, Fischer K, Schmidt M, Watanabe I, Urakawa H, Kajiwara K, Tsukahara Y. Macromolecules 1996;29:978.
[7] Tsukahara Y, Ohta Y, Senoo K. Polymer 1995;36:3413.
[8] Wintermantel M, Fischer K, Gerle M, Ries R, Schmidt M, Kajiwara K, Urakawa H, Wataoka I. Angew Chem Int Ed Engl 1995;34:1472.
[9] Ishizu K, Sunahara K. Polymer 1995;36:4163.
[10] Ishizu K, Kuwahara K. Polymer 1994;35:4907.
[11] Ishizu K, Shimomura K, Fukutomi T. J Polym Sci Polym Chem Ed 1991;29:923.
[12] Mayo FR, Lewis FM. J Am Chem Soc 1944;66:1594.
[13] Kelen T, Tüdos F. J Macromol Sci Chem 1975;A9(1):1.
[14] Lacroix-Desmazes P, Guyot A. Macromolecules 1996;29:4508.
[15] Lewis FM, Mayo FR. J Am Chem Soc 1948;70:1533.
[16] Gaylord NG. J Polym Sci Part D 1970;4:183.
[17] Schulz GO, Milkovich RJ. J Polym Sci Polym Chem Ed 1984;22:1633.