

Reactivity in the Radical Copolymerization of Poly(2-oxazoline) Macromonomers with Methacrylate Monomers

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ABSTRACT: The radical copolymerization of vinylbenzyl-terminated poly(2-methyl-2-oxazoline) macromonomers (**1 Me-*n***; *n* (degree of polymerization) = 3, 15, 28, 31) (M_1) with vinyl monomers (M_2), *i.e.*, methyl methacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA) was performed using 2, 2'-azobis(isobutyronitrile) (AIBN) as an initiator at 60°C in ethanol (EtOH), CD₃OD, or CD₃CN. Monomer reactivity ratios r_1 and r_2 were evaluated based on the terminal model. Copolymerization of **1 Me-3** with MMA gave reactivity ratios as $r_1 = 1.86 \pm 0.15$ and $r_2 = 0.07 \pm 0.03$ in EtOH, and $r_1 = 1.25 \pm 0.10$ and $r_2 = 0.18 \pm 0.05$ in CD₃OD, exhibiting remarkably higher reactivity of the Me-3 compared with the comonomers and corresponding small monomer, styrene. In CD₃CN, however, copolymerization of **1 Me-3** with MMA gave $r_1 = 0.41 \pm 0.10$ and $r_2 = 0.66 \pm 0.10$, showing rather lower reactivity of the macromonomer compared with MMA. With HEMA, **1 Me-3** showed high reactivity in EtOH, *i.e.*, $r_1 = 1.44 \pm 0.10$, $r_2 = 0.04 \pm 0.02$. The reactivity of HEMA against the macromonomers was found higher than that of MMA, possibly due to affinity to aprotic poly(2-methyl-2-oxazoline) graft chains on growing species. The high reactivity of **1 Me-*n*** in EtOH and CD₃OD would be due to the formation of a micelle-like state. The reactivity of macromonomers decreased generally with chain length (*n*).

KEY WORDS Macromonomers / Polyoxazoline / Radical Copolymerization / Monomer Reactivity Ratio / Methyl Methacrylate / 2-Hydroxyethyl Methacrylate /

Poly(2-alkyl-2-oxazoline)s (PROZO) having the poly(*N*-acylethylenimine) structure given by cationic ring-opening polymerization of 2-alkyl-2-oxazoline (ROZO), can be regarded as a polymer homologue of polar aprotic solvents such as *N,N*-dimethylacetamide, showing hydrophilic (R = Me, Et) or hydrophobic (carbon number of R \geq 4) properties.¹ Monodisperse macromonomers of PROZO, *e.g.*, styryl-,² methacryloyl-,³ and vinyl-ester-terminated⁴ macromonomers, have been synthesized using living polymerization of ROZO. Longer alkyl groups (R) in PROZO chain make macromonomers with regularly branched structure.

In general, homopolymerization of macromonomers produces star-like or comb-like polymers, while copolymerization with ordinary vinyl monomers forms graft copolymers. In particular, the synthesis of graft copolymers using the macromonomer method is believed very good for those with well-defined structure. We examined the kinetics of radical homopolymerization of methacryloyl and vinylbenzyl-terminated PROZO macromonomers, and found reactivity to be particularly influenced by longer alkyl (R) branches and remarkably enhanced in water.⁵ Previously, radical copolymerization of hydrophilic PROZO macromonomers was found to produce micron to submicron-size polymer particles using the functions of macromonomers as stabilizers or emulsifiers.⁶ Amphiphilic graft copolymers were obtained by copolymerization of hydrophilic PROZO macromonomers with hydrophobic monomers.⁷ The reactivity of PROZO macromonomers in copolymerizations is of interest, though detailed examination on copolymerizability has not been reported.

In the present study, reactivity of radical copolymerization of *p*-vinylbenzyl (VB)-terminated PMeOZO macro-

monomers (Me-*n*; *n* (degree of polymerization) = 3—31) with ordinary vinyl monomers, methyl methacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA) was examined in ethanol (EtOH), CD₃OD, and CD₃CN. EtOH and CD₃OD must be easy to solvate the aprotic PMeOZO chains. MMA is a hydrophobic monomer, while HEMA is hydrophilic monomer with hydroxyl groups. The effects of the properties on the copolymerization are discussed on the basis of monomer reactivity ratios. The reactivity of macromonomers in copolymerization is essentially the same,⁸ or less than⁹ that of corresponding ordinary vinyl monomers. The most effective factor determining reactivity of macromonomers in copolymerization is the chemical nature of the polymerizable end groups of the macromonomers. Other important factors may be; (1) steric effects¹⁰ including kinetic excluded volume effects,^{9d-f,11} (2) thermodynamic repulsive interactions,^{8b,9a,c} (3) viscosity of polymerization systems, and (4) molecular weights of macromonomers. The reactivity of macromonomers has been found in a few cases higher than that of corresponding small monomers, being interpreted in a term of micelle formation.¹² For the monomer reactivity ratio in copolymerization of macromonomers (M_1) with ordinary vinyl monomers (M_2), only r_2 is generally evaluated because of technical difficulties in determining r_1 and r_2 . On the basis of r_2 , reactivity only with backbone radicals can be discussed and the nature of reactivity with macromonomer-unit-terminated radicals is normally not detectable. PROZO macromonomers possess characteristic features as mentioned above, and thus determination of reactivity and knowing the reactivity of the macromonomer-unit-terminated radicals become essential. r_1 and r_2 in the copolymerization are evaluated and the effects of several factors on reactivity are discussed.

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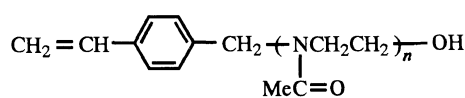
EXPERIMENTAL

Materials

CH₃CN and CD₃CN were purified by distillation over P₂O₅. EtOH was distilled over ethoxide formed using magnesium. *p*-Vinylbenzyl chloride (VBC) was prepared according to the literature.¹³ 2-Methyl-2-oxazoline (MeOZO) was stirred with KOH and distilled. CD₃OD, methyl methacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA) were distilled before use. 2,2'-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol. Diethyl ether (Et₂O) and *n*-hexylbenzene was distilled over sodium wire.

Macromonomers

p-Vinylbenzyl-terminated PMeOZO macromonomers (**1** Me-*n*) having a hydroxyl group at ω end were prepared



1 Me-*n*

Scheme 1.

using the living polymerization of 2-methyl-2-oxazoline (MeOZO).¹⁴ MeOZO was heated with VBC and NaI as an initiator in CH₃CN at 80 °C for 20 h to give living PROZO, whose propagating species (2-oxazolinium salt) was hydrolyzed by heating with H₂O and Na₂CO₃ at 80 °C for 20 h for conversion to the alcohols (**1**). Macromonomers **1** were purified by reprecipitation from CHCl₃ solution with Et₂O as non-solvents, being shown in Table I. Number average molecular weight (M_n) of **1** was determined by ¹H NMR and GPC. In ¹H NMR, signal integration ratios of NCH₂ protons (δ 3.4–3.6) to phenylene protons (δ 7.19–7.47) of styryl groups gave macromonomer chain length *n* (DP_n), from which M_n was calculated. Gel permeation chromatography (GPC) was measured in CHCl₃ as eluent using PMeOZO standards. Molecular weight distributions of the macromonomers were generally narrow, reflecting the living nature of the polymerizations.

Copolymerization

The radical copolymerization of macromonomers with MMA and HEMA was conducted using AIBN as initiator mainly in EtOH. **1** Me-3 and 15 were polymerized in CD₃OD, and CD₃CN.

In polymerization in EtOH, calculated amounts of solutions were mixed in a flask under Ar at 0.05 g total monomers in 2 mL solvent. Each 2 mL of mixture were transferred into glass tubes under Ar and sealed. One tube was kept at –10 °C as the unreacted run for analysis, *i.e.*, UV, gas chromatography (GC), or GPC. Polymerization was carried out at 60 °C. Conversion of macromonomers was determined mainly by change of deviation between an increasing peak at 290 nm and a decreasing peak at 294 nm in UV-second order derivative spectra,^{9f} or by change of the integration ratio of comonomer peak to internal standard peak in GPC. The conversion of vinyl comonomers was determined by change of the integration ratio of comonomer peak to internal standard

Table I. Vinylbenzyl-type macromonomers of poly(2-methyl-2-oxazoline)

Macromonomer (1)	M_n		DP_n^a	M_w^a M_n
	NMR	GPC		
Me-3	410	390	3.0	1.32
Me-15	1380	1370	14.5	1.11
Me-28	2500	2490	27.7	1.16
Me-31	2830	2800	31.4	1.18

^a Determined by GPC.

peak in GC. As the internal standard, *n*-hexylbenzene was used.

In polymerization in CD₃CN and CD₃OD, a solution of 0.01 g total monomers, AIBN, and 0.6 mL solvent was placed into NMR tube (5 mm ϕ) under Ar and sealed. After heating at 60 °C, the solution was analysed by ¹H NMR. Conversion of macromonomers was determined by change of the signal integration ratio of vinyl-methylene protons (δ 5.2–5.3 and 5.8) of styryl group to phenylene protons (δ 7.2–7.5), and that of MMA was assayed by change of the signal integration ratio of vinyl-methylene protons (δ 5.6 and 6.1) of methacryloyl group to the phenylene protons. Monomer reactivity ratios were evaluated using the conversions on a basis of the integrated equation.¹⁵

Measurements

¹H and ¹³C NMR spectra were recorded on a JEOL JNM LA 400 FT NMR spectrometer (¹H: 400 MHz) with tetramethylsilane as standard. ¹H Spin-lattice relaxation times (T_1) in ¹H NMR were measured at $\pi/2$ pulse using the inversion recovery method at 60 °C. Concentrations of macromonomer solutions in T_1 measurement were nearly 25 g L⁻¹ to be analogous to those in actual copolymerization. IR spectra were measured by a JASCO IR-810 spectrophotometer. UV-second order derivative spectra were acquired on a SHIMADZU UV-2200 spectrophotometer. GPC analysis was performed using a SHIMADZU LC-10AD chromatograph equipped with a SHIMADZU RID-6A RI detector. GPC columns, a SHODEX AC-803 and a JASCO Fine Pack Gel-101 were connected in series (M_n at exclusion limit, 7×10^4), and CHCl₃ was used as eluent at 0.8 mL min⁻¹. Molecular weights were determined relative to PMeOZO standards prepared by polymerization of MeOZO by MeOTs as an initiator. GC analysis was carried out with a SHIMADZU GC-R1A gas chromatograph equipped with a flame ionization detector. As stationary phase in GC, Polyester-FF supported on Chromosorb-101 (NISHIO) was employed for MMA analysis, while Thermon-3000 supported on Shincarbon-A (SHIMADZU) was used for analysis of HEMA.

RESULTS AND DISCUSSION

Copolymer Composition

Radical copolymerizations of VB-PMeOZO macromonomers (**1** Me-*n*) with MMA (hydrophobic) and HEMA (hydrophilic and protic) were carried out using AIBN as an initiator in EtOH (*n* = 3, 15, and 31), CD₃OD

Table II. Copolymerization of **1** Me-3 (M_1) with MMA (M_2) in EtOH^a

Run	Feed composition				M_1	Time	Monomer conversion		M_1 in copolymer
	$[M_1]_0$		$[M_2]_0$				M_1^b	M_2^c	
	mg	mol L^{-1} ($\times 10^2$)	mg	mol L^{-1} ($\times 10^2$)					
1	20.66	2.60	29.43	14.70	15.0	10	8.9	1.9	44.7
2	27.10	3.45	23.01	11.50	23.1	16	6.3	1.3	58.8
3	31.38	4.00	18.51	9.25	30.2	22	9.6	2.2	65.2
4	38.06	4.85	11.78	5.90	45.1	32	7.3	2.2	72.9
5	42.90	5.45	7.25	3.60	60.2	36	12.8	5.8	76.9
6	45.08	5.70	5.02	2.50	69.5	36	8.1	5.2	77.9
7	46.01	5.85	3.84	1.90	75.5	44	10.4	8.6	78.7
8	48.65	6.17	1.31	0.65	90.5	48	7.7	10.6	86.7

^a Initiator, AIBN (1.0 mol% to total monomers); solvent, EtOH (2.0 mL); temperature, 60°C. ^b Determined by UV-second order derivative spectroscopy. ^c Determined by GC.

($n=3$ and 15), and CD_3CN ($n=3$ and 15) at 60°C. Copolymerizability is affected by increased viscosity of reaction system resulting from proceeding of the reaction,^{10a} and thus, reactivity at lower conversion of monomers below about 10 % was determined. Monomer reactivity ratios were obtained using the integrated equation on the basis of the copolymerization equation (eq 1).¹⁵

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

where M_1 and M_2 denote monomers **1** and vinyl monomers **2** (MMA and HEMA) and r_1 and r_2 are respective monomer reactivity ratios.

When copolymers can be completely separated from unreacted monomers, compositions can be determined by analysis of them. When complete separation is impossible, it is rather suitable to determine the copolymer composition using monomer conversion.¹⁶ For estimation of monomer conversion, unreacted monomers are largely determined by GPC for macromonomers and by GC for vinyl comonomers. In the present work, the complete separation of copolymers produced from unreacted monomers was impossible. Therefore, copolymer composition was evaluated by monomer conversion. In copolymerization in EtOH, conversions of macromonomers were determined by UV-second order derivative spectra, and those of the vinyl monomers, by GC. UV-fourth order derivative spectra are used for analysis of styryl-type polyamine macromonomers.^{9f} Unreacted macromonomers in polymerization solutions of **1** Me-15 of lower mole fraction were analysed by GPC for confirmation of UV. In the copolymerization in CD_3OD and CD_3CN , conversion of monomers was determined by changes of signal integration ratios of respective vinyl protons to phenylene protons in ¹H NMR spectra.

Copolymerizability

In EtOH, copolymerizations of **1** Me-3 and 15 with MMA or HEMA, of **1** Me-31 with MMA and **1** Me-28 with HEMA were examined. In the copolymerization of **1** Me-3 and 15 with MMA or HEMA, CD_3OD and CD_3CN were used as reaction solvents.

Results of the copolymerization of **1** Me-3 with MMA

Table III. Conversions of **1** Me-15 (M_1) and comonomers (M_2) in copolymerization in EtOH

Run	M_2	M_1	Time	Conversion		
				M_1 %		M_2^a
				mol%	h	
9	MMA	3.6	10	12.1	11.9	2.4
10	MMA	6.2	15	7.8	7.5	1.5
11	HEMA	4.3	17	11.5	11.0	2.7
12	HEMA	7.2	20	9.4	9.9	2.2

^a Determined by GC.

in EtOH are shown in Table II. In the copolymerization of **1** Me-15 with MMA or HEMA in EtOH, macromonomer conversions were determined in part (mole fraction of macromonomers: 3.6 to 7.2) by GPC, being very close to those determined by UV-second order derivative spectroscopy as shown in Table III. Therefore, adequateness of determining macromonomer conversion by UV was confirmed. Copolymerization rate decreased with increase in mole fractions of macromonomers in the feed and macromonomer chain length (n). This is general trend for copolymerizations of macromonomers.

Copolymer composition curves calculated from the monomer reactivity ratios on the basis of eq 1 are shown in Figures 1 and 2 (**1** Me-3, 15, and 31 with MMA in EtOH), Figure 3 (**1** Me-3 and 15 with MMA in CD_3OD), Figure 4 (**1** Me-3 with MMA in CD_3CN), and Figure 5 (**1** Me-3, 15, and 28 with HEMA in EtOH). The plots of feed composition *versus* copolymer composition were generally in agreement with the calculated curves, but, deviated considerably from those for the copolymerization of **1** Me-3 with MMA or HEMA in EtOH.

First, copolymerization with MMA is described below. The polymerization of **1** Me-3 (M_1) with MMA (M_2) in EtOH gave reactivity ratios of $r_1 = 1.86 \pm 0.15$ and $r_2 = 0.07 \pm 0.03$ (Table II, Figure 1). This means that the reactivity of **1** Me-3 is much higher than that of MMA against both of macromonomer-unit-terminated radical ($M_1 \cdot$) and MMA-unit-terminated radical ($M_2 \cdot$), and even than that of styrene in the copolymerization of styrene (M_1) and MMA (M_2) in EtOH; $r_1 = 0.40$ and $r_2 = 0.45$.¹⁷ r_2 suggests probability of mutual bind-

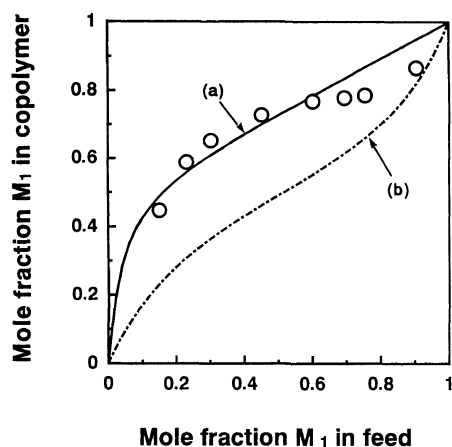


Figure 1. Monomer feed *versus* copolymer composition plots for copolymerization of **1 Me-3** (M_1) with MMA (M_2) in EtOH: (a) calculated curve for the copolymerization ($r_1 = 1.86 \pm 0.15$, $r_2 = 0.07 \pm 0.03$); (b) calculated curve for polymerization of styrene with MMA ($r_1 = 0.40$, $r_2 = 0.45$).

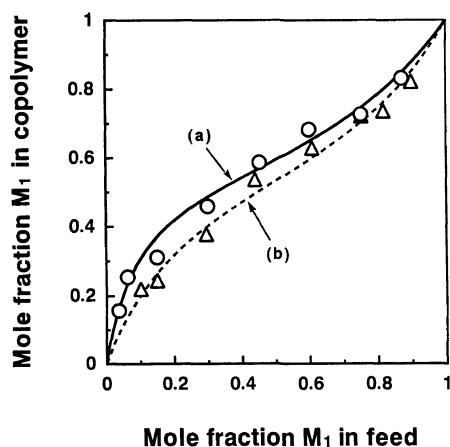


Figure 2. Monomer feed *versus* copolymer composition plots for copolymerization of **1 Me-15** or **1 Me-31** (M_1) with MMA (M_2) in EtOH: (○) plots for **1 Me-15** and MMA; (△) plots for **1 Me-31** and MMA; (a) calculated curve for **1 Me-15** and MMA ($r_1 = 0.70 \pm 0.10$, $r_2 = 0.16 \pm 0.04$); (b) calculated curve for **1 Me-31** and MMA ($r_1 = 0.55 \pm 0.10$, $r_2 = 0.36 \pm 0.05$).

ing of MMA is extremely low. With increase in n , r_1 decreased and r_2 increased (Figure 2). The reactivity of macromonomers (M_1) may thus be lowered with n against both growing radicals, $M_1\cdot$ and $M_2\cdot$. Particularly, large change in r_1 values can be found between at $n=3$ and $n=15$, that is, $r_1 = 0.70 \pm 0.10$ at $n=15$. However at $n=31$, the reactivity ratios were given as $r_1 = 0.55 \pm 0.10$ and $r_2 = 0.36 \pm 0.05$, which showed higher reactivity of VB-PMeOZO macromonomers (M_1) compared with that of styrene in the styrene-MMA copolymerization system¹⁷ even at such large n . In the copolymerization with MMA in CD_3OD , **1 Me-3** gave $r_1 = 1.25 \pm 0.10$ and $r_2 = 0.18 \pm 0.05$, while **1 Me-15** gave $r_1 = 0.53 \pm 0.10$ and $r_2 = 0.31 \pm 0.05$ (Figure 3), to indicate the higher reactivity of **1 Me-3** and decrease in reactivity with increase in n similar to polymerization in EtOH. In the copolymerization with MMA in CD_3CN , **1 Me-3** gave $r_1 = 0.41 \pm 0.10$ and $r_2 = 0.66 \pm 0.10$ (Table IV and Figure 4), while **1 Me-15** gave $r_1 = 0.35 \pm 0.08$ and $r_2 = 0.83 \pm 0.10$, showing extremely lowered reactivity especially in **1 Me-3** compared with that in alcohol

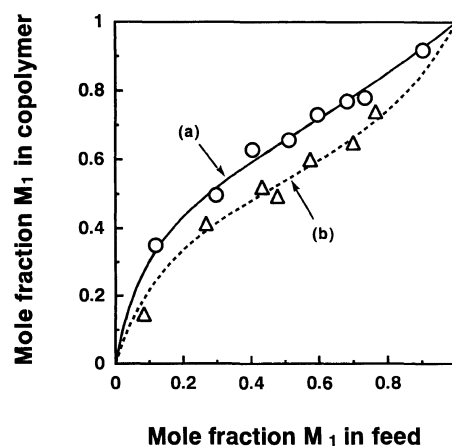


Figure 3. Monomer feed *versus* copolymer composition plots and calculated curve for copolymerization of **1 Me-3** or **1 Me-15** (M_1) with MMA (M_2) in CD_3OD : (○) plots for **1 Me-3** and MMA; (△) plots for **1 Me-15** and MMA; (a) calculated curve for **1 Me-3** and MMA ($r_1 = 1.25 \pm 0.10$, $r_2 = 0.18 \pm 0.05$); (b) calculated curve for **1 Me-15** and MMA ($r_1 = 0.53 \pm 0.10$, $r_2 = 0.31 \pm 0.05$).

solvents.

In many cases reported previously, radical copolymerizability of macromonomers (M_1) has been argued only on the basis of r_2 in copolymerization with large excess of comonomers (M_2), and generally concluded that it does not differ,⁸ or decreases⁹ from that of the corresponding small monomers. However, the present copolymerization in EtOH and CD_3OD indicate PMeOZO macromonomers of smaller n exhibit significantly higher reactivity than that of MMA and even styrene as described above. It is scarcely acceptable that the chemical reactivity of styryl group would be so strongly influenced by PMeOZO chain attached at *para* position in the same molecule. In ^{13}C NMR spectra, chemical shifts of methylene and methine carbons in vinyl groups in CD_3CN were δ 112.22 and 125.94 for 4-methylstyrene (MeSt), 112.87 and 125.88 for **1 Me-3**, and 112.86 and 125.86 for **1 Me-15**, respectively, supporting above concept.

To follow up macromonomer reactivity, spin-lattice relaxation times (T_1) in 1H NMR of the macromonomers and a model compound MeSt were measured in CD_3CN , CD_3OD , and C_2D_5OD by inversion recovery at 400 MHz at 60°C. 1H NMR relaxation is a simple means to estimate the mobility of molecules, although influenced by intermolecular contributions.¹⁸ The results of T_1 measurement on five protons (A–E) are listed in Table V. Relaxation times of the macromonomers were much shorter than those of MeSt and decreased with increase in n . T_1 of the macromonomers in CD_3CN , CD_3OD , and C_2D_5OD decreased in that order. Decrease in T_1 of the macromonomers in C_2D_5OD from that in CD_3CN was much higher than in MeSt. T_1 of MeSt in CD_3OD were rather higher than in CD_3CN . Vinylbenzyl-ended PMeOZO macromonomers **1** ($n=13$ and 34) lowered surface tension (γ) of water to exhibit surfactant properties.¹⁴ T_1 of protons A–C of macromonomers **1** determined in C_2D_5OD were closer to T_1 in D_2O rather than in CD_3CN , and fairly close to those in a C_2D_5OD – D_2O mixture (C_2D_5OD 80 wt%), in which the micellar state of macromonomers may be presumed. In

Table IV. Copolymerization of **1** Me-3 (M_1) with MMA (M_2) in CD_3CN^a

Run	Feed composition				M_1 mol %	Time h	Monomer conversion		M_1 in copolymer mol%
	$[M_1]_0$		$[M_2]_0$				M_1^b %	M_2^c %	
	mg	mol L ⁻¹ ($\times 10^2$)	mg	mol L ⁻¹ ($\times 10^2$)					
13	2.50	1.48	7.62	15.46	9.59	1.5	4.8	4.2	10.0
14	4.48	2.67	5.58	11.34	19.0	4.5	7.1	6.3	21.0
15	5.57	3.33	4.24	8.64	27.8	4.5	6.6	5.0	33.5
16	6.71	3.88	2.98	5.90	39.7	4.5	6.4	5.1	45.1
17	7.77	4.27	2.20	4.12	50.9	1.0	1.7	2.0	46.3
18	8.51	4.99	1.91	3.83	56.6	1.5	2.5	3.1	51.6
19	8.83	5.94	1.34	3.09	65.8	4.5	3.2	4.7	56.0
20	9.58	5.59	0.58	1.16	82.8	4.0	2.2	4.9	68.2

^aTotal monomers, 0.01 g; initiator, AIBN (1.0 mol% to total monomers); solvent, CD_3CN (0.6 ml); temperature, 60°C. ^bDetermined by ¹H NMR.

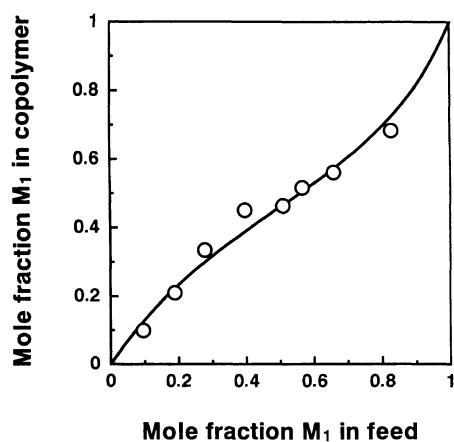


Figure 4. Monomer feed *versus* copolymer composition plots and calculated curve for copolymerization of plots for **1** Me-3 (M_1) with MMA (M_2) in CD_3CN ($r_1 = 0.41 \pm 0.10$, $r_2 = 0.66 \pm 0.10$).

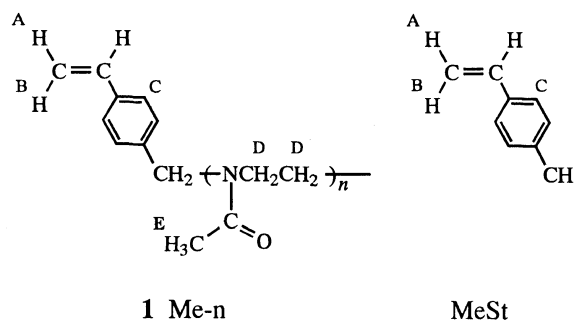
copolymerization of vinylbenzyl-ended poly(4-vinyl-*N*-*n*-butylpyridinium bromide) macromonomer with styrene in an EtOH-H₂O mixture reported by Riza, micelle formation of macromonomers is proposed.^{12c} The relaxation behavior suggests that present macromonomers take on a micelle-like state in C_2D_5OD and CD_3OD , although the state may not be so stable. The alcohols may solvate easily PMeOZO chains of aprotic nature by forming hydrogen bond between hydroxyl and carbonyl groups of PMeOZO. In **1** Me-15 and 31, T_1 of D and E in the alcohol solvents were little different from those in CD_3CN , while T_1 of styryl protons (A, B, and C) in the alcohols differed from those in CD_3CN . This seems to support the micelle-like state of macromonomers, in which styryl groups may aggregate weakly inside. Macromonomers **1** may aggregate with macromonomer units in growing chains.

The higher reactivity of **1** Me-*n* in the copolymerization in EtOH and CD_3OD can be explained on the basis of the aggregation of macromonomers, and that of macromonomers and growing chains. In the latter, macromonomers should be concentrated about growing sites. MMA may disperse homogeneously in EtOH solution. Increase of macromonomer reactivity by micelle formation in copolymerization with conventional small monomers has been reported.¹² In CD_3CN , macro-

Table V. ¹H Spin-lattice relaxation times (T_1) of macromonomers and 4-methylstyrene (MeSt) measured at 400 MHz (60.0°C)

Entry	Monomer	Solvent	Relaxation time/s				
			A	B	C	D	E
1	MeSt	CD_3CN	7.63	7.49	9.86	—	—
2	MeSt	CD_3OD	9.79	8.93	13.25	—	—
3	MeSt	C_2D_5OD	6.05	5.76	7.34	—	—
4	Me-3	CD_3CN	3.02	2.38	3.89	0.58	2.02
5	Me-3	CD_3OD	2.09	1.73	2.74	0.50	1.30
6	Me-3	C_2D_5OD	1.73	1.30	2.16	0.35	0.86
7	Me-15	CD_3CN	2.30	1.87	3.17	0.36	0.86
8	Me-15	CD_3OD	1.80	1.44	2.45	0.33	0.86
9	Me-15	C_2D_5OD	1.51	1.15	2.16	0.30	0.86
10	Me-31	CD_3CN	2.02	1.66	2.88	0.32	0.79
11	Me-31	C_2D_5OD	1.44	1.08	2.02	0.29	0.79
12	Me-3	C_2D_5OD					
		D_2O^a	1.44	1.15	1.73	0.32	0.86
13	Me-15	C_2D_5OD					
		D_2O^a	1.22	1.01	1.73	0.32	0.72
14	Me-15	D_2O	0.95	0.86	1.44	0.30	0.72

^a C_2D_5OD 80 wt%.



monomers **1** may constitute a homogeneous solution.

The apparent reactivity of PMeOZO macromonomers in the present copolymerization decreased with increase in *n*, but the chemical reactivity of the VB group cannot be considered to decrease so easily. The most probable cause for this may be steric hindrance due to augmentation in segment density around growing sites. By increase in segment density and macromonomer chain length (*n*), interpenetration of growing ends and polymerizable end groups must be sterically depressed.

Poly(methyl methacrylate)(PMMA) is incompatible

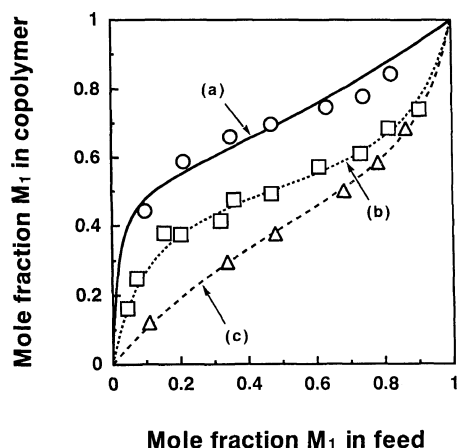


Figure 5. Monomer feed versus copolymer composition plots for copolymerization of **1 Me-3**, **1 Me-15** or **1 Me-28** (M_1) with HEMA (M_2) in EtOH: (○) plots for **1 Me-3** and HEMA; (□) plots for **1 Me-15** and HEMA; (△) plots for **1 Me-28** and HEMA; (a) calculated curve for **1 Me-3** and HEMA ($r_1 = 1.44 \pm 0.10$, $r_2 = 0.04 \pm 0.02$); (b) calculated curve for **1 Me-15** and HEMA ($r_1 = 0.26 \pm 0.05$, $r_2 = 0.20 \pm 0.05$); (c) calculated curve for **1 Me-28** and HEMA ($r_1 = 0.21 \pm 0.05$, $r_2 = 0.86 \pm 0.10$).

Table VI. Monomer reactivity ratios^a

Macromonomer ^b (M_1)	Comonomer ^c (M_2)	Solvent	r_1	r_2
Me-3	MMA	EtOH	1.86 ± 0.15	0.07 ± 0.03
Me-15	MMA	EtOH	0.70 ± 0.10	0.16 ± 0.04
Me-31	MMA	EtOH	0.55 ± 0.10	0.36 ± 0.05
Me-3	MMA	CD ₃ OD	1.25 ± 0.10	0.18 ± 0.05
Me-15	MMA	CD ₃ OD	0.53 ± 0.10	0.31 ± 0.05
Me-3	MMA	CD ₃ CN	0.41 ± 0.10	0.66 ± 0.10
Me-15	MMA	CD ₃ CN	0.35 ± 0.08	0.83 ± 0.10
Me-3	HEMA	EtOH	1.44 ± 0.10	0.04 ± 0.02
Me-15	HEMA	EtOH	0.26 ± 0.05	0.20 ± 0.05
Me-28	HEMA	EtOH	0.21 ± 0.05	0.86 ± 0.10
Me-3	HEMA	CD ₃ CN	0.38 ± 0.08	0.75 ± 0.10
Me-15	HEMA	CD ₃ CN	0.30 ± 0.05	0.93 ± 0.10

^a Evaluated based on macromonomer conversions using integrated equation. ^b Conversions were determined by UV-second order derivative spectra (reaction in EtOH) or ¹H NMR (reaction in CD₃OD and CD₃CN). ^c Conversions were determined by GC (reaction in EtOH) or ¹H NMR (reaction in CD₃OD and CD₃CN).

with poly(2-ethyl-2-oxazoline),¹⁹ and thus should also be with PMeOZO. Consequently, if PMMA chain length at a growing site increases in the copolymerization of PMeOZO macromonomers (M_1) with MMA (M_2), incompatibility of macromonomers with the MMA-terminated radicals ($M_2\cdot$) should cause greater decrease in macromonomer reactivity. The present copolymerization is not of a comonomer-large-excess system to be generally used. Therefore, it may be little influenced by the incompatible effect proposed by Ito in the copolymerization of poly(ethylene oxide) macromonomers.^{9a}

The copolymerization of **1 Me-*n*** (M_1) with HEMA (M_2) was examined. HEMA may possess affinity to aprotic PMeOZO branches on growing chains by forming hydrogen bonds of hydroxyl groups with *N*-acetyl groups. In copolymerization in EtOH, r_1 was 1.44 ± 0.10 at $n = 3$ showing unusual reactivity of the macromonomer as in polymerization with MMA (Figure 5). The value fell to 0.26 ± 0.05 at $n = 15$ indicating remarkable decrease in macromonomer reactivity toward $M_1\cdot$. r_2

increased with n , exhibiting decrease in macromonomer reactivity toward $M_2\cdot$. At $n = 28$, relative reactivity of VB-PMeOZO macromonomers with HEMA can be lower than that of styrene in the copolymerization of styrene (M_1) and HEMA (M_2) in 2-propanol in which $r_1 = 0.53$ and $r_2 = 0.59$.²⁰ The relative reactivity of HEMA should be somewhat higher than that of MMA toward $M_1\cdot$ and $M_2\cdot$. The reason for the higher relative reactivity of HEMA compared with MMA is that HEMA should access more easily propagating sites by forming hydrogen bonds to PMeOZO branches. The decrease of macromonomer reactivity with increase in n can be interpreted similarly to the copolymerization with MMA. In copolymerization with HEMA in CD₃CN, such higher reactivity of **1 Me-3** as in EtOH was not observed and with increase in n , reactivity of **1 Me-*n*** toward $M_1\cdot$ and $M_2\cdot$ decreased (Table VI).

Monomer reactivity ratios in the present polymerization using feed composition and monomer conversion are listed in Table VI.

Thus, hydrophilic PMeOZO macromonomers exhibited unusually higher reactivity in copolymerization with MMA and HEMA in EtOH especially at smaller n , possibly due to "macromonomer concentration effect". The shapes of copolymer composition curves in copolymerizations **1 Me-3**-MMA and **1 Me-3**-HEMA were remarkably similar to those in the "bootstrap model" of Harwood,²¹ suggesting copolymerization behavior to deviate from the terminal model. Also other cases in the present copolymerization of **1 Me-*n*** in the alcohol solvents, may be regarded incompatible with the terminal model, although copolymer composition curves from r_1 and r_2 appeared consistent with plots of mole fraction macromonomers in copolymer versus mole fraction macromonomers in the feed.

CONCLUSIONS

The reactivity of radical copolymerization of macromonomers **1 Me-*n*** (M_1) possessing aprotic nature with MMA and HEMA (M_2) was examined in EtOH, CD₃OD, and CD₃CN. Monomer reactivity ratios r_1 and r_2 were evaluated on the basis of the terminal model.

In alcohol solvents, **1 Me-*n*** with especially the shortest chain length ($n = 3$) exhibited remarkably higher reactivity than MMA, toward $M_1\cdot$ and $M_2\cdot$. In copolymerization with HEMA, **1 Me-3** showed high reactivity in EtOH. The reason for the high reactivity of the macromonomers is the micelle-like state.

Reactivity of macromonomers decreased with n , probably due to increase in steric hindrance to interpenetration of polymerizable end groups and growing sites.

The reactivity of HEMA in the present copolymerizations was higher than that of MMA, possibly due to forming hydrogen bonds in PMeOZO graft chains.

In copolymerization in CD₃CN, macromonomers of even $n = 3$, showed lower reactivity than comonomers.

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