Polymer Journal, Vol. 31, No. 3, pp 219—225 (1999)

Reactivity in Radical Polymerization of Poly(2-oxazoline) Macromonomers

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(Received June 5, 1998)

ABSTRACT: Reactivity in radical homopolymerization of vinylbenzyl-ended poly(2-alkyl-2-oxazoline) macromonomers (VB-PROZO-*n*; *n* (degree of polymerization) = 3—34) and methacryloyl-ended macromonomers (MA-PROZO-*n*; *n* = 4—34) was examined at 60°C in CD_3CN, $CDCl_3$, or D_2O using 2,2′-azobis(isobutyronitrile) (in organic solvents) or 2,2′-azobis(2-amidinopropane) dihydrochloride (in D_2O) as initiator. R was Me, Bu, or *n*-octyl (Oc) group. In CD_3CN (R = Me, Bu), macromonomers were polymerized faster with increase in *n*. Higher R_p was observed for Bu group and MA end group than Me group or VB end group, respectively. In $CDCl_3$, polymerization of VB-ended POcOZO macromonomers showed higher R_p than PBuOZO macromonomers. The rate increased with in *n*, whereas, polymerization of MA-ended POcOZO macromonomers showed lower *R*p than PBuOZO macromonomers of similar *n*, and rate decreased with increase in *n*. In D_2O, PMeOZO macromonomers were polymerized 9 to 14 times faster than CD_3CN. Kinetic orders of monomer concentration were 1.55 to 1.73 in organic solvents, while nearly 1.0 in water, and those of initiator concentration were close to 0.5 in CD_3CN. R_p is thus affected by carbon number of acyl side chains in PROZO and by *n*, and D_2O increases enormously R_p of PMeOZO macromonomers by micelle formation.

KEY WORDS Macromonomers / Polyoxazoline / Radical Polymerization / Kinetics / Reactivity /

Cationic ring-opening polymerization of 2-alkyl-2-oxazoline (ROZO) gives poly(2-alkyl-2-oxazoline) (PROZO) having poly(*N*-acylethylenimine) structure. PROZO can be regarded as a polymer homologue of polar aprotic solvents such as *N*,*N*-dimethylacetamide, exhibiting hydrophilic (R = Me, Et) or hydrophobic (carbon number of R ≥ 4) properties.[1] Macromonomers of PROZO, *e.g.*, styryl-[2], methacryloyl-[3], and vinylester-terminated[4] macromonomers have been synthesized using living polymerization of ROZO.

Macromonomers possess large importance and potential as building block for functional polymeric materials. Copolymerization with small-sized monomers produces graft copolymers with well-defined structure, and homopolymerization forms star-like or comb-like polymers. In contrast to polymerization of small monomers, polymerization systems of macromonomers have the following characteristics; (1) propagation reactions are polymer–polymer reactions, (2) concentrations of polymerizable end groups are low, (3) viscosity of polymerization systems is high from the initial stage of the reaction,[5] and (4) segment density around the propagating species is high.[5] These factors (1)—(4) have been found to affect greatly polymerization rates and molecular weights of poly(macromonomer)s.[5ab,6] Radical copolymerizations of PROZO macromonomers produce micron or submicron-size polymer particles utilizing macromonomers as stabilizer or emulsifier,[7] and form amphiphilic polymers from hydrophilic macromonomers and hydrophobic small monomers, *i.e.*, styrene and methyl methacrylate (MMA).[8] It is essential to know the characteristics of macromonomer reactivity in polymerization to obtain well-defined polymers. Many studies on copolymerizations[6,9] and homopolymerizations[2b,5,6] of macromonomers have been reported mainly in radical polymerization. The factor predominating polymerizability of macromonomers in copolymerization is primarily chemical reactivity of polymerizable end groups.[2b,5ab,10]

Homopolymerization of PROZO macromonomers has not been reported so far for radical and ionic polymerizations. Polymerizability of PROZO macromonomers is of interest first in radical homopolymerization. Homopolymerization may be strongly subject to solvent effect, since macromonomers with polymer homologue structure of aprotic amide solvent can possess hydrophilic or hydrophobic nature. Consequently, polymerization behavior of macromonomers in organic solvents and/or water is of interest. In radical polymerization of poly(ethylene oxide) macromonomers in water, Ito and co-workers propose the micellar polymerization.[5b] Polymerization of macromonomers with long side chains has not been reported extensively. PROZO macromonomers with long acyl groups can easily be obtained and acyl side chains may affect sterically reactivity in growing sites and/or polymerizable end groups such as by increasing segment density. This paper reports reactivity in radical homopolymerization of vinylbenzyl- and methacryloyl-terminated PROZO macromonomers (R = Me, Bu, Oc), for different chain lengths of PROZO, reaction solvents (acetonitrile, chloroform, and water), and macromonomer concentrations.

EXPERIMENTAL

Materials

CH_3CN was purified by distillation after refluxing with P_2O_5. Et_2O was distilled over sodium wire. Commercial reagents 2-methyl-2-oxazoline (MeOZO) and methacryloyl chloride were purified by distillation. 2-*n*-Butyl-

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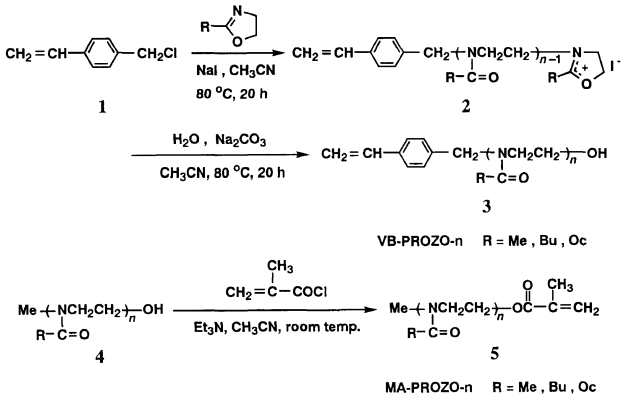

Scheme 1.

2-oxazoline (BuOZO),[11] 2-*n*-octyl-2-oxazoline (OcOZO),[11] and *p*-vinylbenzyl chloride (VBC)[12] were prepared according to the literature. Commercial initiator 2,2′-azobis(2-amidinopropane) dihydrochloride (V-50) and deuterated solvents CD_3CN, $CDCl_3$, and D_2O were used as received. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized from MeOH.

Measurements

^1H NMR spectra were recorded on a JEOL JNM FX60Q FT NMR spectrometer at 24°C with tetramethylsilane as standard. GPC was performed using a SHIMADZU LC-10AD chromatograph equipped with a SHIMADZU RID-6A RI detector. GPC columns, SHODEX AC-803 and JASCO FINE PACK GEL-101(Column A; M_n at exclusion limit, 7×10^4), or two columns of TOSOH TSKgel $GMH_{HR}M$ (Column B; M_n at exclusion limit, 4×10^6) were connected in series, and $CHCl_3$ was used as an eluent at a flow rate of 0.8 mL min^{-1} in the former, and *N*,*N*-dimethylformamide (DMF) was used at the same flow rate at 60°C in the latter. Surface tension of aqueous macromonomer solutions was measured by a KYOWA CBVP-A3 tensiometer (Wilhelmy method).

Macromonomers

p-Vinylbenzyl(VB)-terminated PROZO (VB-PROZO) macromonomers (**3**) and MA-terminated PROZO(MA-PROZO) macromonomers (**5**) were prepared by the living polymerization of 2-alkyl-2-oxazoline (ROZO) (Scheme 1).

ROZO was heated with VBC and NaI as initiator in CH_3CN to give rise to living PROZO (**2**),[2a] which was hydrolyzed to alcohol (**3**). Macromonomers **3** were purified by reprecipitation from $CHCl_3$ solution with Et_2O (R = Me) or hexane (R = Bu and Oc) as nonsolvents. For preparation of MA-PROZO macromonomers (**5**), ROZO was polymerized with methyl tosylate as an initiator and the living PROZO was hydrolyzed to give a PROZO-alcohol (**4**), which was acylated with methacryloyl chloride.[3] **5** was purified similarly to **3**.

The results are shown in Table I. Code names of the macromonomers are VB-PROZO-*n* and MA-PROZO-*n*, whose *n* is DP_n of ROZO. M_n of **3** and **5** was determined by ^1H NMR and GPC. In ^1H NMR, signal integration ratios of NCH_2 protons (δ 3.4—3.6) to phenylene protons (δ 7.19—7.47) in **3** and NCH_3 protons (δ 3.0) at ω ends

Table I. Macromonomers of poly(2-alkyl-2-oxazoline)(PROZO)

Macromonomer[a]	M_n		DP_n[b]	M_w/M_n[b]	F[c]
	NMR	GPC			
VB-PMeOZO-3	470	440	3.3	1.31	1.00
VB-PMeOZO-13	1230	1140	12.8	1.10	1.00
VB-PMeOZO-34	3030	2910	34.0	1.16	1.00
VB-PBuOZO-13	1810	1760	13.2	1.12	1.00
VB-PBuOZO-24	3120	3190	23.5	1.15	1.00
VB-POcOZO-3	730	680	3.0	1.34	1.00
VB-POcOZO-16	3100	3010	15.7	1.17	1.00
MA-PMeOZO-8	800	830	8.2	1.18	1.00
MA-PMeOZO-15	1340	1410	14.6	1.12	0.98
MA-PMeOZO-32	2820	2730	32.0	1.17	0.99
MA-PBuOZO-7	1010	960	7.2	1.15	1.00
MA-PBuOZO-14	1920	1840	14.3	1.13	1.00
MA-PBuOZO-34	4390	4020	33.7	1.19	0.99
MA-POcOZO-4	800	880	3.8	1.30	1.00
MA-POcOZO-8	1660	1740	8.5	1.16	1.00
MA-POcOZO-11	2140	2230	11.1	1.17	1.00

[a] POcOZO: poly(2-*n*-octyl-2-oxazoline). [b] Determined by GPC. [c] *F*: functionality of polymerizable end groups determined by ^1H NMR.

in **5** gave macromonomer chain length *n* (DP_n), from which M_n was calculated. GPC was measured with GPC columns SHODEX AC-803 and JASCO FINE PACK GEL-101 connected in series (Column A) in $CHCl_3$ as eluent using PMeOZO standards prepared by polymerization of MeOZO by MeOTs as initiator. Molecular weight distribution was generally narrow reflecting the living nature of the polymerization; $M_w/M_n = 1.10$—1.34. Functionality (*F*), *i.e.*, the number of vinylbenzyl or methacryloyl groups per molecules of macromonomers **3** and **5** was evaluated as follows. *F* of **3** was calculated from signal integration ratios of phenylene protons (δ 7.19—7.47) to OCH_2 protons (δ 4.07) at ω ends, and that of **5** was calculated from signal integration ratios of both vinyl protons (δ 5.60—6.03) of methacryloyl groups to NCH_3 protons (δ 3.0) at ω ends.

Polymerization

Radical polymerization of macromonomers was carried out under Ar in organic solvents (CD_3CN, $CDCl_3$) or D_2O in a sealed 5 mmϕ NMR tube at 60°C, using AIBN (in organic solvents) or V-50 (in D_2O) as initiator. Conversion of macromonomers was mainly determined by change of signal integration ratios in ^1H NMR of the reaction mixture, *i.e.*, CH_2 signal (δ5.80, 5.25) of vinyl group to CH_2 signal (δ4.28) of benzyl group in VB-PROZO, and CH_2 signal (δ 5.60—6.03) of vinyl group to CH_2 signal (δ4.24) of OCH_2 signal in MA-PROZO. For confirmation of NMR, macromonomer conversion was determined also by GPC in the homopolymerization of VB-PMeOZO-13 and MA-PMeOZO-15 in CD_3CN. The reaction solutions were evaporated *in vacuo* to dryness to give mixtures of poly(macromonomer)s and unreacted macromonomers, which were analyzed by GPC using two columns of TOSOH TSKgel $GMH_{HR}M$ connected in series(Column B) in DMF as eluent. Conversion *p* of the macromonomer was calculated from eq 1 under the assumption that peak area per ROZO unit by RI detector is equal for a macromonomer and a poly(macromonomer).

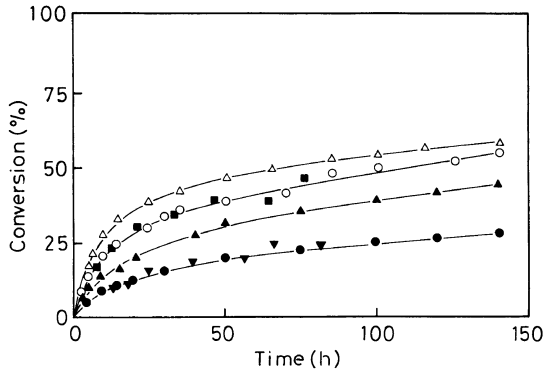

Figure 1. Time *versus* conversion plots in the polymerization of MA-PMeOZO-15 (○ by NMR, ■ by GPC), MA-PMeOZO-32 (△ by NMR), VB-PMeOZO-13 (● by NMR, ▼ by GPC), and VB-PMeOZO-34 (▲ by NMR) in CD_3CN at 60°C with $[M]_0=44$ mmol L^{-1} and $[I]_0=2.20$ mmol L^{-1}.

$$p=A_p/(A_m+A_p) \quad (1)$$

where A_m is the peak area of a macromonomer, while A_p, that of poly(macromonomer). Polymerization rate R_p was obtained from the initial slope of time-conversion plots. After polymerization reaction mixtures were analyzed by GPC using the Column B in the same manner as described above using polystyrene as standard.

In Figure 1, time *versus* conversion plots of polymerization of PMeOZO macromonomers in CD_3CN are shown. Plots given by GPC in VB-PMeOZO-13 and MA-PMeOZO-13 agree well with those by ^1H NMR. Therefore, NMR was mainly used for determining conversion.

RESULTS AND DISCUSSION

Polymerization Rate

PBuOZO macromonomers were insoluble in D_2O, and POcOZO macromonomers were insoluble in D_2O and CD_3CN. Both macromonomers were readily soluble in $CDCl_3$. PMeOZO macromonomers were soluble in three solvent. The resulting poly(macromonomer)s were insoluble in $CDCl_3$.

Time *versus* conversion plots in Figure 1 suggest that polymerization proceeds faster with chain length (n) for VB-PMeOZO and MA-PMeOZO macromonomers within the range of n examined. The apparent rates of polymerization (R_p) from those curves (Table II) were higher than that for model small monomers (VB-PMeOZO-3), and increased with n. Time *versus* conversion plots in organic solvents leveled off with reaction time, ascribable to dead-end polymerization because of low concentrations of the monomers.[13] In the radical polymerization of vinylbenzyl-ended poly(ethylene oxide) macromonomers with chain length n of 32—45 in benzene reported by Ito *et al.*, R_p was higher than for model monomers with n of 4.[5b] Our results seem basically consistent with their data. In MA and VB-ended polystyrene macromonomers, R_p was observed to be larger for the macromonomers with longer chain length than for shorter chain length by Tsukahara *et al.*, which was explained by higher gel effect.[5a]

In the polymerization of macromonomers, higher viscosity and segment density than the ordinary polymerization system must depress translational diffusion and segmental diffusion of growing sites and macromonomers, and mutual diffusion of growing sites.[14] These effects are expected to decrease propagation and termination rates. Bimolecular termination reactions between growing ends with high segment density should be strongly suppressed by depression of diffusion.[14]

Table II. Polymerization rates of PMeOZO and PBuOZO macromonomers in organic solvents[a]

Entry	Macromonomer	Polymerization solvent	$R_p \times 10^{7}$ [b] / mol L^{-1} s^{-1}
1	VB-PMeOZO-3	CD_3CN	0.74
2	VB-PMeOZO-13	CD_3CN	1.09
3	VB-PMeOZO-34	CD_3CN	2.22
4	VB-PBuOZO-13	CD_3CN	4.45
5	VB-PBuOZO-13	$CDCl_3$	0.84
6	VB-PBuOZO-24	CD_3CN	5.85
7	VB-POcOZO-3	$CDCl_3$	11.30
8	VB-POcOZO-16	$CDCl_3$	19.73
9	MA-PMeOZO-8	CD_3CN	1.00
10	MA-PMeOZO-15	CD_3CN	3.34
11	MA-PMeOZO-32	CD_3CN	5.64
12	MA-PBuOZO-7	CD_3CN	1.64
13	MA-PBuOZO-14	CD_3CN	7.47
14	MA-PBuOZO-14	$CDCl_3$	3.50
15	MA-PBuOZO-34	CD_3CN	9.41
16	MA-POcOZO-4	$CDCl_3$	2.11
17	MA-POcOZO-8	$CDCl_3$	0.95
18	MA-POcOZO-11	$CDCl_3$	0.68

[a] $[M]_0=44$ mmol L^{-1}; $[I]_0=2.2$ mmol L^{-1}; temperature, 60 °C. [b] Initial rate of polymerization.

Radical polymerization rate R_p in ordinary monomers is defined by[15]

$$R_p=k_p(2fk_d/k_t)^{0.5}\,[M][I]^{0.5} \quad (2)$$

where k_p, k_t, and k_d are rate constants for propagation, termination, and initiator decomposition, respectively, and f is initiator efficiency. In polymerization of macromonomers, decrease of termination reactivity results in increase in polymerization rate.[5b,14] Tsukahara *et al.* reported that k_p and k_t (L mol^{-1} s^{-1}) of radical polymerization of MA-terminated polystyrene macromonomer ($M_n=4400$) were 1/20 and 1/3000 of those of MMA, respectively.[5a] When R_p of PMeOZO and PBuOZO macromonomers of similar chain length (n) are compared as shown in Table II, the polymerization of PBuOZO macromonomers is faster than that of PMeOZO macromonomers for VB and MA polymerizable groups (entry 2, 4, and 10, 13). With similar chain length (n), molecular weight of PBuOZO macromonomer is higher than that of PMeOZO macromonomers. PBuOZO macromonomers with lower molecular weight polymerize faster than PMeOZO macromonomers with higher molecular weight (entry 4, 3 and 13, 11). PROZO macromonomers with pentanoyl side chains can be considered to possess higher reactivity than macromonomers with acetyl side chains in these reaction conditions and ranges of n. This can be mainly ascribed to depress termination caused by retarding translational diffusion and interpenetration of propagating sites with highly increased segment density (Figure 2).

Comparing reactivity of polymerizable end groups,

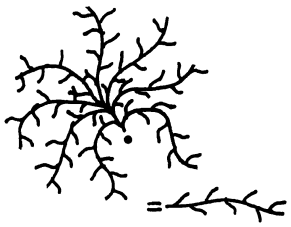

Figure 2. Models for growing chains and macromonomers.

MA-terminated macromonomers exhibited higher initial rates of polymerization than VB-terminated macromonomers with same alkyl groups (R) and similar chain length (n). This agrees with results for MMA and styrene monomers.[15]

Polymerizability of POcOZO macromonomers with longer branch (pelargonoyl group) was examined and compared with that of PBuOZO macromonomers using $CDCl_3$ as solvent, since POcOZO macromonomers were insoluble in CD_3CN. The results are given in Table II. The polymerizability of PBuOZO macromonomers in $CDCl_3$ is lower than in CD_3CN (entry 4, 5 and 13, 14). PBuOZO macromonomers were more readily soluble in $CDCl_3$ than in CD_3CN, forming transparent solutions in $CDCl_3$ but slightly cloudy solution in CD_3CN. Consequently, lower rates in $CDCl_3$ can be explained as follows: higher solubility of PBuOZO chains in $CDCl_3$ increases the coil size of growing chain than in CD_3CN, favoring interpenetration between growing sites to lead to inefficient retardation of termination reaction. In VB-ended macromonomers, even VB-POcOZO-3 of shorter chain length (n) and lower molecular weight exhibited significantly higher initial rate (11.30×10^{-7} mol $L^{-1} s^{-1}$), being polymerized faster than VB-PBuOZO-13 of longer chain length and of higher molecular weight. R_p of VB-POcOZO-16 was further higher, *i.e.*, 19.73×10^{-7} mol $L^{-1} s^{-1}$. Such high R_p of VB-POcOZO macromonomers are very noticeable in the present polymerization in organic solvents. The reason for these results can be considered basically the same as the reactivity of PBuOZO macromonomers as described above, and further acceleration of reactivity in VB-POcOZO macromonomers must be achieved by stronger depression of termination caused by highly increased segment density around growing sites (Figure 2). MA-terminated POcOZO macromonomers showed quite different tendency. R_p of MA-POcOZO-4, whose chain length is shortest in MA-POcOZO macromonomers, is 2.11×10^{-7} mol $L^{-1} s^{-1}$, being lower than that of MA-PBuOZO-14. R_p of MA-POcOZO macromonomers decreased with increase in chain length (n). In various macromonomers, MA-ended macromonomers are usually polymerized with higher reactivity than VB-ended ones as already discussed. The reverse results were observed in POcOZO macromonomers. Decrease in polymerizability of MA-POcOZO macromonomers may be explained as follows: in MA-POcOZO macromonomers or their polymer radicals, linkages from vinyl groups or growing ends to POcOZO segments are wholly single bonds that are flexible in contrast to VB-POcOZO macromonomers or their radicals, and accordingly steric effect of the long acyl chains (pelargonoyl groups) seems highly exerted at reaction

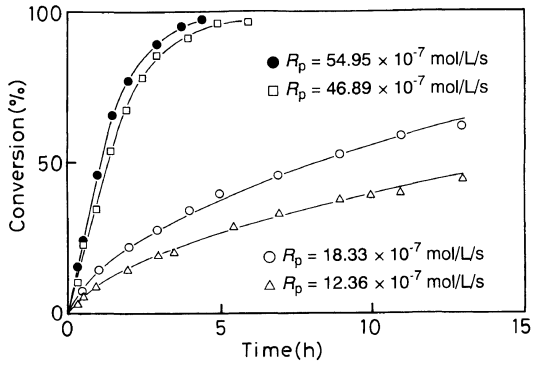

Figure 3. Time *versus* conversion plots in the polymerization of MA-PMeOZO-32 (●), MA-PMeOZO-15 (□), VB-PMeOZO-34 (○), and VB-PMeOZO-13 (△) in D_2O at 60°C with $[M]_0 = 44$ mmol L^{-1} and $[I]_0 = 0.44$ mmol L^{-1}. Conversion was followed by NMR.

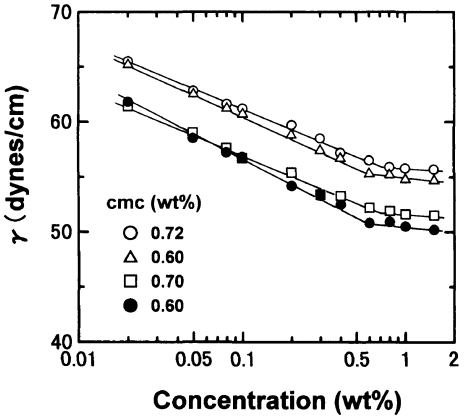

Figure 4. Relationship of surface tension (γ) to solution concentration in macromonomers; MA-PMeOZO-32 (○), VB-PMeOZO-34 (△), MA-PMeOZO-15 (□), and VB-PMeOZO-13 (●).

sites to retard strongly propagation reactions. In the radical polymerization of VB and MA-ended poly(ethylene oxide) macromonomers, bulky alkyl groups such as n-octyl groups at ω ends show little effect on polymerizability.[5b]

The reactivity of radical polymerization of PMeOZO macromonomers in D_2O increased enormously, compared with CD_3CN, as shown in Figure 3. For VB-PMeOZO-13 and 34, ratios of R_p in D_2O to that in CD_3CN were 11.3 and 9.27, respectively. Ito *et al.* proposes the micellar polymerization of poly(ethylene oxide) macromonomers in water.[5b] The polymerization rate was extremely higher than that in benzene, mainly due to increased propagation and decreased termination.[16] VB-PMeOZO macromonomers act also as emulsifiers in soap-free emulsion copolymerization with styrene in water.[7b] To examine the ability of micelle formation of PMeOZO macromonomers in water, surface tension (γ) of aqueous solutions of VB and MA-ended macromonomers (n: 13—34) was measured. γ of 1.0 wt% solutions of VB-PMeOZO-13, VB-PMeOZO-34, MA-PMeOZO-15, and MA-PMeOZO-32 were 50.5, 54.8, 51.6, and 55.8 dynes cm^{-1}, respectively, exhibiting surfactant properties of PMeOZO macromonomers and were lower at n of 13—15 than 32—34. Critical micelle concentrations (cmc) were observed at 0.60—0.72 wt% (Figure 4). Those results show that the PMeOZO macromonomers should aggregate in aqueous

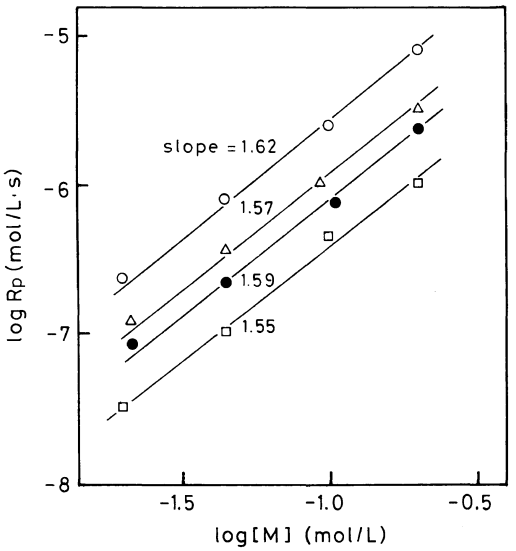

Figure 5. Log–log plots of R_p *versus* $[M]$ in the polymerization of MA-PBuOZO-14 (○), MA-PMeOZO-15 (△), VB-PMeOZO-34 (●), and VB-PMeOZO-13 (□) in CD_3CN at 60°C with $[I]_0 = 2.20$ mmol L^{-1}.

solution to form micelles in the range of monomer concentrations in actual polymerization solutions. Reactivities of propagation and termination should increase and decrease, respectively, to accelerate polymerization.

For MA-PMeOZO-15 and 32, ratios of R_p in D_2O to that in CD_3CN were 14.1 and 9.8, respectively. The polymerization of MA-PMeOZO macromonomers in D_2O can also be taken as micellar polymerization and was observed to proceed at higher rate than that of VB-PMeOZO macromonomers. Ratios of R_p of MA-PMeOZO-*n* to that of VB-PMeOZO-*n* at similar *n* in D_2O were higher than in CD_3CN. It is not easy to explain this trend, because k_p and k_t are unknown. The enhancing effect of water solvent on polymerization rate was observed to be higher for chain length *n* around 13, probably due to fitting for micelle formation of macromonomers as described above.

Concentration Dependence of Polymerization Rate

The radical polymerization rate of PROZO macromonomers is influenced by macromonomer chain length (*n*) and carbon number of alkyl chains. The effects of concentrations of monomer and initiator on the present polymerization system were examined.

The effects of monomer concentrations on the polymerization rate R_p are shown in Figure 5. Whole plots of log $[M]$ *versus* log R_p gave straight lines. Reaction orders of macromonomer concentration $[M]$ obtained from the slopes of the straight lines are listed in Table III. The values given in polymerization of PMeOZO macromonomers in CD_3CN are in the range of 1.55—1.63, and higher than for convensional small monomers in radical polymerization.

Tsukahara *et al.*[14a] and Ito *et al.*[5b] obtained kinetic orders of $[M]$ to be 2.1 and 1.40—1.49 for the MA-ended polystyrene macromonomer of a M_n of 12400 and VB-ended poly(ethylene oxide) macromonomers of a molecular weight around 1200 respectively, in the homopolymerization in organic solvents. They explained the

Table III. Reaction orders of macromonomer concentrations[a]

Macromonomer	Polymerization solvent	Kinetic order[b]
VB-PMeOZO-13	CD_3CN	1.55
VB-PMeOZO-34	CD_3CN	1.59
VB-PBuOZO-13	CD_3CN	1.61
MA-PMeOZO-15	CD_3CN	1.57
MA-PMeOZO-32	CD_3CN	1.63
MA-PBuOZO-14	CD_3CN	1.62
VB-PBuOZO-13	$CDCl_3$	1.65
VB-POcOZO-16	$CDCl_3$	1.72
MA-PBuOZO-14	$CDCl_3$	1.68
MA-POcOZO-11	$CDCl_3$	1.73
VB-PMeOZO-13	D_2O	1.04
MA-PMeOZO-15	D_2O	0.97

[a] $[M]_0 = 44$ mmol L^{-1}; $[I]_0 = 2.2$ mmol L^{-1}; temperature, 60°C. [b] Kinetic order of $[M]$.

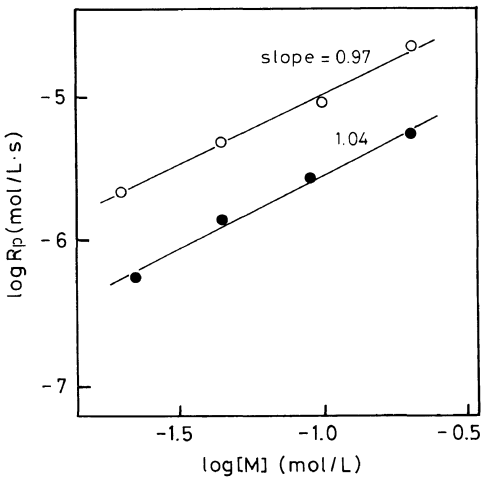

Figure 6. Log–log plots of R_p *versus* $[M]$ in the polymerization of MA-PMeOZO-15 (○) and VB-PMeOZO-13 (●) in D_2O at 60°C with $[I]_0 = 0.44$ mmol L^{-1}.

higher kinetic orders on the basis of increased viscosity of polymerization media by higher concentrations of macromonomers, resulting in retardation of termination reactions. Kinetic orders in the present polymerization can be interpreted by the same gel effect, because of similar M_n of the PROZO macromonomers for poly(ethylene oxide) macromonomers. In macromonomers with longer acyl groups (R = Bu, Oc), slightly higher kinetic orders were observed, probably due to stronger depression in termination brought about by increased suppression of diffusions with segment density of growing radicals.

Log–log plots of R_p *versus* $[M]$ in the polymerization of VB-PMeOZO-13 and MA-PMeOZO-15 in D_2O also gave straight lines (Figure 6), showing higher rates than in organic solvents. The kinetic orders of $[M]$ were close to 1.0, as normally observed for convensional small monomers. Under the assumption that polymerization in water proceeds in micelles, monomer concentration should affect the number of micelles in reaction system. There would be no influence on the diffusion control in micelle. Thus, kinetic order is the same as the small monomer system.

The dependence of R_p of VB-PMeOZO-13 and MA-PMeOZO-15 in CD_3CN on initiator concentration $[I]$

at $[M]_0 = 44\,\text{mmol}\,L^{-1}$ is given in Figure 7. Log–log plots of R_p *versus* $[I]$ gave straight lines, from whose slopes kinetic orders were determined as 0.50 (MA-PMeOZO-15) and as 0.54 (VB-PMeOZO-13). These orders appear compatible with the square root rule in eq 2. Thus, the result suggests that the termination in CD_3CN involves mainly bimolecular reaction at the $[M]_0$.

Molecular Weights of Poly(macromonomer)s

After polymerization in NMR tube, molecular weights of produced poly(macromonomer)s were measured by GPC using an RI detector (Table IV). The values increased with macromonomer concentration under the same conditions of macromonomers (polymerizable end group and R), probably due to depression of termination by increasing the viscosity of the polymerization system. Tsukahara *et al.* reported that molecular weight of a poly(macromonomer) is strongly affected by monomer concentration in radical polymerization of polystyrene macromonomers.[14] GPC of the product obtained from MA-PBuOZO-14 with $[M]_0$ of $200\,\text{mmol}\,L^{-1}$ showed poly(macromonomer) peaks at M_n of 90350 and 364000 (Figure 8). This can be explained by increased viscosity due to smaller polymer formed with consequent increase in the molecular weight of the polymer given by polymerization. Examination of MA-PBuOZO-34 with $[M]_0$ of $200\,\text{mmol}\,L^{-1}$ exhibited no polymerization, probably due to remarkable depression of diffusion of growing radicals and macromonomers by increased viscosity and higher segment density. In contrast, VB-PMeOZO-34 polymerized even with $[M]_0$ of $200\,\text{mmol}\,L^{-1}$ (Figure 5). The polymerization of PBuOZO macromonomers in $CDCl_3$ gave poly(macromonomer)s of higher molecular weights than in CD_3CN. This can be explained by considering that the expanded coils of growing chains in $CDCl_3$ favor penetration of macromonomers to accelerate propagation, resulting in increased molecular weights of poly(macromonomer)s.

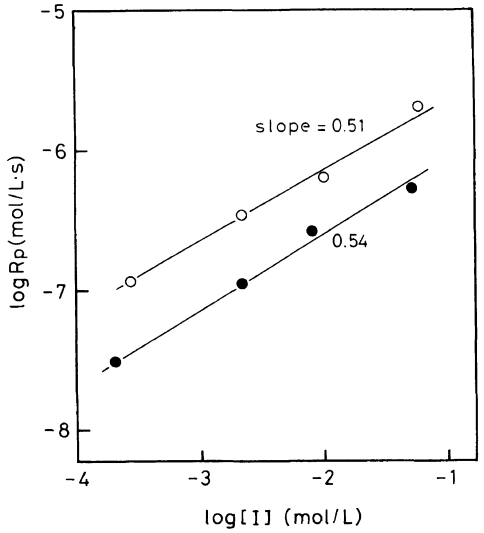

Figure 7. Log–log plots of R_p *versus* $[I]$ in the polymerization of MA-PMeOZO-14 (○) and VB-PMeOZO-13 (●) in CD_3CN at 60°C with $[M]_0 = 44\,\text{mmol}\,L^{-1}$.

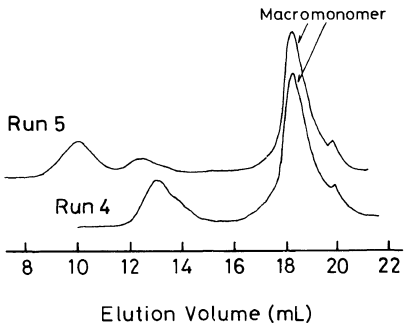

Figure 8. GPC curves of reaction mixtures in the polymerization of MA-PBuOZO-14 in CD_3CN at 60°C (Runs 4 and 5). GPC: column, TOSOH TSKgel $GMH_{HR\text{-}M}$ (×2); solvent, DMF (LiCl); temp, 58°C; flow rate, 0.8 mL min.$^{-1}$ Run 4: $[M]_0 = 44\,\text{mmol}\,L^{-1}$; $[I]_0 = 2.2$ mmol L^{-1}; reaction time, 130 h. Run 5: $[M]_0 = 200\,\text{mmol}\,L^{-1}$; $[I]_0 = 2.2$ mmol L^{-1}; reaction time, 130 h.

Table IV. Molecular weights of poly(macromonomer)s[a]

Run	Macromonomer	Entry	Polymerization[b]			M_n	DP_n
			Solvent	$[M]_0$ / mmol L^{-1}	Time / h		
1	MA-PBuOZO-7	12	CD_3CN	44	140	54400	57
2	MA-PBuOZO-7	—	CD_3CN	200	140	132000	137
3	MA-PBuOZO-14	—	CD_3CN	20	140	38200	21
4	MA-PBuOZO-14	13	CD_3CN	44	140	63500	35
5	MA-PBuOZO-14	—	CD_3CN	200	140	90400	49
						364000	198
6	MA-PBuOZO-34	—	CD_3CN	100	140	116000	29
7	MA-PBuOZO-34	—	CD_3CN	200	140	—[c]	—
8	VB-PBuOZO-13	4	CD_3CN	44	140	32500	19
9	VB-PBuOZO-24	6	CD_3CN	44	140	35400	11
10	MA-PBuOZO-14	14	$CDCl_3$	44	130	82700	45
11	MA-POcOZO-8	17	$CDCl_3$	44	130	89450	51
12	MA-PMeOZO-15	10	CD_3CN	44	140	33900	24
13	VB-PMeOZO-13	2	CD_3CN	44	140	28700	25
14	MA-PMeOZO-15	21	D_2O	44	6	48600	35
15	VB-PMeOZO-13	19	D_2O	44	13	39700	35

[a] Determined by GPC: column, TOSOH TSKgel $GMH_{HR}M$(×2)(Column B); solvent, DMF(LiCl); temp, 60°C; flow rate, 0.8 mL min^{-1}. [b] $[I]_0 = 2.2\,\text{mmol}\,L^{-1}$ (in organic solvents) and $0.44\,\text{mmol}\,L^{-1}$ (in D_2O); temp, 60°C. [c] No polymerization observed.

CONCLUSIONS

Reactivity of radical homopolymerization of VB-PROZO and MA-PROZO macromonomers was examined. In CD_3CN or $CDCl_3$, polymerization rate of the macromonomers increased with macromonomer chain length (*n*) and/or in carbon number of alkyl groups (R), except in the case of MA-POcOZO-*n*. This can be explained that higher solution viscosity and segment density around the growing sites depress the translational diffusion and segmental diffusion of the growing chains to retard bimolecular termination.

In POcOZO macromonomers, polymerization rates of MA-type monomers were slower than for VB-type monomers, in contrast to present macromonomers and convensional small monomers and other macromonomers. With increase in *n*, polymerization rate of VB-POcOZO-*n* increased, whereas that of MA-POcOZO-*n* decreased. This may be interpreted that the growing ends or the vinyl groups of MA-POcOZO-*n* are more susceptible to steric effects of POcOZO segment having long acyl chains than those of VB-POcOZO-*n*.

PMeOZO macromonomers were polymerized in D_2O 9 to 14 times faster than CD_3CN, probably due to micelle formation of macromonomers.

Kinetic orders of monomer concentration were determined as 1.55 to 1.73 in organic solvents and closely 1.0 in water. The higher orders in organic solvents would result from increased retardation of termination caused by increased viscosity. The orders of initiator concentration were close to 0.5, suggesting termination was mainly bimolecular reaction.

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