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Radical Polymerization Kinetics of Poly(ethylene oxide) Macromonomers

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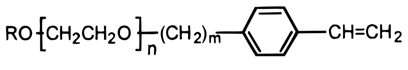
ABSTRACT: Radical polymerization of poly(ethylene oxide) macromonomers carrying a methoxy group on the one end and a *p*-vinylbenzyl or a (*p*-vinylphenyl)butyl group on the other end was investigated in benzene and water. The overall rate of polymerization was found to be more than 50 times higher in water than that in benzene. Apparent rate constants of propagation and termination were evaluated based on ESR measurements under irradiation, while initiator efficiency was estimated from inhibition period measurements. Very rapid polymerization in water was then reasonably attributed to a combined result of locally concentrated propagating radicals and monomers in their micellar organization, together with high initiator efficiency, enhanced rate of propagation, and reduced rate of termination there.

Introduction

We have reported an unusually rapid radical polymerization in water of poly(ethylene oxide) macromonomers of the general structure[2-5]



(**1**) **R-PEO-VB-n** (m=1)

(**2**) **R-PEO-Cm-S-n** (m>1)

where R stands for alkyl group as an ω-end, PEO for poly(ethylene oxide), VB for *p*-vinylbenzyl, Cm-S for *p*-styrylbutyl ($m = 4$) or -heptyl ($m = 7$) as an α-end, and n for the number-average degree of polymerization of PEO. Because of their amphiphilic constitution (PEO chains are soluble in water while *p*-styrylalkyl groups are insoluble in water), they organize into micelles with the polymerizing end groups locally concentrated in the cores, which apparently enhances their polymerization. Their aggregation has in fact been confirmed by means of static light scattering[2] and fluorescence probe methods.[6]

Meanwhile, interesting polymerization behaviors have recently been reported with a number of micelle-forming, surface-active monomers.[7-10] Also of interest to us, polymerization of some macromonomers such as polystyrene[11,12] and poly(methyl methacrylate)[13,14] with *p*-vinylbenzyl or methacrylate end-groups has been characterized by a lower rate of propagation and a much lower rate of termination, and thus by a comparable or rather higher overall rate of polymerization, as compared to that of conventional monomers such as styrene or methyl methacrylate, respectively. Therefore we considered it important and interesting to study the micellar polymerization of the PEO macromonomers in more details including determination of propagation radicals by ESR to estimate rate constants of propagation, k_p, and termination, k_t. Here we report the results with Cl-PEO-VB-48 (**1**, R = CH_3, $n = 48$) and Cl-PEO-C4-S-48 (**2**, R = CH_3, $m = 4$, $n = 48$) and discuss their micellar polymerization characteristics in comparison with their isotropic polymerization in benzene.[15]

Experimental Section

Materials. The PEO macromonomers were prepared from poly(ethylene glycol) monomethyl ether (MPEG, from Aldrich, $M_n = 2000$) by alkoxidation with sodium hydride, followed by reaction with excess *p*-vinylbenzyl chloride or *p*-(4-bromobutyl)styrene.[4] For example, Cl-PEO-VB-48 was obtained as

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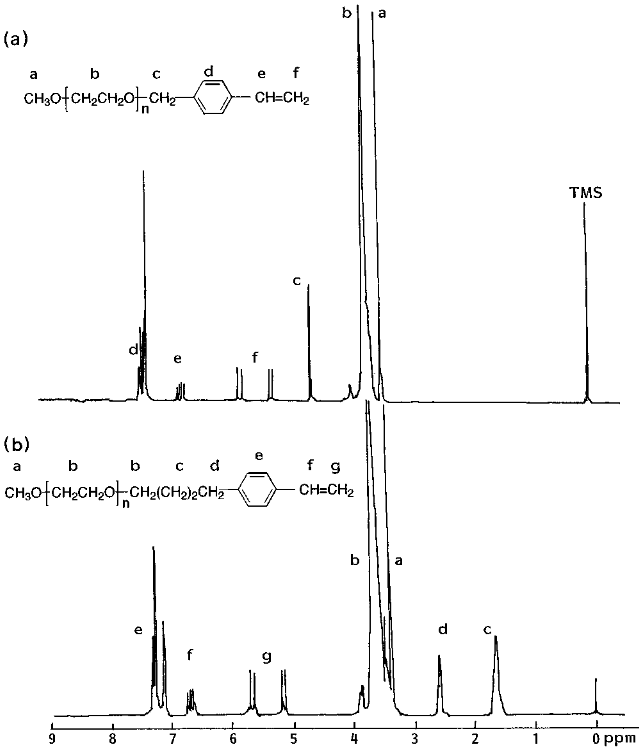

Figure 1. ^{1}H NMR spectra of PEO macromonomers in $CDCl_3$: (a) Cl-PEO-VB-48 and (b) Cl-PEO-C4-S-48.

Table 1. Characterization of the PEO Macromonomers Used

code	M_n	n ^{1}H NMR[a]	n GPC	M_w/M_n GPC	functionality ^{1}H NMR[b]
Cl-PEO-VB-48	2260	48	48	1.04	0.96
Cl-PEO-C4-S-48	2300	48	48	1.13	0.95

[a] Determined from the peak area ratio of oxyethylene to double bond methylene. [b] Determined from the peak area ratio of double bond methylene to ω-methoxy.

follows. In a three-necked, 500 mL flask under argon atmosphere was placed 0.6 g (25 mmol) of sodium hydride and dry tetrahydrofuran (THF) (50 mL), and a solution of 10 g (5 mmol) of MPEG in THF (100 mL) was dropped in at room temperature and stirred for 2 h. After this mixture was cooled to 0 °C, 5 g (33 mmol) of *p*-vinylbenzyl chloride was dropped in and stirred at room temperature for 24 h. The solution was poured into excess acetone to precipitate the resulting sodium chloride, which was filtered out. The filtrate was evaporated under a reduced pressure to remove almost all of acetone and then poured into hexane to precipitate the macromonomer, which was recovered by centrifuge (~3000 rpm). After two reprecipitations from benzene into hexane and freeze-drying from benzene, the macromonomer was obtained in more than 90% yield. Cl-PEO-C4-S-48 was obtained similarly but by a coupling reaction with *p*-(4-bromobutyl)styrene conducted at 30 °C for 72 h. Their ^{1}H NMR spectra and results of the characterization are given in Figure 1 and Table 1, respectively.

2,2′-Azobisisobutyronitrile (AIBN, from Kishida Chemicals) was recrystallized from ethanol. 4,4′-Azobis(4-cyanovaleric acid) (AVA) from Aldrich, di-*tert*-butyl peroxide (tBPO) from Kishida Chemicals, 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPOL) from Aldrich, and deuterated solvents, $CDCl_3$, C_6D_6, and D_2O from Aldrich were used as supplied commercially.

Polymerization. The radical polymerization of the macromonomers both in water and in benzene proceeded apparently cleanly (transparently) without any precipitation. The rate of polymerization, R_p, at 60 °C either in D_2O with AVA or in C_6D_6 with AIBN was determined from the initial slope of the time−conversion plot obtained by ^{1}H NMR following the disappearance of the double bond peak in reference to the oxyethylene peak according to a similar procedure as described.[1,4] Polymerization at 20 °C in H_2O or in C_6H_6 under irradiation was also carried out to monitor the propagating radicals to determine k_p by ESR measurements. Water or benzene solution of a macromonomer and an initiator were placed under argon into a flat ESR cell of 0.2 mm thickness or into an ESR tube of 5 mm diameter, respectively. Irradiation with an USHIO 500 W ultrahigh-pressure mercury lamp was turned on to induce the stationary polymerization. Conversions of the photopolymerization were determined with the aliquots diluted in THF by taking GPC from the area ratio of polymer to monomer peaks. Satisfactory agreement between the conversions estimated by ^{1}H NMR and GPC within experimental errors was previously reported.[2] Irradiation was turned off to monitor the decay of the radicals for evaluating k_t.

Measurements. ^{1}H NMR was recorded on a JEOL JNM-GX 270 FT spectrometer as described before.[2−4] Characterization of the macromonomers by GPC was made with a JASCO PU980 chromatograph, equipped with an RI detector, JASCO RI930, and Shodex A-802 and A-803 columns. THF was used as an eluent at a flow rate of 1 mL/min at 40 °C. Molecular weight was calibrated with standard samples of PEO from Tosoh Co., Ltd. GPCs on a TOSOH PS-8010 chromatograph with a TOSOH RI-8012 detector were taken to monitor the conversions of the macromonomers in the polymerization under irradiation, as described above. ESR spectra were recorded at 20 °C on a JEOL JES-RE2X spectrometer with a JEOL ESPRIT 330 data processor. Concentrations of the propagating radicals were determined by calibration of the signal intensity with that from a known amount of TEMPOL as a standard.

Results and Discussion

Overall Polymerization Kinetics. The macromonomers, Cl-PEO-VB-48 and Cl-PEO-C4-S-48, were polymerized in NMR tubes at 60 °C in C_6D_6 and in D_2O with AIBN and AVA as the initiators, respectively. The decrease in the intensities of the double bond peaks relative to the oxyethylene peaks was followed to determine the conversion−time plots, the initial slope of which allowed us to estimate the overall rate of polymerization, R_p. The results are given as the double logalithmic plots of R_p against initial initiator, [I], and monomer concentrations, [M], as in Figures 2 and 3, respectively. It is clearly seen that R_p in water is more than 50 times higher than that in benzene under the same condition and that Cl-PEO-C4-S-48, carrying a more hydrophobic polymerizing end group, polymerized in water more rapidly than Cl-PEO-VB-48, supportingagain the micellar polymerization mechanism in water as proposed.[2−5]

The slopes in the logarithmic plots in Figures 2 and 3 indicate the following power-law relationships, which were observed in the polymerization of the ω-*tert*-butoxy macromonomers,[2] to hold approximately also in all of the present systems at least within the concentration range studied.

$$R_p \sim [M][I]^{1/2} \quad \text{in water} \tag{1}$$

and

$$R_p \sim [M]^{1.5}[I]^{1/2} \quad \text{in benzene} \tag{2}$$

The former is in apparent accordance with the conventional rate relationship in radical polymerization[16] as follows:

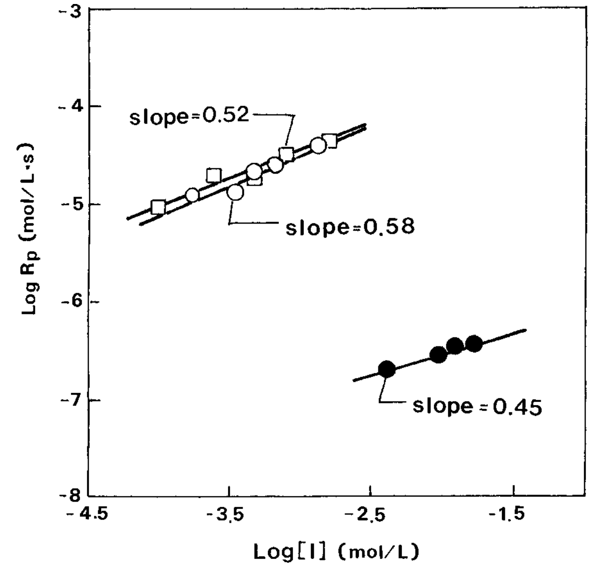

Figure 2. Plots of log R_p against log [I]: (○) Cl-PEO-VB-48, [M] = 50 mmol/L, with AVA in D_2O at 60 °C; (□) Cl-PEO-C4-S-48, [M] = 50 mmol/L, with AVA in D_2O at 60 °C; (●) Cl-PEO-VB-48, [M] = 22.9 mmol/L, with AIBN in C_6D_6 at 60 °C.

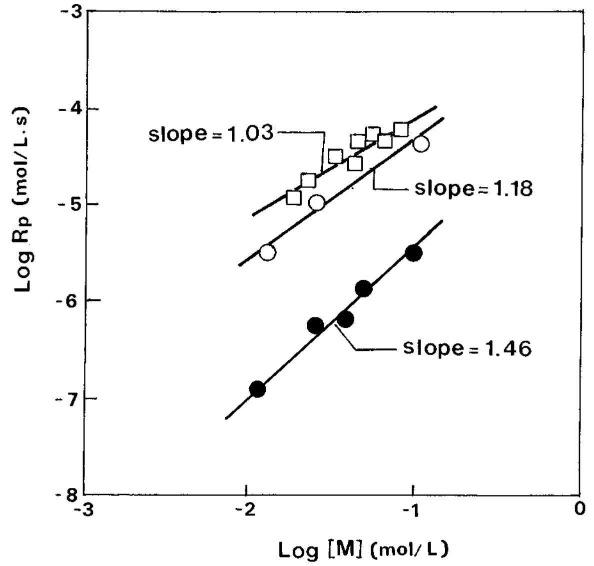

Figure 3. Plots of log R_p against log [M]: (○) Cl-PEO-VB-48 with AVA, [I] = 0.375 mmol/L, in D_2O at 60 °C; (□) Cl-PEO-C4-S-48 with AVA, [I] = 0.494 mmol/L, in D_2O at 60 °C; (●) Cl-PEO-VB-48 with AIBN, [I] = 16.6 mmol/L, in C_6D_6 at 60 °C.

$$R_p = k_p(2k_d f/k_t)^{1/2}[\mathrm{M}][\mathrm{I}]^{1/2} \qquad (3)$$

where k_p and k_t are the rate constants of propagation and termination, respectively, while k_d and f are the decomposition rate constant of the initiator and the initiator efficiency, respectively.

The square-root dependence on [I], as observed both in benzene and in water, clearly supports the conventional bimolecular termination of the polymer radicals to prevail also for the present polymerizations. Since the radical termination reactions are diffusion-controlled,[16] they should be retarded by increasing medium viscosity which would restrict the segmental motion of the involved polymer radicals. This effect can be more pronounced in polymerization of macromonomers involving the termination between highly branched polymer radicals, as has been reported.[2,11-14] The one-and-half-order dependence of R_p on [M] as observed in benzene can be explained by assuming the inverse dependence of k_t on the solution viscosity which increases linearly with [M].[2]

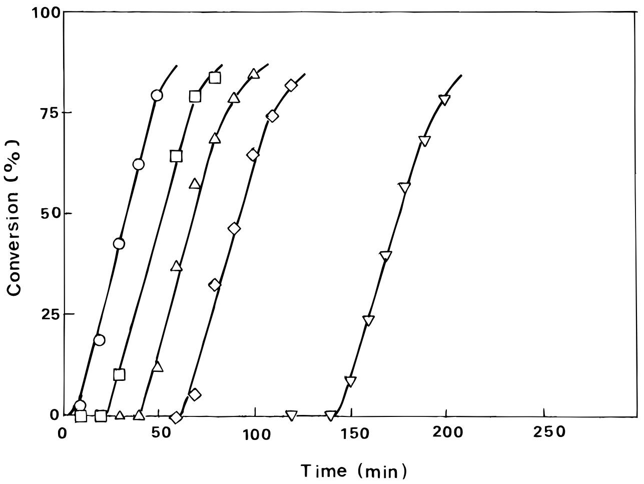

Figure 4. Conversion–time plots for polymerization of Cl-PEO-VB-48 with AVA, [I] = 0.5 mmol/L, in the presence of TEMPOL in D_2O at 60 °C to estimate t_{inh}. $[\mathrm{TEMPOL}]_0$ (mmol/L): (○) 0, (□) 0.0131, (△) 0.0164, (◇) 0.0328, and (▽) 0.0656.

In water an apparently normal kinetic dependence, eq 1, was observed with an unusually high polymerization rate. Essentially similar kinetics has been reported with some micelle-forming surfactant monomers.[7,17] Since the decomposition rate constant, k_d, of AVA in water is almost comparable to, or rather slightly smaller than, that of AIBN in benzene,[2] very rapid polymerization of the PEO macromonomers in water must be attributed to enhanced f or k_p and/or to reduced k_t by virtue of eq 3, assuming [M] and [I] as the corresponding overall concentrations as charged. Similarly,[5] very high degrees of polymerization, *DP*, of the polymacromonomers obtained in water followed essentially the conventional kinetic dependence,[16] i.e., $DP \sim [\mathrm{M}]/[\mathrm{I}]^{1/2}$, supporting the same context except for f. Now a question arises about which factor(s) may control to what extent the very rapid micellar polymerization of the PEO macromonomers in water. Also, what are the effects of possible enhancement in the local concentrations of the monomers and the radicals involved in the polymerization sites? So we attempted here to determine these kinetic parameters independently and to discuss the characteristic behavior of the macromonomers in micellar polymerization as compared to that in benzene, as follows.

Initiator Efficiency. We followed a conventional procedure[16,18,19] to estimate f by measurements of inhibition period, t_{inh}, of polymerization in the presence of a known amount of an *N*-oxy stable radical, TEMPOL, as an inhibitor. Thus the rate of initiation, R_i, can be given by

$$R_i = -\mathrm{d}[\mathrm{TEMPOL}]/\mathrm{d}t = [\mathrm{TEMPOL}]_0/t_{inh} \qquad (4)$$

Then f was calculated from the definition, the ratio of R_i to the rate of the production of the primary radicals, according to

$$R_i = 2k_d f[\mathrm{I}] \qquad (5)$$

Figure 4 shows the time-conversion curves of polymerization of Cl-PEO-VB-48 at 60 °C with various amounts of TEMPOL to determine t_{inh} and Figure 5 shows the plots of t_{inh} against $[\mathrm{TEMPOL}]_0$ to estimate R_i from their

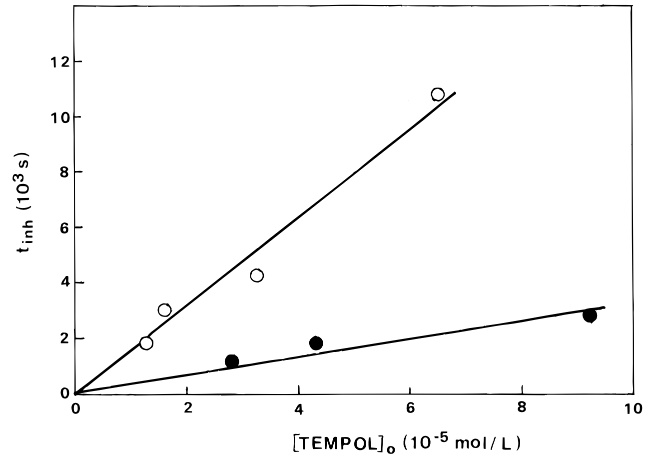

Figure 5. Plots of t_{inh} for polymerization of Cl-PEO-VB-48 at 60 °C against [TEMPOL]$_0$ according to eq 4 to estimate R_i: (○) in D_2O with AVA, [I] = 0.5 mmol/L; (●) in C_6D_6 with AIBN, [I] = 10 mmol/L.

slopes. We used the k_d values as 6.0×10^{-6} and 8.3×10^{-6} s^{-1} for AVA in water and AIBN in benzene,[2] respectively, and obtained f as 0.90 and 0.15, respectively.

The initiator efficiency less than unity comes from a so-called cage effect[16] and indeed values as small as 0.1−0.3 have been found in the solution polymerization of polystyrene and poly(methyl methacrylate) macromonomers,[12,14] possibly as a result of the high viscosities involved. This may be also true here for $f = 0.15$ in the polymerization of the PEO macromonomer in benzene. In contrast, the very high value, $f = 0.9$, observed for the polymerization in water is clearly partly responsible for the very high R_p. We speculate that the micellar organization of the macromonomers in water may exert little cage effect on the primary radicals generated in the continuous phase or near the periphery of the micelles to make them so effective. The negative charge of the primary radicals from AVA may be also a factor for making their escape from the cage more effective.

Propagation and Termination Rate Constants. For direct measurements of these rate constants, ESR[20] is one of the most reliable methods also for the macromonomers.[11−14] We here followed the propagating radicals in polymerization of the macromonomers under irradiation at 20 °C. Figure 6 shows the ESR spectra in polymerization of the macromonomers, Cl-PEO-VB-48 and Cl-PEO-C4-S-48, and of styrene for comparison, in benzene and in bulk, respectively. Clearly the presence of polystyryl and substituted polystyryl radicals is identified. Similarly, Figure 7 proves the propagating radicals of the macromonomers in water, though with no hyperfine splittings observed probably due to dielectric loss or micellar organization in water.

The concentration of the overall propagating radicals, [P$^\bullet$], in the stationary state of polymerization under irradiation was estimated from the corresponding spectrum in reference with the signal from a known amount of TEMPOL. Then the propagation rate constant, k_p, was directly calculated from the equation

$$R_p = -d[M]/dt = k_p[P^\bullet][M] \qquad (6)$$

Here R_p was determined from the initial conversion by GPC measurement and [M] was taken as the overall monomer concentration in feed.

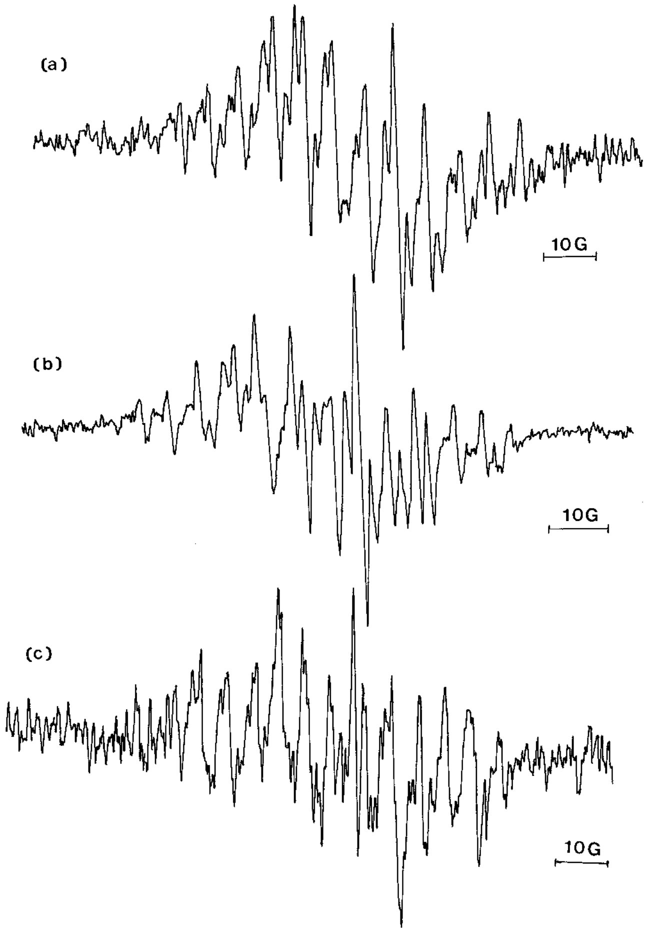

Figure 6. ESR spectra of propagating radicals in polymerization with tBPO under irradiation at 20 °C: (a) Cl-PEO-VB-48 in benzene with [M] = 50 mmol/L and [I] = 2.5 mol/L; (b) Cl-PEO-C4-S-48 in benzene with [M] = 50 mmol/L and [I] = 2.5 mmol/L; (c) styrene in bulk with [I] = 0.2 mol/L.

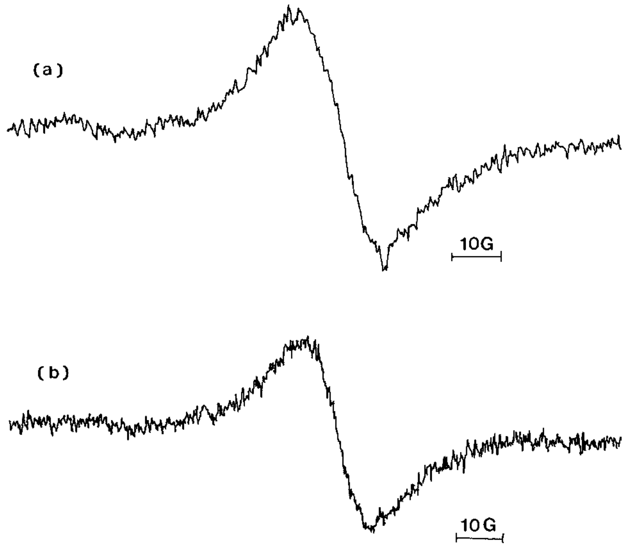

Figure 7. ESR spectra of propagating radicals in polymerization in water with AVA under irradiation at 20 °C: (a) Cl-PEO-VB-48 with [M] = 50 mmol/L and [I] = 2.5 mmol/L; (b) Cl-PEO-C4-S-48 with [M] = 50 mmol/L and [I] = 2.5 mmol/L.

The rate of termination, R_t, is defined by

$$R_t = -d[P^\bullet]/dt = k_t[P^\bullet]^2 \qquad (7)$$

The conventional overall rate expression, eq 3, of course

Table 2. Kinetic Parameters of Radical Polymerization Under Irradiation at 20 °C[a]

monomer/solvent	initiator	$R_p \times 10^6$, mol L^{-1} s^{-1}	$[P^\bullet] \times 10^6$, mol L^{-1}	k_p, L mol^{-1} s^{-1}	k_t, L mol^{-1} s^{-1}
Cl-PEO-VB-48/benzene	tBPO	3.9	2	40	1800
Cl-PEO-VB-48/water	AVA	210	4	1100	5400
Cl-PEO-C4-S-48/benzene	tBPO	15	5	45	4500
Cl-PEO-C4-S-48/water	AVA	510	5	2100	9000
styrene/bulk[b]	tBPO	940	0.6	35	1.9×10^7

[a] $[M] = 50 \times 10^{-3}$ mol L^{-1}, $[I] = 2.5 \times 10^{-3}$ mol L^{-1} for the macromonomers, and $[I] = 0.2$ mol L^{-1} for styrene. Values of R_p, $[P^\bullet]$, k_p, and k_t of the macromonomers in this work may include errors of 10–30%. [b] Data at 25 °C from Burnett et al.[21]

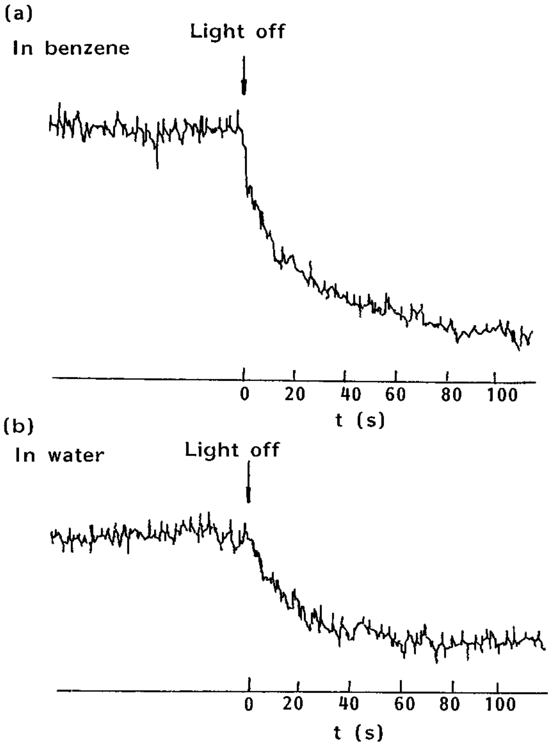

Figure 8. Decay of propagating radicals of C1-PEO-VB-48 on turning off of irradiation at 20 °C: (a) in benzene; (b) in water.

holds under the stationary condition of $R_i = R_t$ together with eqs 5–7. The rate constant of termination, k_t, was then directly evaluated from the nonstationary decay curve of $[P^\bullet]$ upon turning off the irradiation, according to the integrated form of eq 7

$$([P^\bullet] - [P^\bullet]_t)/[P^\bullet]_t = k_t[P^\bullet]t \qquad (8)$$

where $[P^\bullet]_t$ is the concentration of the polymer radicals at time, t, after the irradiation is turned off and $[P^\bullet]$ is now the concentration at $t = 0$ or the stationary concentration under the irradiation. Figures 8 and 9 show the ESR decay and the corresponding second-order plots for Cl-PEO-VB-48, respectively.

Table 2 summarizes the relevant kinetic data obtained for polymerization of the PEO macromonomers in comparison with those reported for styrene in bulk.[21] It can be clearly seen that the macromonomers are characterized by k_t, which is much smaller by a factor of $1/10^3$ to $1/10^4$ than that for styrene, indicating a severely hindered, diffusion-controlled bimolecular termination between the highly branched polymacromonomer radicals, as already reported.[11–14] On the other hand, k_p of the macromonomer in benzene is almost comparable to that of styrene, indicating a rather easy access of the macromonomer double bond to the polymacromonomer radical to perform a normal chemically-controlled propagation.

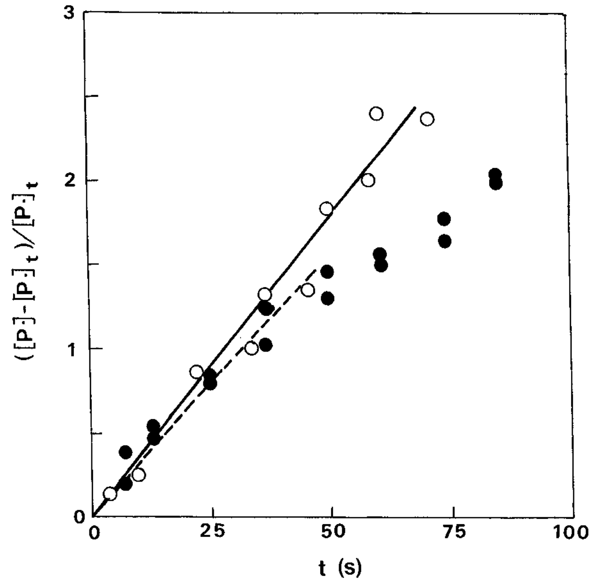

Figure 9. Second-order plots of decay of poly(Cl-PEO-VB-48) radicals at 20 °C according to eq 8 to evaluate k_t from the slopes: (○) in water; (●) in benzene.

Most interesting here is the fact that the values of k_p of the macromonomers in water are about 30–50 times higher as compared to those in benzene, while the corresponding k_t's are not so much different. This fact, together with the about 6-fold increase in f, as described above, may apparently account for the observed enhancement in R_p in water, by a factor of more than 50, by virtue of eq 3. Also a significantly higher R_p of Cl-PEO-C4-S-48 than of Cl-PEO-VB-48 may be reasonably accounted for by a higher k_p of the former, which has a more hydrophobic styryl end group and is apparently more favored for micellar organization than the latter. Thus we conclude that the observed very rapid polymerization of the PEO macromonomers in water results from their micellar organization with an enhanced k_p and f.

We have to recall here that evaluation of k_p and k_t is based on eqs 6 and 7 using [M] and $[P^\bullet]$ taken as the overall concentrations in a whole solution, as is usually done. This poses no problem in the isotropic solution polymerization as reasonably expected in benzene.[2] In water, however, micellar polymerization as proposed assumes a micelle as a polymerization locus which should involve locally concentrated radical and monomer. In this sense, the k_p and k_t values obtained as above are apparent ones. So we will attempt to evaluate their "true" values in the micellar environment as follows.

Micellar Polymerization Kinetics. Let $k_{p,m}$ and $k_{t,m}$ be "true" propagation and termination rate constants, respectively, for a polymerization within a hypothetically isolated micelle in water. Then, "true" or local rates of propagation and termination within this micelle are given by

$$R_{p,m} = -d[M]_m/dt = k_{p,m}[P^\bullet]_m[M]_m \tag{9}$$

and

$$R_{t,m} = -d[P^\bullet]_m/dt = k_t[P^\bullet]_m{}^2 \tag{10}$$

respectively. Here $[P^\bullet]_m$ and $[M]_m$ denote the "true" or local concentrations of the propagating radical and the monomer within the micelle, respectively. Now if we assume that all the propagating radicals and the monomers are present within the micelles,[22] then we have from the mass balance, with ϕ_m as the volume fraction of the whole micelles

$$[M] = [M]_m\phi_m \tag{11}$$

and

$$[P^\bullet] = [P^\bullet]_m\phi_m \tag{12}$$

Equations 9 and 10 combined with eqs 6, 7, 11, and 12 then give

$$R_{p,m} = R_p/\phi_m = k_{p,m}[P^\bullet][M]/\phi_m{}^2 \tag{13}$$

$$R_{t,m} = R_t/\phi_m = k_{t,m}[P^\bullet]^2/\phi_m{}^2 \tag{14}$$

Or

$$R_p = (k_{p,m}/\phi_m)[P^\bullet][M] \tag{15}$$

$$R_t = (k_{t,m}/\phi_m)[P^\bullet]^2 \tag{16}$$

Comparison with eqs 6 and 7 then gives the relationship between the apparent and "true" rate constants as follows.

$$k_p = k_{p,m}/\phi_m \tag{17}$$

$$k_t = k_{t,m}/\phi_m \tag{18}$$

Now we can convert the apparent rate constants in Table 2 to the "true" rate constants even very roughly by assuming ϕ_m to be equal to the weight fraction, ϕ_w, of the macromonomers in water, which is 0.11, and then we have $k_{p,m} = 120$ and $k_{t,m} = 590$ L mol^{-1} s^{-1} for Cl-PEO-VB-48, and $k_{p,m} = 230$ and $k_{t,m} = 990$ L mol^{-1} s^{-1} for Cl-PEO-C4-S-48. Since ϕ_m appears to be larger than ϕ_w by any occlusion of water in the micelle, the "true" values as above may have been underestimated. However, by comparison of these values with those for polymerization in benzene, it is reasonable to conclude that the propagation is favored while the termination is hindered in the micellar environment as compared to the corresponding reactions in the isotropic circumstance. Thus the micellar organization of the PEO macromonomers in water, with the hydrophobic polymerizing end groups in the core and the hydrophilic PEO segments in the shell, appears to enhance propagation and reduce termination there.

Another consequence of eqs 17 and 18 is that the apparent k_p and k_t are not constant coefficients but are inverse functions of ϕ_m; thus, they should increase with dilution as an apparently increasing deviation from an hypothetically pure micellar condition, $\phi_m = 1$. Although the exact relationship between ϕ_m and [M] is not clear at present, Figure 10 shows in fact that k_p and k_t decrease with increasing macromonomer concentration, supporting the micellar polymerization mechanism even qualitatively.

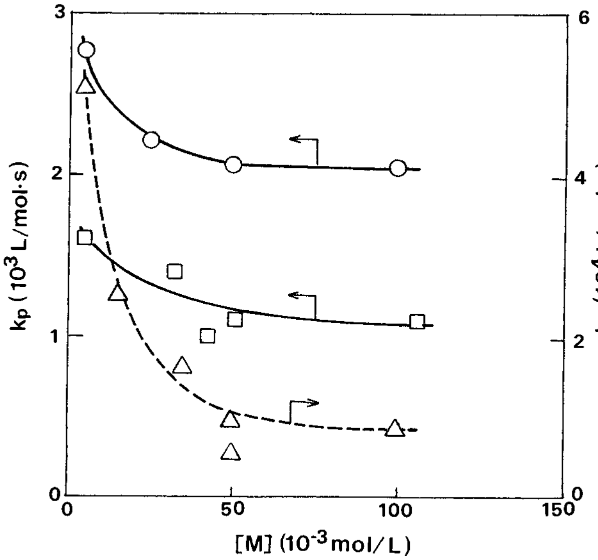

Figure 10. Dependence of k_p and k_t in D_2O at 20 °C on [M]: (□) k_p of Cl-PEO-VB-48; (○) k_p of Cl-PEO-C4-S-48; (△) k_t of Cl-PEO-VB-48.

Now the micellar polymerization mechanism as above should take an alternative form for the overall rate expression, different from the conventional eq 3. Thus by assuming the stationary condition that $R_i = R_t$, eq 6 with eqs 17 and 18 yields

$$R_p = k_{p,m}(2k_df/k_{t,m})^{1/2}[I]^{1/2}[M]\phi_m{}^{-1/2} \tag{19}$$

Experimental rate dependence as in eq 1 can be in accord with eq 19 only if we assume that $\phi_m \sim [M]^{1/2}$, with $k_{p,m}$ and $k_{t,m}$ being constant, independent of [M]. Another possibility to meet the dependence of $R_p \sim [M]$ is to assume $k_{t,m} \sim \phi_m{}^{-1}$, which means $k_t \sim \phi_m{}^{-2}$ with eq 18. Correspondingly, the data in Figure 10 show a more pronounced decrease in k_t than k_p, which might be plausible in view of the diffusion-control in the termination. Further study, however, is clearly needed to know more about the micelle organization of the present macromonomer systems, including a possible change in the micelle structure with the overall concentration, which may afect the kinetics in a complicated manner. Also, a complicating factor is micellization dynamics during polymerization,[7] which have to be considered since the *DP*'s of the polymacromonomers obtained have been found to be significantly higher than the average number of aggregation of the macromonomers in the corresponding micelle,[2,5,6] indicating a chain cycle of initiation−propagation−termination extending beyond an average, static micellar size.

In conclusion, the radical polymerization of the PEO macromonomers was characterized by a very low rate of diffusion-controlled termination between highly branched polymer radicals as compared to that of conventional monomers. Their polymerization in water was more than 50 times faster than that in benzene. Micellar organization of these amphiphilic macromonomers in water is most reasonably expected to be responsible for the fact as a combined result of locally concentrated polymer radical and monomers, together with a high initiator efficiency, enhanced rate of propagation, and reduced rate of termination in such an apparently isolated environment.

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References and Notes

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(22) A reasonable assumption since the critical micelle concentration (cmc) of the macromonomers are very low as compared to the overall concentrations used and polymerization below the cmc is negligibly slow.[2]

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