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

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Abstract

Free-radical copolymerizations of vinylbenzyl-terminated polystyrene (PS-VM; M_1) and methacryloyl-terminated poly(ethylene glycol methylether) (PEG-MC; M_2) were carried out in various solvents (benzene, 1,4-dioxane and *N*,*N*-dimethylformamide). The reactivity ratios obtained for the binary macromonomer systems were different from corresponding model system of styrene and methyl methacrylate ($r_1 = 0.52$ and $r_2 = 0.46$) due to phase separation. PEG macromonomers could not interpenetrate sufficiently into propagating copolymer chains that had radical sites due to phase separation. On the other hand, the reactivity ratios ($r_1 = 0.25$ and $r_2 = 0.02$) obtained for the binary copolymerizations of PS-VM and PEG-MC/tin tetrachloride macromonomers showed strong alternation. It was suggested that alternation results from the homopolymerization of 1:1 complexs formed between the donor and acceptor monomers. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Free-radical copolymerization; Macromonomer; Comb-shaped copolymer

1. Introduction

Homopolymerization of macromonomers provides regular multi-branched polymers with a branch density. Since both the degree of polymerization and the length of branches are varied, poly(macromonomer)s are interesting models for the study of branched polymers [1–4]. Recent structural characterization of such long-chain poly(macromonomer)s revealed that the main chain exhibits an almost rod-like conformation [5,6].

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 [7], 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. More recently, free-radical copolymerizations of vinylbenzyl-terminated PS (PS-VM; M_1) and maleate-terminated poly(ethylene glycol methylether) (PEG-MM; M_2) were carried out in benzene, in order to achieve alternative reactivity [8]. 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.

In this article, free-radical copolymerizations of methacryloyl-terminated poly(ethylene glycol methylether) (PEG-MC) with PS-VM macromonomers were carried out in various solvents. In order to achieve alternative reactivity, such copolymerizations were also carried out under the addition of Lewis acid. The copolymerization reactivity was estimated from the distribution function by gel permeation chromatography (GPC) of the comb-shaped copolymer produced.

2. Experimental

2.1. Synthesis and characterization of macromonomers

PS-VM was synthesized by the coupling reaction of polystyryl lithium living anion with an excess amount of

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p-chloromethylstyrene (CMS) in a benzene–tetrahydrofuran (THF) mixed solvent. Details concerning the synthesis and characterization have been given elsewhere [9,10].

PEG-MC macromonomer was prepared under nitrogen from commercially available PEG (Aldrich: $\bar{M}_n = 5000$) by alkoxidation with sodium hydride in toluene followed by reaction with methacryloyl chloride (for 12 h at 45°C) [11]. Reaction product was poured by a large excess of diethyl ether. PEG-MM was separated by filtration. The content of terminal methacryloyl group was determined by ^{1}H NMR (500 MHz JEOL GSX-500 NMR spectrometer) in $CDCl_3$.

2.2. Free-radical copolymerization of binary macromonomers

Free-radical copolymerization of binary macromonomers was carried out in various solvent (benzene, 1,4-dioxane and *N*,*N*-dimethylformamide (DMF)) at 60°C using 2,2′-azobisisobutyronitrile (AIBN) as an initiator in a sealed glass apparatus under high vacuum. The copolymerization system under the addition of tin (IV) tetrachloride ($SnCl_4$) as a Lewis acid was also carried out in benzene. After polymerization, the copolymerization solution was poured into a large excess of *n*-heptane.

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 methacryloyl-terminated PEG (PEG-MC) macromonomers, respectively. Each propagation reaction has a characteristic rate constant, k_{ab}, where the first subscript refers to the active center 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:

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

By integration of Eq. (1) between the limits $[M_1]_0$ and $[M_2]_0$ at the time before starting the copolymerization, one obtains:

$$r_2 = \frac{\log\frac{[M_2]_0}{[M_2]} - \frac{1}{P}\log\frac{-P[M_1]/[M_2]}{1 - P[M_1]_0/[M_2]_0}}{\log\frac{[M_1]_0}{[M_1]} + \log\frac{1 - P[M_1]/[M_2]}{1 - P[M_1]_0/[M_2]_0}} \quad (2)$$

where $P = (1 - r_1)/(1 - r_2)$.

Eq. (2) describes the course of the whole copolymerization up to high conversion. Therefore, r_1 and r_2 can be calculated by determination of the monomer ratios $[M_1]/[M_1]_0$ and $[M_2]/[M_2]_0$ at any time after starting the copolymerization; the determination can be done with sufficient precision by GPC The reactivity ratios can be estimated by a graphical r_1–r_2 determination. We deduced the GPC distribution (refractive index (r.i.) chart) of the homopolymers of PS-VM and PEG-MC macromonomers from that of the copolymerization product by using a personal computer, because the GPC distributions of PS-VM and PEG-MC macromonomers are the known curves. On the other hand, the conversion was estimated from the relationship between the separated weight ratio of comb-shaped copolymer to homopolymers of PS-VM and PEG-MC macromonomers. The GPC 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 methacryloyl-terminated PEG macromonomers

Code	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$ [a]	Functional group (number per molecule)
PS-VM	2300[b]	1.08	1.04[c] (1.03)[d]
PEG-MC	5000	1.06	1.00[d]

[a] Determined by GPC distributions.
[b] Determined by vapor pressure osmometry in benzene.
[c] Determined by GPC eqipped with IR and UV (254 nm) double detectors using *p*-methylstyrene as the model compound.
[d] Determined by ^{1}H NMR in $CDCl_3$.

3. Results and discussion

Chao et al. [11] reported the synthesis of PEG-MC macromonomers by the reaction of alkoxidated PEG with methacryloyl chloride. We also followed the above method for the preparation of PEG-MC. The content of terminal methacryloyl group was determined by ^{1}H NMR in $CDCl_3$. 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 exhibited 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)), the double bond protons (6.10 ppm; 1H, =CH and 5.54 ppm; 1H, =CH), and the α-methyl protons (1.92 ppm; 3H, CH_3). From the integrated peak intensities, the PEG-MC macromonomer possessed one methacryloyl group at the terminal end. Table 1 lists the characteristics of PS-VM and PEG-MC macromonomers.

Free-radical copolymerizations of binary PS-VM and PEG-MC macromonomers were carried out in various solvents (benzene, 1,4-dioxane and DMF). Table 2 lists the cohesive energy densities [13] of the polymers and solvents employed in this work. It is not desirable to choose the solvent system leading the phase separation during copolymerization. First, free-radical copolymerizations of binary PS-VM and PEG-MC macromonomers were carried out in benzene, varying the feed molar ratio of PS-VM (M_1) to PEG-MC (M_2) macromonomers (CPB series). All of the experimental series showed phase separation, because the

Table 2
Cohesive energy densities of polymers and solvents

Code	Cohesive energy density δ (cal cm^{-3})$^{1/2}$
PS	9.1
PEG	8.5–14.7
Benzene	9.2
1,4-Dioxane	10.2
DMF	12.1

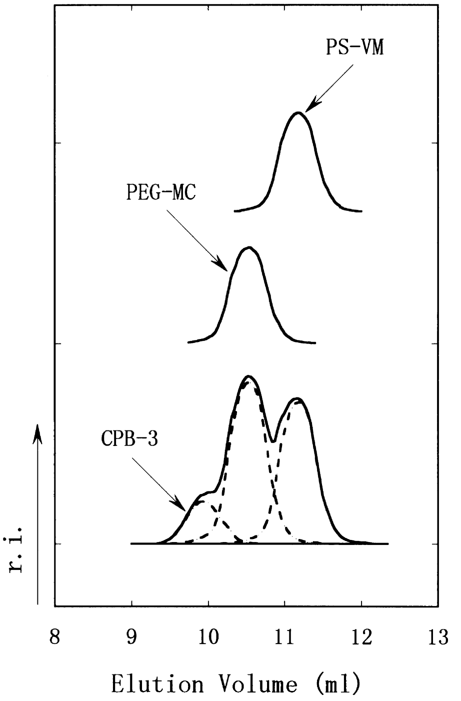

Fig. 1. GPC profiles of CPB-3, PS-VM and PEG-MC macromonomers.

copolymerization mixture indicated turbidity in solution. Table 3 lists the copolymerization conditions and composition of comb-shaped copolymers (*F* and *f* indicate the feed ratio of macromonomer concentrations, $[M_1]_0/[M_2]_0$ and the copolymer composition, $d[M_1]/d[M_2]$, respectively).

Typical GPC profiles of CPB-3, PS-VM and PEG-MC macromonomers are shown in Fig. 1. In this copolymerization, new peak appears at the high-molecular-weight side compared to PS-VM and PEG-MC macromonomers. After separation of the distributions of comb-shaped copolymer and both unreacted macromonomers by simulation, the conversion of each macromonomer was determined from the PS or PEG calibration curve, respectively. Subsequently, the value of *f* was determined from both conversions of PS-VM and PEG-MC macromonomers. The values of *f* are also listed in Table 3.

Fig. 2 shows the graphical r_1–r_2 determination plot for CPB series. Reactivity ratios ($r_1 = 2.16 \pm 0.2$ and $r_2 = 0.02 \pm 0.01$) were derived from this plot. On the other hand, the reactivity ratios for styrene (M_1) and methyl methacrylate (MMA; M_2) as a model system were $r_1 = 0.52$ and $r_2 = 0.46$ (60°C) [14]. Copolymerization reactivity of styrene–MMA system leads to random nature. However, it is found that copolymerization reactivity of binary PS-VM and PEG-MC macromonomers does not show random nature. 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 [15]. 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 (CPB-1–CPB-5) 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. As mentioned earlier, the reactivity ratios for styrene (M_1) and MMA (M_2) as a model system were $r_1 = 0.52$ and $r_2 = 0.46$. The relative propagation constant of the methacryloyl end group of PEG-MC is almost equal to that of the styrene end group of PS-VM.

Table 3
Copolymerization conditions and composition of comb-shaped copolymers (CPB series; polymerized in benzene initiated by AIBN (0.01 mol l^{-1}) at 60°C)

No.	Macromonomer concentration (mmol l^{-1})				Feed ratio of macromonomers *F* (mol mol^{-1})	Conversion of macromonomers (%)		Comb-shaped copolymer *f* (mol mol^{-1})
	Feed		After 8 h					
	$[M_1]_0$	$[M_2]_0$	M_1	M_2		M_1	M_2	
CPB-1	37.5	12.5	29.34	12.38	3.0	21.8	1.0	65.80
CPB-2	33.4	16.7	24.15	15.41	2.0	27.7	7.7	7.15
CPB-3	25.0	25.0	16.34	22.40	1.0	34.6	10.4	3.33
CPB-4	16.7	33.4	11.58	28.39	0.5	30.7	15.0	1.02
CPB-5	12.5	37.5	10.68	30.28	0.33	14.6	19.2	0.25

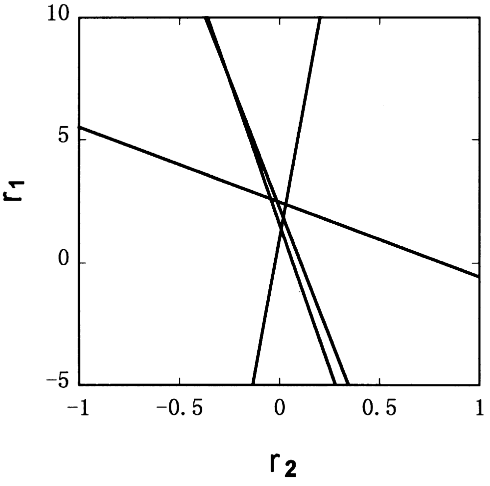

Fig. 2. Graphical r_1–r_2 determination plot for the CPB series.

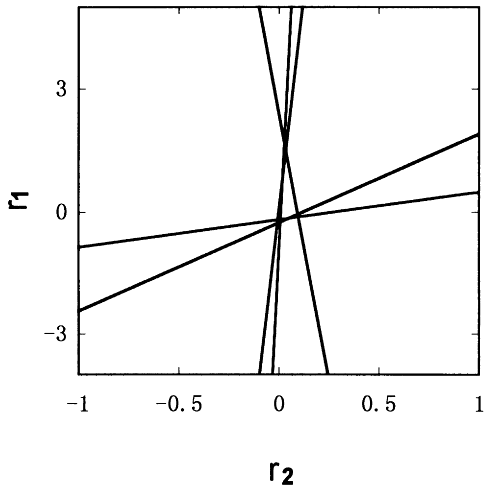

Fig. 3. Graphical r_1–r_2 determination plot for the CPLB series.

PEG-MC macromonomers are difficult to dissolve homogeneously in benzene compared to PS-VM. It seems therefore that the propagating copolymer at the initial stage have a high PS content. 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.

Tables 4 and 5 (CPO and CPD series, respectively) list the copolymerization conditions and composition of comb-shaped copolymers in 1,4-dioxane and in DMF, respectively. The reactivity ratios were estimated from the graphical r_1–r_2 determination plots to be $r_1 = 2.20 \pm 0.20$ and $r_2 = 0.02 \pm 0.01$ for the CPO series and $r_1 = 1.80$ and $r_2 = 0.01$ for the CPD series. The reactivity ratios obtained in both solvent systems were very similar to that obtained in benzene. All of the experimental series (CPO and CPD series) showed phase separation during copolymerization. As the compatibility between PS and PEG segments was too poor, the copolymerizations proceeded in heterogeneous phase regardless of employing the solvent systems possessing

Table 4
Copolymerization conditions and composition of comb-shaped copolymers (CPO series; polymerized in 1,4-dioxane initiated by AIBN (0.01 mol l^{-1}) at 60°C)

No.	Macromonomer concentration (mmol l^{-1})				Feed ratio of macromonomers F (mol mol^{-1})	Conversion of macromonomers (%)		Comb-shaped copolymer f (mol mol^{-1})
	Feed		After 8 h					
	$[M_1]_0$	$[M_2]_0$	M_1	M_2		M_1	M_2	
CPO-1	37.5	12.5	28.77	12.45	3.0	23.3	0.4	164.6
CPO-2	33.4	16.7	25.86	16.56	2.0	22.6	0.9	52.01
CPO-3	25.0	25.0	16.34	24.34	1.0	34.6	2.6	13.08
CPO-4	16.7	33.4	11.08	30.75	0.5	33.6	7.9	2.12
CPO-5	12.5	37.5	7.76	33.25	0.33	37.9	11.3	1.12

Table 5
Copolymerization conditions and composition of comb-shaped copolymers (CPD series; polymerized in DMF initiated by AIBN (0.01 mol l^{-1}) at 60°C)

No.	Macromonomer concentration (mmol l^{-1})				Feed ratio of macromonomers F (mol mol^{-1})	Conversion of macromonomers (%)		Comb-shaped copolymer f (mol mol^{-1})
	Feed		After 8 h					
	$[M_1]_0$	$[M_2]_0$	M_1	M_2		M_1	M_2	
CPD-1	37.5	12.5	27.29	12.27	3.0	27.2	1.9	43.81
CPD-2	33.4	16.7	22.89	16.17	2.0	31.5	3.2	19.94
CPD-3	25.0	25.0	17.18	23.83	1.0	31.3	4.7	6.66
CPD-4	16.7	33.4	10.79	29.25	0.5	35.4	12.4	1.43
CPD-5	12.5	37.5	6.91	33.15	0.33	44.7	11.6	1.28

Table 6
Copolymerization conditions and composition of comb-shaped copolymers (CPLB series; polymerized in benzene under the addition of $SnCl_4$ initiated by AIBN (0.01 mol l^{-1}) at 60°C)

No.	Macromonomer concentration (mmol l^{-1})				Feed ratio of macromonomers F (mol mol^{-1})	Conversion of macromonomers (%)		Comb-shaped copolymer f (mol mol^{-1})
	Feed		After 8 h					
	$[M_1]_0$	$[M_2]_0$[a]	M_1	M_2		M_1	M_2	
CPLB-1	37.5	12.5	32.52	8.10	3.0	13.3	35.2	1.13
CPLB-2	33.4	16.7	25.64	10.09	2.0	23.2	39.6	1.17
CPLB-3	25.0	25.0	20.36	20.64	1.0	18.6	17.4	1.07
CPLB-4	16.7	33.4	12.93	29.59	0.5	22.6	11.4	0.99
CPLB-5	12.5	37.5	8.74	32.89	0.33	30.1	12.3	0.82

[a] Concentration of PEG-MC/$SnCl_4$ 1:1 complexes.

various cohesive energy densities. It is also noticed that the conversions of PEG-MC in Tables 3–5 increase much with increase in the feed composition of PEG-MC. The propagating copolymers at the initial stage have relatively high PEG content due to high feed composition of PEG-MC. The compatibility between comb-shaped copolymer micelle and PEG-MC seems to increase with increase in the conversion of propagating copolymers.

It is well known that highly alternating copolymers are prepared by copolymerizing strongly electron-accepting monomers such as MMA/Lewis acid complex with electron-donating monomers such as styrene [16]. It has been suggested that alternation results from the homopolymerization of 1:1 complexes formed between the donor and acceptor monomers. Table 6 lists the copolymerization conditions and composition of comb-shaped copolymers under the addition of $SnCl_4$ in benzene (CPLB series). Fig. 3 shows the graphical r_1–r_2 determination plot for CPLB series. Reactivity ratios ($r_1 = 0.25 \pm 0.10$ and $r_2 = 0.02 \pm 0.01$) were derived from this plot. It is found that copolymerization reactivity of binary PS-VM and PEG-MC/$SnCl_4$ macromonomers shows strong alternation. It has been found that the structure of a copolymer is greatly modified by the incorporation of a Lewis acid in the reaction mixture. Methacrylic monomers which by themselves are thought to be too weak to act as acceptor molecules, became active in the presence of complexing agents such as $SnCl_4$ thereby enabling them to form alternating copolymers with electron-donating monomers. In this copolymerization system, the propagating copolymer radicals proceed always with the homopolymerization of 1:1 complexes formed between the donor and acceptor macromonomers. In fact, copolymerization systems did not show phase separation at the final stage of reaction. Thus copolymerization system is one of the best methods to prepare the well-defined comb-shaped copolymers.

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

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