Photo-Initiated Post-Polymerization in Micellar System of Amphiphilic Poly(ethylene oxide) Macromonomers

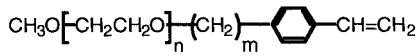
*Ryuta Maruyama,[1] Mohd. Maniruzzaman,[2] Seigou Kawaguchi,[3] Koichi Ito**

Department of Materials Science, Toyohashi University of Technology, Tempaku-cho, Toyohashi 441-8580, Japan
[1] Present Address: Rohm Hamamatsu Co., Ltd., 10 Sanwa-cho, Hamamatsu 435-0038, Japan
[2] Present Address: Department of Applied Chemistry and Chemical Technology, Islamic University, P. O. University, Kushtia, 7003 Bangladesh
[3] Present Address: Department of Polymer Science and Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa 992-8510, Japan

Summary: Aqueous micellar polymerization of amphiphilic poly(ethylene oxide) macromonomers carrying *p*-vinylphenylheptyl end-group has been found to persist to proceed after turning-off of the UV-irradiation. Simulation of the kinetics revealed a high propagation rate constant coupled with a low termination constant, supporting a living-like polymerization at the initial stage. Micellar copolymerization with equimolar styrene also proceeded after UV-irradiation. Polymer molecular weights in MALLS-SEC were also found to evolve with time after irradiation.

Introduction

We have reported very rapid radical polymerization to a very high molecular weight of poly(ethylene oxide) (PEO) macromonomers, **1**, in aqueous micellar system.[1,2] Association of the hydrophobic *p*-vinylphenylalkyl end-groups into the micelle core[3] appears to be a key factor for the enhanced polymerization. Copolymerization with equimolar styrene proceeded even faster to a unimolecular polymeric nanoparticle, a fact suggesting us to propose a quasi-living polymerization in a compartmentalized micellar



1 (C1-PEO-Cm-S-n)

system.[4]

These results tempted us to apply photo-initiation to the above micellar system. Photo-irradiation will almost instantly produce an amount of initiating-radicals which will then polymerize the monomers present within the micelles. Thus we are concerned

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with only propagation and, if any, termination. The kinetics will be simple to simulate and we might even expect a clean living "compartmentalized" polymerization if we could have a system with no termination or no transfer there.

This paper presents the results of the kinetics of post-polymerization at room temperature of the PEO macromononers in water with 4,4'-azobis[4-cyanovaleric acid] (AVA) as an initiator after UV irradiation.

Experimental

The PEO macromonomers, **1** (C1-PEO-Cm-S-n), were prepared similarly as before[1-3, 5] from poly(ethylene glycol) monomethyl ether by reaction with sodium hydride followed by 4-(*p*-vinylphenyl)butyl bromide (m = 4), or 7-(*p*-vinylphenyl)heptyl bromide (m = 7). In the case of m = 14, the coupling with 1,10-dibromodecane was followed by that with the Grignard reagent from 4-(*p*-vinylphenyl)butyl bromide. Their characterization by ^{1}H-NMR and SEC, given in Table 1, confirms satisfactorily their structures.

Table 1. Characterization of macromonomers, **1** (C1-PEO-Cm-S-n)

Macromonomer code	n[a)]	$10^{-3}M_n$[b)]	M_w/M_n[b)]	Functionality[a)] %
C1-PEO-C4-S-18	17.2	1.17	1.04	100
C1-PEO-C7-S-18	18.0	1.20	1.05	86.5
C1-PEO-C14-S-18	18.6	1.46	1.08	96.3
C1-PEO-C7-S-45	50.3	2.20	1.06	97.3

[a)] Number-average degree of polymerization of ethylene oxide (n) and functionality (%) of the double bond, as determined by ^{1}H NMR from the peak area of oxyethylene and double bond, respectively, relative to methoxy protons.

[b)] Number-average molecular weight and the polydispersity, as determined by SEC calibrated with standard poly(ethylene glycol)s.

The other reagents and characterization of the polymers followed our previous papers.[1-5]

Photo-initiated polymerization was carried out in an NMR tube to follow the conversion by ^{1}H-NMR.[1] The macromonomers and the initiator (AVA) were respectively dissolved in D_2O under sonication and mixed together into an NMR tube under Argon and sealed. The NMR spectrum was taken to have the data for the 0 % conversion. UV irradiation at 350-365 nm was made through a super high pressure mercury lamp, Wacom HX-500, Type BMO-500D1, Wacom R&D Corp., Japan. After irradiation for a desired time, usually 1 min., the light was turned off and from this time on (t = 0) the polymerization conversion was monitored by NMR. The temperature during UV irradiation and post-polymerization was as ambient (20-30 °C). SEC-MALLS data were taken with the samples similarly obtained.

Results and Discussion

The PEO macromonomers, **1**, with m = 4, 7, 14, and n = 18, in water with AVA were UV-irradiated for 1 min and after turning-off of the light their polymerization was monitored by following the disappearance of their double bonds in ^{1}H-NMR. Time-evolution curves are given Figure 1.

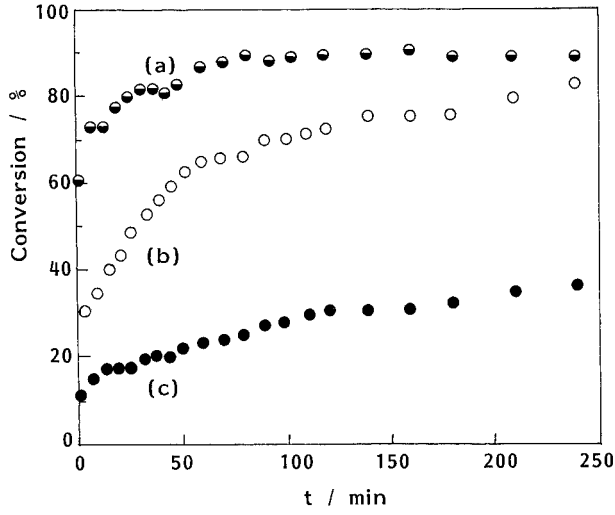

Figure 1. Conversion vs time plots for the post-polymerization of (a) C1-PEO-C14-S-18, (b) C1-PEO-C7-S-18, and (c) C1-PEO-C4-S-18 after UV irradiation for 1min. $[M]_o$ = 22.7 mmol dm^{-3}, $[AVA]_o$ = 1.0 mmol dm^{-3}.

Clearly, the polymerization of the PEO macromonomers persisted over hours after turning-off of the light, in contrast the conventional photo-initiated post-polymerization which fades very rapidly in seconds due to frequent terminations. In particular, the macromonomers with longer alkylene length (m = 7 and 14) polymerize more etensively, probably because they tend to organize into more clear-cut, more rigid core-shell micelles and so appear to disfavor their bimolecular (inter-micellar) termination due to steric stabilization effect of the abundant PEO chains covering the micelles. The most hydrophobic macromonomer with m = 14 polymerized most rapidly to already 60 % conversion at the first monitoring, clearly indicating its extensive polymerization already during the irradiation, making the post-polymerization (the timing of t = 0) difficultly assigned.

By assuming that all the initiating radicals formed during the irradiation time and that the events thereafter are only propagation and bimolecular termination, then we can have the relations for the rates of propagation and termination in the post-polymerization:

$$\text{Propagation;} \quad R_p = -d[M]/dt = k_p[M][P^{\cdot}] \tag{1}$$

$$\text{Termination;} \quad R_t = -d[P^{\cdot}]/dt = 2\,k_t[P^{\cdot}]^2 \tag{2}$$

By combining these and integrating over time = 0 to t, we have

$$ln([M]_o/[M]) = (k_p/2k_t)[\ln(1 + 2\,k_t[P^{\cdot}]_o\,t)] \tag{3}$$

where $[M]_o$ and $[M]$ are the monomer concentrations at t = 0 and t, respectively, and $[P^{\cdot}]_o$ and $[P^{\cdot}]$ the corresponding radical concentrations, and k_p and k_t are the rate constants of propagation and termination, respectively. Here, however, it must be mentioned that the relations strictly hold for a homegeneous system. Since we are concerned with a micellar organized system, the concentrations and the parameters involved are apparent ones in order to discuss the relevant kinetic picture in at most qualitative sence.

Figure 2 shows the first-order plot of $ln[M]_o/[M]$ against time t for the post-polymerization of C1-PEO-C4-S-18, C1-PEO-C7-S-18, and C1-PEO-C7-S-45, together with the corresponding theoretical curves by eq (3) with the parameters given in Table 2. Simulation has been made to minimize the sum of the squares of the differences between

the observed $[M]_o/[M]$ and the calculated values assuming k_p, k_t, and $[P^\cdot]_o$ varying in the range of 0-10^4 $dm^3 mol^{-1} s^{-1}$, 0-10^4 $dm^3 mol^{-1} s^{-1}$, and 10^{-8}-10^{-5} mole dm^{-3}, respectively. The agreements between experimental and calculation are satisfactorily good. The parameters obtained are also in fair accord in the order of magnitude with those previously estimated by ESR determination of the steady-state propagating radicals under photo irradiation at room temperature.[2]

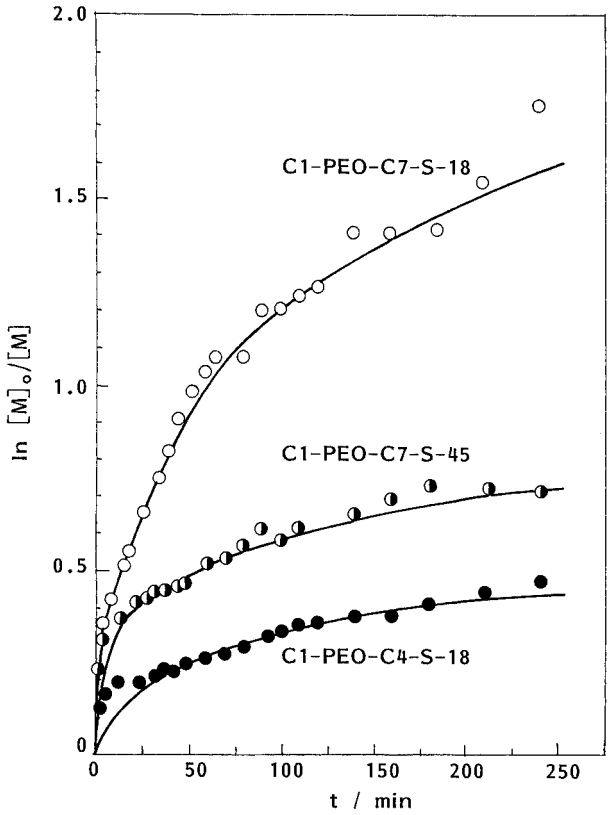

Figure 2. First-order plots of the polymerization of the macromonomers with the theoretical curves simulated with the parameters given in Table 2.

The above results clearly indicate that the post-polymerization persists more definitely with increasing hydrophobicity of the macromonomer, i. e., with increasing m (the spacer alkylene length) and decreasing n (PEO length).

Table 2. Kinetic parameters simulated for best fit to the photo-initiated post-polymerizaion in water[a)]

Macromonomer	k_p	k_t	$10^7[P^{\cdot}]_o$
	$dm^3\ mol^{-1}\ s^{-1}$	$dm^3\ mol^{-1}\ s^{-1}$	$mol\ dm^{-3}$
C1-PEO-C4-S-18	1000	4200	3.2
C1-PEO-C7-S-18	1200	1300	8.0
C1-PEO-C7-S-45	2000	7300	8.5

a) $[M]_o$ = 22.7 mmol dm^{-3}, $[AVA]_o$ = 1.0 mmol dm^{-3}, at room temp.

Too short PEO length (low n), however, makes the macromonomer insoluble in water while too long PEO (high n) will disfavor the organization into micelles, so that a proper balance of n relative to m (HLB of the macromonomer) can be a key factor for the long life of the propagating radicals in micellar system. In fact, the first-order plot for the polymerization of C1-PEO-C7-S-18 in Figure 2 appears linear with time for the initial one hour, just like a living polymerization with no termination. Formally by using the parameters in Table 2, the average life of their radicals is calculated as $[P^{\cdot}]_o / R_t$ = 16 min., very long as compared to less than 1 sec for the conventional radical polymerization.

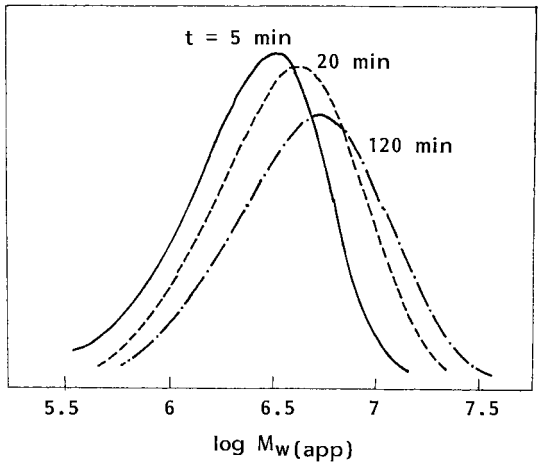

Figure 3. Change in SEC-MALLS curves with polymerization time for the poly(C1-PEO-C7-S-18) obtained by post-polymerization after UV-irradiation for 1 min.

The SEC-MALLS curves in Figure 3 also clearly show evolution in the size of the poly(macromonomer) with post-polymerization time. The final polymer was characterized by the apparent molecular weight, $M_{w(app)}$, as high as 5.8 x 10^6, with $M_w/M_{n(app)}$ = 1.6

Micellar copolymerization of C1-PEO-C7-S-18 with equimolar styrene solubilized in water was also conducted after turning-off of the UV irradiation, with the result shown in Figure 4. The conversions of the macromonomer and styrene are similar in accord with the azeotropic behavior just as observed for their thermal copolymerization with AVA at 60 °C.[4] The apparent molecular weight, $M_{w(app)}$ by SEC-MALLS, was also observed to increase with conversion, supporting the quasi-living mechanism as proposed before.

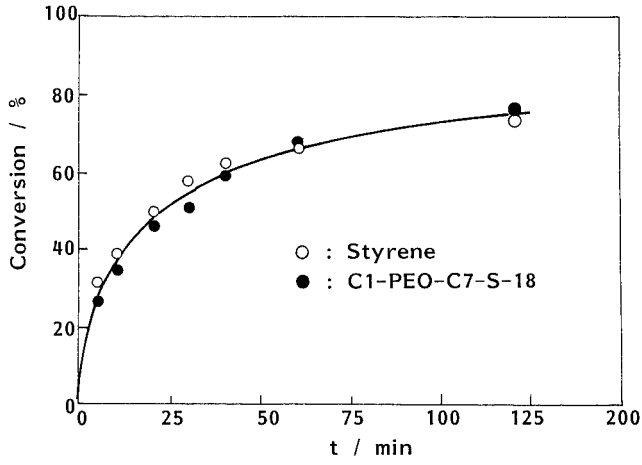

Figure 4. Conversion vs time plots for the post-copolymerization of C1-PEO-C7-S-18 with styrene after UV irradiation for 1min. $[C1\text{-}PEO\text{-}C7\text{-}S\text{-}18]_o$ = $[styrene]_o$ = 22.7 mmol dm^{-3}, $[AVA]_o$ = 0.11 mmol dm^{-3}.

Conclusion

The micellar system from the amphiphilic PEO macromonomers with sufficiently hydrophobic styryl moiety (*p*-vinylphenylheptyl or -tetradecyl) was found to persist polymerization at room temperature even after turning-off of the UV irradiation, supporting significantly long life of the radicals compartmentallized there. The living-

like behavior, observed at least in the initial stage, may be expected to find some interesting applications to polymeric design.

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