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Micellar Copolymerization of Styrene with Poly(ethylene oxide) Macromonomer in Water: Approach to Unimolecular Nanoparticles via Pseudo-Living Radical Polymerization

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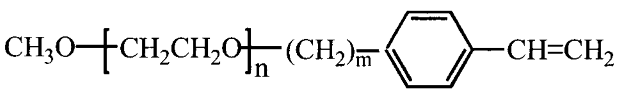
ABSTRACT: Micellar copolymerizations of amphiphilic ω-methoxy-α-*p*-styrylalkyl poly(ethylene oxide) (PEO) macromonomers **1** (C_1−PEO−C_m−S-*n*, $m = 1, 4, 7$ and $n = 18$) with a limited amount of styrene solubilized therein have been investigated. The reactions were carried out with 4,4′-azobis(4-cyanovaleric acid) (AVA) as a water-soluble initiator and 2,2′-azobis(isobutyronitrile) (AIBN) as an oil-soluble initiator at 60 °C. Fractional time-evolution experiments revealed that the copolymerization rate of styrene is greatly enhanced by the presence of macromonomer micelles and that the rate increases with hydrophobicity (increase of *m*) of α-end group of **1**. The characterization of the resulting graft copolymers revealed that the organized copolymerization proceeds in the manner of a pseudo-living radical copolymerization with highly limited terminations between compartmentalized (isolated) propagating radicals. That is, the molecular weight of the graft copolymers increased with the conversion of monomers. At an equimolar styrene with **1** ($n = 18$, $m = 7$) the copolymerization proceeded apparently transparently and azeotropically to afford a highly branched graft copolymer of poly(styrene-*graft*-PEO), which in water formed a "unimolecular particle" with 15 nm radius and $7.4_4 \times 10^6$ apparent molecular weight. A plausible mechanism for the present organized copolymerization behavior is presented and discussed.

Introduction

The macromonomer technique has widely been appreciated as one of most convenient and promising methods to prepare well-defined branched polymers.[1,2] The macromonomer homopolymerizes to provide a regular star- or comb-shaped polymer with an extremely high branch density. Some unique properties of the poly(macromonomer) have very recently been reported by some research groups.[3−8] This material is particularly interesting for understanding the influence of the branching architecture on the polymer properties.

On the other hand, macromonomer copolymerizes with a commodity monomer to give also a well-defined graft copolymer to the point that the branched chain is precharacterized. This polymer is also important in the field of polymer blend industry. Strictly speaking, however, the graft copolymers prepared by conventional radical copolymerization with a macromonomer usually have large heterogeneity in the composition due to the difference in the reactivity ratio. For this reason, very limited fundamental studies have been carried out for precise characterization of molecular weight and compositional distribution of the resulting graft copolymers.[9] Our interest is focused on establishment of a "designed synthesis" of graft copolymers using the macromonomer technique. If possible, we intend to prepare a model graft copolymer, i.e., that with well-defined branched chain length and sequence as well as narrow molecular weight distribution. The well-defined graft copolymers have quite recently been prepared by the multistep anionic polymerization technique.[10,11] This technique, however, is extremely limited in the number of branched chains in a polymer chain. A recent controlled radical polymerization of macromonomer[12] and living ring-opening methathesis polymerization[13] may promise one to prepare such a well-defined branched polymer with narrow molecular weight distribution.

We have been interested in amphiphilic poly(ethylene oxide) (PEO) macromonomers **1** with a hydrophobic polymerizing end group. Their radical co- and homopolymerizabilities have systematically been investigated in various media including homogeneous, organized, and heterogeneous (emulsion and dispersion) systems.[1,2] Their (co)polymerization behavior was markedly influenced by their organization state. Indeed, the macromonomers polymerized unusually rapidly in water, due to their organization of hydrophobic, polymerizing groups into the micelle core, so-called "micellar, organized polymerization".[14−17] The kinetic studies by ESR clearly demonstrated that very rapid polymerization is attributed to locally concentrated propagating radical and monomers, together with enhanced rate of propagation and reduced rate of termination.[18] These results motivated the authors to start a new project, "*design of graft copolymer synthesis through an organized polymerizing system*". We use the system positively as a (co)polymerization locus, which is different from either the homogeneous or bulk system, enabling one to control the molecular weight and reactivity of the components therein. We expected here that one could prepare graft copolymers which can be prepared with difficulty in the other conventional systems.



(1) C_1-PEO-C_m-S-n: n=18; m= 1,4, 7)

The present paper deals with the copolymerization behavior in an organized, micellar copolymerization

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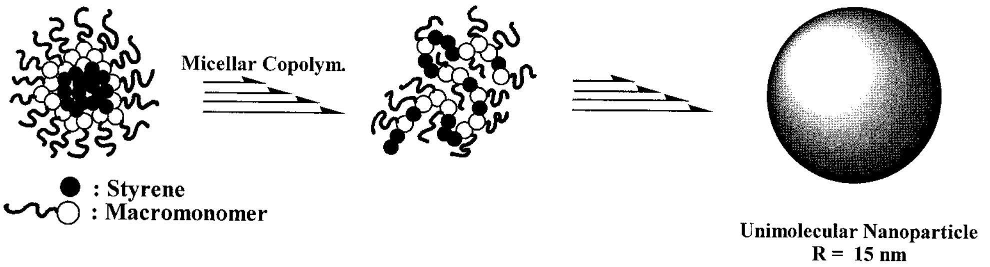
Scheme 1



system in water, consisting of the macromonomer micelles and a very limited amount of styrene solubilized therein. We call this type of copolymerization "micellar copolymerization" which is different from the conventional copolymerizations in homogeneous and bulk systems as well as in emulsion and dispersion systems. The copolymerization proceeds in micellar organization but apparently homogeneously throughout polymerization. The mechanism of this micellar copolymerization might be similar to that of microemulsion polymerization in which, however, a conventional surfactant is used at a concentration considerably high up to ~10 wt % with a higher alcohol as a cosurfactant frequently added. The mechanism of microemulsion polymerization is still open for question.[19]

One interesting point to be noted in the present organized copolymerization system is "*compartmentalization effects*" by polymerizing micelles. Under a favorable circumstance as will be presented, one could obtain nanoparticles, each composed of one graft copolymer as shown in Scheme 1, via a pseudo-living radical copolymerization with highly limited termination reactions between the compartmentalized radicals.

In this work, we investigated the micellar copolymerization behavior with macromonomers **1** and a hydrophobic monomer, styrene, solubilized therein under several conditions. We intend to clarify the kinetics and the copolymerizabilities in such an organized copolymerization system.

Experimental Section

Materials. Macromonomers **1** were prepared by the method reported in a previous paper.[16] In short, C_1−PEO−C_1−S-18 was prepared under argon by reaction of sodium alkoxide of poly(ethylene glycol) monomethyl ether with *p*-vinylbenzyl chloride (VBC, from Seimi Chemical Co., Japan) in dry tetrahydrofuran (THF) at room temperature. *p*-(4-Bromobutyl)styrene and *p*-(7-bromoheptyl) styrene were prepared by reactions of (*p*-vinylbenzyl)magnesium chloride with 1,3-dibromopropane and 1,6-dibromohexane, respectively, in dry ether at 0 °C. C_1−PEO−C_4−S-18 and C_1−PEO−C_7−S-18 were prepared in dry THF by reacting of poly(ethylene glycol) monomethyl ether with a 5-fold excess amount of either *p*-(4-bromobutyl)styrene or *p*-(7-bromoheptyl)styrene in the presence of a 5-fold excess of sodium hydride at room temperature. The reaction solutions were twice poured into benzene to precipitate salts. The filtrates were recovered by precipitation into hexane and purified by three precipitation cycles from THF to hexane. The macromonomers were finally freeze-dried from benzene. The molecular characteristics of the macromonomers prepared are presented in Table 1. The degree of polymerization of the PEO chain (n) determined by SEC was 17 ± 1, in agreement with the results obtained from end group analysis by ^{1}H NMR. The functionalities (f) of the double bond determined by ^{1}H NMR were satisfactorily high ($f > 93\%$).

Styrene was washed with aqueous sodium thiosulfate and aqueous sodium hydroxide and distilled over calcium hydride under a reduced pressure just before use. The initiator, 2,2′-azobis(isobutyronitrile), AIBN, from Kishida Chemicals was purified by recrystallization three times from anhydrous methanol, and 4,4′-azobis(4-cyanovaleric acid), AVA, from Aldrich was used as supplied commercially. Water was purified by a Millipore Milli-Q purification system. All the other reagents and solvents were purified according to the procedures as described before.[15]

Table 1. Characteristics of PEO Macromonomers

macromonomers	n^a(SEC)	M_w/M_n(SEC)	n^b	f (%)^c
C_1−PEO−C_1−S-18	16	1.1_2	18	$96._2$
C_1−PEO−C_4−S-18	17	1.1_2	18	$94._4$
C_1−PEO−C_7−S-18	18	1.0_9	19	$92._9$

[a] Determined by SEC calibrated with poly(ethylene glycol) standard samples. [b] Determined by ^{1}H NMR from the ratio of peak areas of oxyethylene to ω-methoxy protons. [c] Functionality of the double bonds determined by ^{1}H NMR from the ratio of peak areas of vinyl to ω-methoxy protons.

Micellar (Co)polymerization. Micellar homopolymerization and copolymerization were performed at 60 °C with a 100 mL three-necked round-bottom flask fitted with a condenser and a magnetic stirrer under nitrogen. A typical recipe for the copolymerization is 22.7 mmol/L of macromonomer, 22.7 or 45.4 mmol/L of styrene, and 0.10_7 mmol/L of AVA or AIBN in 40 mL of water. Water, macromonomer, and styrene were first loaded into the reactor. After purging with nitrogen for 30 min at room temperature, the reactor was immersed in an oil bath thermostated at 60 °C, and an initiator solution was added to start the polymerization. In the case of copolymerization with AIBN as an initiator, it was dissolved in styrene and added to the reactor. In time-evolution experiments, a precise amount of the reaction mixture was taken out of the reactor at different reaction times and immediately freeze-dried at least for 4 days, followed by further drying in a vacuum at room temperature until the weight change was less than 1×10^{-4} g. The styrene conversion was then determined by the weight method with the following equation:

$$\text{conv(styrene) (\%)} = \frac{W(t) - W_0(\text{macromonomer})}{W_0(\text{styrene})} \times 100 \quad (1)$$

where $W_0(i)$ is the weight of the component i included in the amount sampled out and $W(t)$ is the weight of the reaction mixture recovered after each polymerization time (t). The conversion of the macromonomer was determined from the disappearance of the double-bond peaks in ^{1}H NMR. The precision and reproducibility were examined by three times run and confirmed to be within less than 3% for each conversion.

Measurements. ^{1}H NMR spectra were recorded on a JEOL JNM-GX-270 FT spectrometer in $CDCl_3$ at 20 °C. The condition was 16 times accumulation and 30 s pulse delay time. Size exclusion chromatography (SEC) for characterization of macromonomers was run at 40 °C with JASCO PU980 as a pump, JASCO RI-930 as a refractive index detector, and Shodex A-802 and A-803 as columns. The signals are recorded on a computer and analyzed with a SIC 480 data station software (Ver. 2.1A, SIC Inc., Japan). THF was used as an eluent at a flow rate of 1 mL min^{-1}. The elution volume was calibrated with standard samples of PEO from Tosoh Co., Ltd.

Surface tension measurement was carried out with a surface tensiometer, CBV-A3 type (Kyowa Interface Science Co. Ltd.). All the measurements were carried out at 22 °C. To confirm precision for our experimental procedures, the surface tension of sodium dodecyl sulfate (SDS) solution was measured and its critical micelle concentration (cmc) determined to be 0.21 ± 0.01 wt %, in agreement with reference value of 0.21 wt %.[20]

Static light scattering (SLS) measurements were performed with an intensity monitor of an ELS-8000 (Otsuka Electronics Co., Ltd) equipped with a vertically polarized light of a 10 mW He−Ne laser of 632.8 nm as an incident beam at 25 °C. The Rayleigh ratio of the scattered light was based on the Rayleigh ratio $R(90) = 11.84 \times 10^{-6}$ cm^{-1} at a scattered angle of 90° of pure benzene at 25 °C.[21] Dynamic light scattering (DLS) experiments were also carried out with the same equipment. Measurements were made at a scattered angle of 90° in a temperature-controlled cell maintained via a thermostatically controlled water bath. For an optical purification, the solution was filtered slowly with a membrane filter of 0.1−0.45 μm in pore size (Toyo Roshi Co., Ltd.) directly into light scattering cells using a microfeeder.[22]

Apparent molecular weights of the graft copolymers were determined at 30 °C with SEC (Tosoh Co. Ltd., two Shodex KD-806M) connected to a refractive index detector and a multiangle laser light scattering instrument (MALLS) (Wyatt Technology Co. Ltd., DAWN-DSP).[7,23] The eluent was a spectroscopic grade DMF containing 50 mmol L^{-1} LiCl, and the rate was 1 mL min^{-1}. The Rayleigh ratio $R(90)$ was based on the Rayleigh ratio of pure toluene at 25 °C. The scattered volume correction for the detector at angles other than 90° was performed using the scattering intensities of a solution of the poly(methyl methacrylate) standard sample. The data analysis was carried out using the software ASTRA (Ver. 4.70.07, Wyatt Technology). The precision and reliability of the SEC-MALLS were reported elsewhere.[23]

Excess refractive index increments (dn/dc) were measured using a refractometer, RM-102 (Otsuka Electrons Co. Ltd.). The value of dn/dc for macromonomers in water was determined to be 0.13_3 (mL/g) for C_1−PEO−C_1−S-18, 0.13_5 for C_1−PEO−C_4−S-18, and 0.13_9 for C_1−PEO−C_7−S-18 at 25 °C and for the graft copolymers of styrene with PEO macromonomers (1:1 mole ratio) in DMF containing 50 mmol L^{-1} LiCl to be 0.050_5 for C_1−PEO−C_1−S-18, 0.053_0 for C_1−PEO−C_4−S-18, and 0.056_4 for C_1−PEO−C_7−S-18 at 30 °C.

Results and Discussion

We first report aggregation characteristics of PEO macromonomers in water. The cmc and aggregation number in water were characterized by surface tension and light scattering experiments. Second, homopolymerization of the macromonomer and styrene in water and copolymerization of their mixture are studied together with their organization states. A possible mechanistic approach to the interesting behavior observed will be presented in terms of “compartmentalization effects”. Characterization and solution properties of the resulting graft copolymers studied by means of dynamic and static light scattering experiments will be given in order to discuss the copolymerization behavior and the formation of unimolecular nanoparticle in a selective solvent for branched chains.

Aggregation Behavior of PEO Macromonomers into Micelles in Water. Characterization of the present micellar copolymerization system is essential to understanding the polymerization behavior more deeply. The characterization was carried out by means of two methods, i.e., surface tension and static light scattering.

Figure 1 represents semilogarithmic plots of surface tension of aqueous macromonomer solution with the concentration, [macromonomer], at 22 °C. With increasing [macromonomer] the surface tension decreases almost linearly and becomes constant above a certain concentration which may correspond to the critical micelle concentration (cmc). The cmc values determined from an inflection point are collected in Table 2.

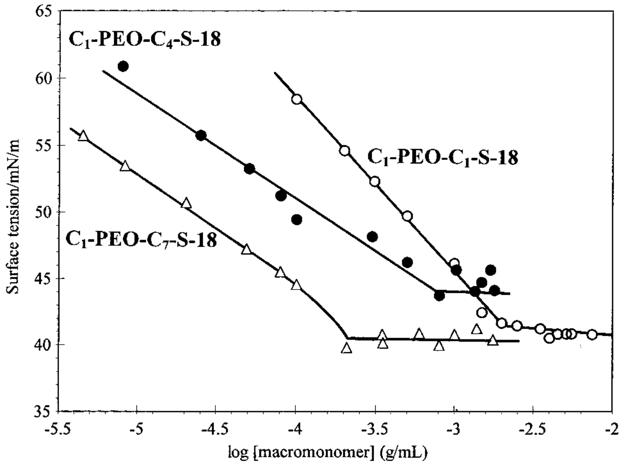


Figure 1. Semilogarithmic plots of surface tension of macromonomer solution with [macromonomer] at 22 °C: (○) C_1−PEO−C_1−S-18, (●) C_1−PEO−C_4−S-18, and (△) C_1−PEO−C_7−S-18.

The cmc was also determined by a static light scattering experiment at 25 °C, as shown in Figure 2. The Rayleigh ratio $R(90)$ of aqueous macromonomer solution at scattered angle of 90° was plotted against the concentration. The scattered intensity or $R(90)$ increased steeply with a concentration above that to be identified as cmc. The values are also given in Table 2. One sees a reasonable agreement between the cmc's by the two methods and that the cmc decreases with increasing hydrophobicity of α-end group of the macromonomer. An interesting point to be noted in Figure 2 is that below cmc $R(90)$ of C_1−PEO−C_1−S-18 solution is much higher than that of C_1−PEO−C_4-18 or C_1−PEO−C_7-18.[14,15] This behavior was also observed in our previous studies, most likely due to formation of loose aggregates of less hydrophobic surfactant molecules at concentration below cmc.[24]

When particle size of the aggregates is sufficiently small compared to the wavelength of incident light, their molecular weight may be evaluated by the equation

$$\frac{K(C - \text{cmc})}{R(90)} = \frac{1}{M_{\text{w}}^{\text{agg}}}\{1 + 2A_2(C - \text{cmc}) + ...\} \quad (2)$$

where $M_{\text{w}}^{\text{agg}}$ is the weight-averaged molecular weight of aggregates, A_2 is the second virial coefficient, and $K = 4\pi^2 n_0^2(\mathrm{d}n/\mathrm{d}c)^2/(\lambda_0^4 N_{\text{A}})$ with the refractive index of the solvent (n_0), the excess refractive index increment (dn/dc), the wavelength (λ_0), and Avogadro's number (N_{A}).

A typical plot of eq 2 is given for C_1−PEO−C_4−S-18 macromonomer solution in Figure 3. The weight-averaged molecular weight and aggregation number ($N_{\text{w}}^{\text{agg}}$) of the micelle determined from an intercept in this plot are presented in Table 2. The value of $N_{\text{w}}^{\text{agg}}$ decreases a little but not so much with increase in the hydrophobic alkylene chain length of the α-end group. We reported previously that number-averaged aggregation numbers ($N_{\text{n}}^{\text{agg}}$) of the macromonomer **1** (n = 53 and m = 4, 7) are 38−27 through analysis of a fluorescence decay

Table 2. Characterization of Macromonomer Micelle in Water

macromonomers	10^4cmc (g/mL)^a	10^4cmc (g/mL)^b	$10^{-4}M_w^{agg\ b}$	$N_w^{agg\ b}$	N_s^c
C_1−PEO−C_1−S-18	20	20	8.3 ± 0.6	105 ± 7	
C_1−PEO−C_4−S-18	7.8	9.0	7.4 ± 0.3	78 ± 3	22
C_1−PEO−C_7−S-18	2.1	3.0	7.3 ± 0.2	69 ± 2	31

[a] Determined by surface tension measurements at 22 °C. [b] Determined by static light scattering at 25 °C. [c] Calculated from an oil drop model.[24]

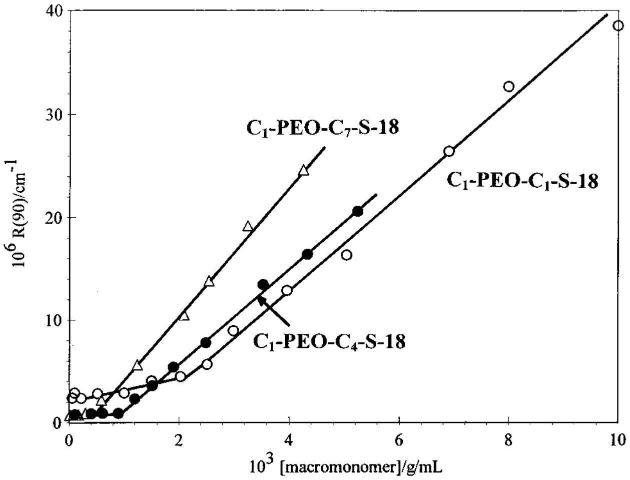


Figure 2. Rayleigh ratio at 90° $R(90)$ vs concentration for C_1−PEO−C_1−S-18 (○), C_1−PEO−C_4−S-18 (●), and C_1−PEO−C_7−S-18 (△) at 25 °C.

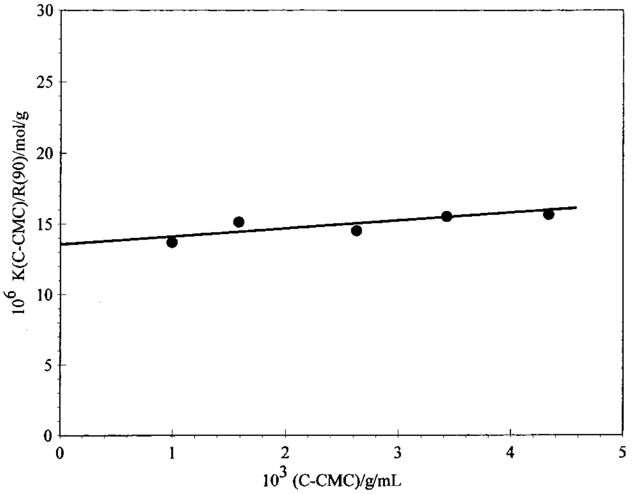


Figure 3. $K(C - \text{cmc})/R(90)$ vs concentration for C_1−PEO−C_4−S-18 at 25 °C.

curve of pyrene as a probe.[24] The present weight-averaged values (N_w^{agg}) are significantly higher than the N_n^{agg} and also those calculated from an ideal oil drop model. This can be expected because light scattering is more sensitive to larger species than smaller ones in a polydisperse aggregate sample.

Since light scattering is sensitive only to the size and mass of objects in the solution, it does not inform one of the details of the hydrophobic domain of the aggregates. In our previous study,[24] the partitioning experiments and steady-state fluorescence spectroscopy of pyrene in the micelles clearly revealed that the increase in alkylene chain length results in the micelles with a more hydrophobic core (a decrease of the vibrational fine structure intensity ratio (I_1/I_3)) and with higher solubility of a hydrophobe (high partitioning coefficient of pyrene). Therefore, the present micellar homopolymerization and copolymerization behavior would be expected to be remarkably affected by the structure of macromonomer used.

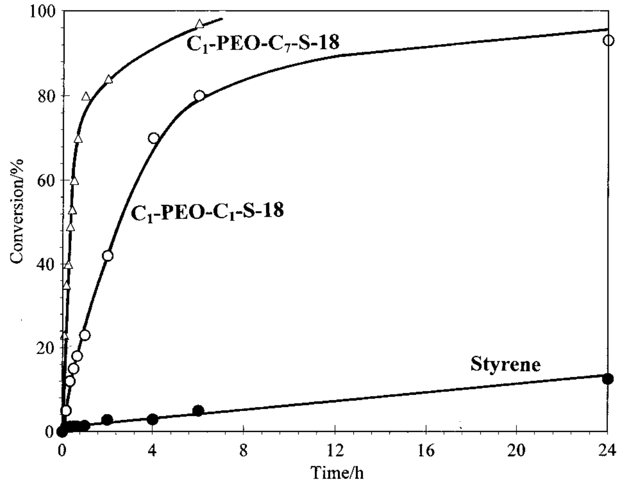


Figure 4. Fractional conversion vs time plots for homopolymerization of C_1−PEO−C_1−S 18 (○), C_1−PEO−C_7−S 18 (△), and styrene (●) in water with [styrene] = 22.7 mmol/L, [macromonomer] = 22.7 mmol/L, and [AVA] = 0.10_7 mmol/L at 60 °C.

Micellar Homopolymerization and Copolymerization. First, we have examined homopolymerization of the PEO macromonomers and also of styrene in water at the same concentration as that used in copolymerization. The macromonomer polymerized apparently transparently while styrene with droplets polymerized to precipitate. Figure 4 represents a time-evolution curve of the homopolymerization in water with AVA as an initiator at 60 °C. Two interesting observations are that homopolymerization of macromonomers proceeds with a rate much higher than styrene and that fractional conversion rate of C_1−PEO−C_7−S-18 is higher than C_1−PEO−C_1−S-18, supporting micellar polymerization. What we intend to claim in this experiment with AVA as an initiator is that in water styrene never polymerizes rapidly. This is because of low solubility of styrene (low monomer concentration) and its oligomers in water. The solubility of styrene molecules in water is about 5×10^{-3} mol L^{-1}, and the critical chain length (J_{crit}) of polystyrene above which polymer precipitates is about 5 at 60 °C.[25] In addition, the oligostyrenes with a carboxylic acid group formed from initiator-derived entities in the aqueous phase is too low in the surface activity to form in situ micelles (nuclei), in contrast to surface-active oligostyrenes formed in a soap-free emulsion polymerization with potassium persulfate as an initiator. In the absence of macromonomer micelles, therefore, termination reactions between unstable oligostyrene radicals formed in water phase may significantly take place.

The copolymerization results for a mixture of macromonomer micelles and an equimolar amount of styrene solubilized therein are indicated in Figure 5.

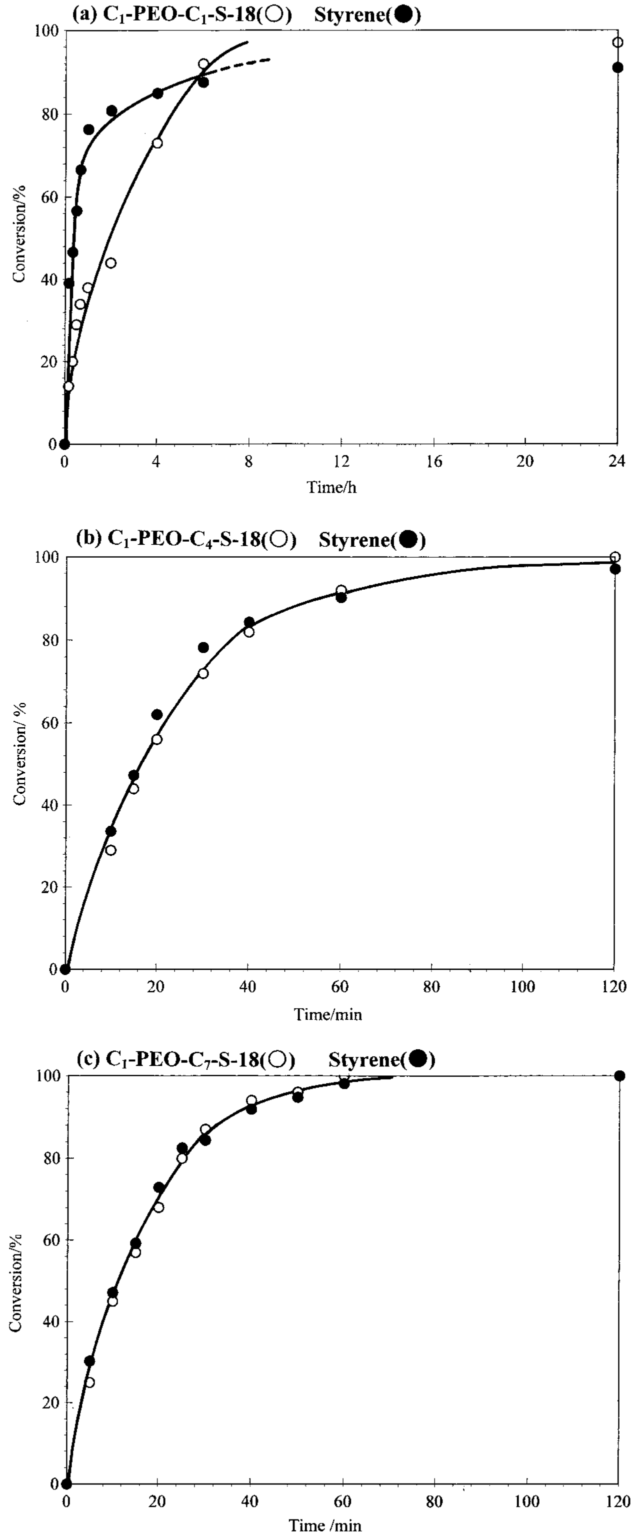


Figure 5. Fractional conversion vs time plots for radical copolymerization of styrene (●) with (a) C_1−PEO−C_1−S-18 (○), (b) C_1−PEO−C_4−S-18 (○), and (c) C_1−PEO−C_7−S-18 (○) with AVA at 60 °C; [styrene] = 22.7 mmol/L, [macromonomer] = 22.7 mmol/L, and [AVA] = 0.10_7 mmol/L.

Copolymerizations were carried out with AVA as a water-soluble initiator at 60 °C. Each fractional conversion was plotted against the copolymerization time. It might be emphasized that all the copolymerizations proceeded apparently transparently at 60 °C before and after copolymerization.

Interestingly, the fractional conversion rate of styrene was remarkably accelerated by the presence of the polymerizable macromonomer micelles. The extent of the acceleration increased with alkylene chain length of the macromonomer, i.e., $C_7 > C_4 > C_1$ (note that time scale in Figure 5a is different from (b) and (c)). Correspondingly, the conversion rate of macromonomer also increased by the presence of small amount of hydrophobic styrene solubilized therein. These results imply that the micelle structure plays apparently an important role in their copolymerization behavior. It is, however, difficult to explain this unusual acceleration in terms of the kinetics based on a conventional terminal model in homogeneous copolymerization.

A question should be addressed why both copolymerization rates of styrene and macromonomer are accelerated in the present organized copolymerization media. Very rapid conversion rate of styrene clearly indicates that styrene molecules solubilized in micelles are exclusively copolymerized; that is, a major locus of the copolymerization is in the copolymerizable micelles and/or the resulting graft copolymer micelles but not in aqueous phase. That is, the compartmentalization effects by the micelles correspond to the acceleration in the rate in the present copolymerization. These effects increase the copolymerization rate through retardation of the termination reactions between compartmentalized graft copolymer radicals. Therefore, the answer should be provided based on a reliable knowledge for the mechanisms of nucleation, i.e., of particle formation in emulsion, microemulsion, and dispersion polymerization systems, whereas the present copolymerization proceeded apparently transparently. Unfortunately, the nucleation is a complex process, and major topics in the heterogeneous polymerization are but still a matter of discussion. The micellar entry, homogeneous, and homogeneous-coagulative nucleations are thought to simultaneously take place for the nucleation process in the present system. In any event, since the copolymerization affords amphiphilic graft copolymers, the nucleation may thus depend on the composition of the graft copolymers formed in both phases, continuous and micelle phases.

An explanation for the experimental observation begins with the idea that polymerizable micelles will efficiently capture the oligomer radicals formed in water phase and compartmentalize (isolate) them, that is, "micellar entry", a major nucleation mechanism for emulsion polymerization of hydrophobic monomer at the surfactant concentration higher than cmc. The stabilization of the primary nuclei by the macromonomer and the events taking place in water phase will be discussed later.

The fractional conversion of total monomers into copolymers per unit polymerization time, dx/dt, in the present micellar, compartmentalized copolymerization may be given by the same equation as conventional emulsion polymerization as follows.[25]

$$\frac{dx}{dt} = \frac{\langle k_p \rangle C_p \bar{n} N_{\mathrm{micelle}}}{n_0^{\mathrm{M}} N_{\mathrm{A}}} \tag{3}$$

where $\langle k_p \rangle$ is the average propagation rate coefficient, C_p the local styrene and macromonomer concentrations in the micelle (mol/micelle volume·L), $\bar{n}$ the average number of free radical per micelle, N_{micelle} the number concentration of micelle (L^{-1}), and n_0^{M} the initial

Table 3. Monomer Composition of Styrene and Macromonomer in Water and Micelle Phases[a]

macromonomer	$[\text{styrene}]_0/[\text{macromonomer}]_0$ in feed (mol ratio)	$10^{-20}N_{\text{micelle}}$ (number/L)	$[\text{styrene}]_w/[\text{macromonomer}]_w$ in water (mol ratio)	$[\text{styrene}]_M/[\text{macromonomer}]_M$ in a micelle (mol ratio)
C_1−PEO−C_1−S-18	1.0	1.1_6	1.9_8	0.8_8
C_1−PEO−C_4−S-18	1.0	1.6_8	5.2_6	0.8_1
C_1−PEO−C_7−S-18	1.0	1.9_6	$17._2$	0.7_9
C_1−PEO−C_7−S-18	2.0	1.9_6	$17._2$	$1._8$
C_1−PEO−C_7−S-18	4.0			*b*

[a] $[\text{macromonomer}]_0 = 2.27 \times 10^{-2}$ mol L^{-1}. $N_{\text{micelle}} = ([\text{macromonomer}]_0 - \text{cmc})N_A/N_w^{\text{agg}}$. $[\text{styrene}]_M = [\text{styrene}]_0 - [\text{styrene}]_w$, where $[\text{styrene}]_w = 5.0 \times 10^{-3}$ mol L^{-1} at 60 °C. $[\text{macromonomer}]_w$ = cmc at 25 °C. $[\text{macromonomer}]_M = [\text{macromonomer}]_0 - \text{cmc}$. [b] Heterogeneous (emulsion).

concentration of styrene and macromonomer (mol/L). Equation 3 may also be rewritten as

$$\frac{dx}{dt} = \frac{\bar{n}\langle k_p\rangle}{N_{\text{agg}}}\left(\frac{[\text{macromonomer}]_M + [\text{styrene}]_M}{[\text{macromonomer}]_0 + [\text{styrene}]_0}\right) \times ([\text{macromonomer}]_0 - \text{cmc}) \quad (4)$$

and for the rate of polymerization,

$$R_p = -\frac{d[M]}{dt} = \frac{dx}{dt}n_0{}^M = \frac{\bar{n}\langle k_p\rangle}{N_{\text{agg}}}([\text{macromonomer}]_M + [\text{styrene}]_M)([\text{macromonomer}]_0 - \text{cmc}) \quad (5)$$

where subscripts 0 and M represent initial concentration and local concentration per micelle volume, respectively.

The increase of the fractional copolymerization rate with alkyl chain length of the macromonomer is thought to come from the following origin: (1) the decrease of N_{agg} and cmc, that is, the increase of the number of micelle, (2) the increase of local concentration, (3) and the increase of $\bar{n}$. In fact, the number of micelle (N_{micelle}) increases from 1.2×10^{20} to 2×10^{20} L^{-1} with alkylene chain length from C_1 to C_7, as listed in Table 3. The further increase in the number of micelles might come from the fact that hydrophobic styrene molecules solubilized into the micelles can force original, loose micelles which "reorganize" into ones with denser cores to enhance both N_{micelle} and local concentration.

The local concentrations of styrene and macromonomer (mol/micelle volume) are estimated with great difficulty from the present experimental data. The average composition of styrene or macromonomer in a micelle is calculated and listed in Table 3. This value is around 0.8−0.9 and varies little with the alkylene chain length. The unusually high aggregation number in a C_1−PEO−C_1−S-18 micelle, however, results in a micelle having a large micelle volume. As a result, the local concentration in the micelle is thought to be lower than those of the other macromonomer micelles.

The $\bar{n}$, which is determined by the extent of the rate of radicals "entry into" and "exit from" a micelle as well as the rate of termination, is also a variable. Since the average ratio of styrene to macromonomer in a micelle is almost constant, the rate of exit of small radicals due to chain transfers in a micelle should not be so different with the alkylene chain length. The entry rate, on the other hand, may depend on the styrene composition of oligo-graft-copolymer radicals formed in a continuous phase, i.e., water phase. We listed in Table 3 the monomer composition of styrene and macromonomers in water phase before the copolymerization. The average styrene composition in the graft copolymers from C_1−PEO−C_1−S-18 in water phase should be much smaller than those with the other macromonomers, if one assumes a reasonably similar reactivity ratio. Introduction of one PEO macromonomer chain to an oligostyrene chain remarkably increases its water solubility (increase in J_{crit}). Thus, the copolymer radicals from C_1−PEO−C_1−S-18 would be considerably soluble in the water phase to self-organize into inter- and/or intramolecular aggregates. They are not so efficiently captured by the less hydrophobic micelles to decrease the number of radical and particle. On the other hand, the graft copolymer radicals from C_1−PEO−C_7-18 with much higher styrene composition may be efficiently captured by the styrene-swollen micelles before they precipitate ($J_{\text{crit}} \approx 5$). Therefore, the $\bar{n}$ may decrease on the order of $C_7 \approx C_4 > C_1$.

An alternative explanation is based on the events taking place in water phase, that is, homogeneous and/or homogeneous coagulative nucleation. We call again the composition of styrene and macromonomer in water phase in Table 3. Table 3 shows that C_1−PEO−C_1−S-18 is ca. 8.7 times more soluble in water phase than C_1−PEO−C_7−S-18. Since the micelles are considered as dynamic entities in equilibrium with unimers in solution, the unimers participate to exchange between micelles and also adsorb on the amphiphilic graft macroradicals. This implies two points. First is that much more macroradicals are formed in the water phase of C_1−PEO−C_1−S-18, and their termination rate must be higher than that of C_1−PEO−C_7−S-18, leading to lower R_p. Second is that the primary nuclei formed in the water phase is stabilized by adsorption of macromonomer, and C_1−PEO−C_7−S-18 being a more efficient stabilizer than C_1−PEO−C_1−S-18 is able to stabilize more nuclei to increase R_p. In the macromonomer with high cmc, the contribution of the graft copolymers formed in the water phase to the nucleation becomes crucial.

The higher fractional conversion rate of styrene than C_1−PEO−C_1−S-18 in Figure 5a may be deduced from the difference in the local concentration between the loose aggregates of the macromonomer and styrene solubilized therein. The copolymerization of styrene with C_1−PEO−C_1−S-18 will increase the surface activity and absorb a higher amount of styrene than the original micelle to increase the local concentration of styrene. The fractional conversion rate of styrene approaches to that of macromonomer with increasing alkyl chain length, as shown in Figure 5b,c. With C_1−PEO−C_7−S-18 macromonomers, both conversions are the same within experimental error over all copolymerization time. That is, azeotrope copolymerization took place to afford highly branched amphiphilic graft copolymers with a relatively low compositional heterogeneity. We conclude that designing the organization states will control the copolymerization behavior.

The time−conversion plots for the copolymerization at the different molar ratio of styrene to C_1−PEO−C_7-

Table 4. Characterization Results of Poly(styrene-*graft*-PEO)$^{a)}$

macromonomer	initiator	$10^{-6}M_{w(app)}{}^{b}$ g/mol	$M_w/M_{n(app)}{}^{b}$	$\langle S^2\rangle_z{}^{1/2}{}_{(app)}{}^{b}$ (nm)	R_h in DMF^c (nm)	R_h in H_2O^d (nm)
C_1−PEO−C_1−S-18	AVA	1.7_4	2.5 ± 0.1	49	43	89
C_1−PEO−C_1−S-18	AIBN	1.7_4	2.4 ± 0.1	50	42	88
C_1−PEO−C_4−S-18	AVA	6.7_6	1.7 ± 0.1	92	71	34
C_1−PEO−C_4−S-18	AIBN	6.7_1	1.7 ± 0.1	90	60	36
C_1−PEO−C_7−S-18	AVA	7.4_4	1.7 ± 0.1	94	74	15
C_1−PEO−C_7−S-18	AIBN	7.2_7	1.8 ± 0.1	93	63	20

[a] Copolymerizations were carried out for the solution of the macromonomer and equivalent amount of styrene at 60 °C. Copolymerization conditions are the same as in Figure 5. [b] Determined by SEC-MALLS at 30 °C. [c] Determined by DLS at 20 °C. [d] Determined by DLS at 25 °C.

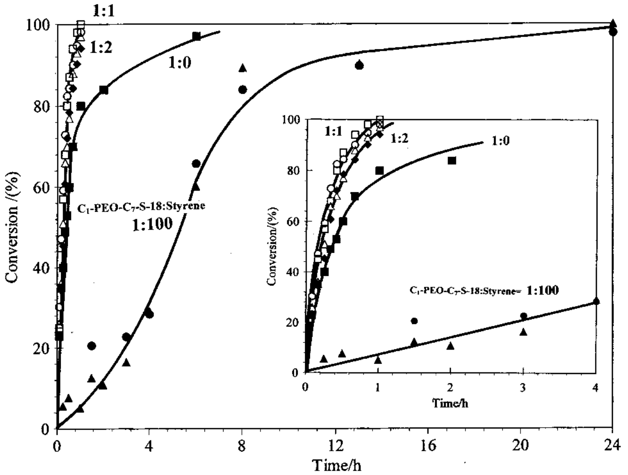


Figure 6. Fractional conversion vs time plots for radical homopolymerization of C_1−PEO−C_7−S-18 and the copolymerization with different mol ratio of styrene: (1:0); [C_1−PEO−C_7−S-18] = 22.7 mmol/L (■), [styrene] = 0 mmol/L, [AVA] = 0.10_7mmol/L, (1:1); [C_1−PEO−C_7−S-18] = 22.7 mmol/L (□), [styrene] = 22.7 mmol/L (○), [AVA] = 0.10_7mmol/L, (1:2); [C_1−PEO−C_7−S-18] = 22.7 mmol/L (△), [styrene] = 45.4 mmol/L (◆) [AVA] = 0.10_7mmol/L, and (1:100); emulsion copolymerization, [C_1−PEO−C_7−S-18] = 1.40 mmol/L (●), [styrene] = 140 mmol/L (▲), [KPS] = 0.657 mmol/L.

18 macromonomer are shown in Figure 6. The copolymerization proceeded apparently homogeneously up to twice the molar amount of styrene. The results of the emulsion copolymerization of 100 times molar amount of styrene to macromonomer are also shown for the comparison, where potassium persulfate was used as an initiator at 65 °C. The last data cannot be directly compared with the former, because the macromonomer concentration decreased to 1.40 mmol/L. There are two interesting observations to be noted. First is that in all the feed compositions the fractional conversions of styrene are almost the same as those of the macromonomer, implying azeotrope copolymerization. Second is that the copolymerization in an equivalent amount of monomer mixture proceeds fastest in terms of the fractional conversion rate. This is most likely due to reorganization of the original micelle by a limited amount of the solublilized hydrophobic styrene molecules. Another explanation is that the excess amount of styrene results in the graft copolymer radicals with higher styrene composition by micellar entry. They are unstable in water to coalesce some extent and bring about the decrease in the number of radical and nuclei. In fact, the fractional slope in the stage II of emulsion copolymerization (1:100) is much smaller than that of the homogeneous micellar copolymerization because of the lower number density of particles. The copolymerization afforded monodisperse, core−shell latex particles with 275 nm diameter and with a number density of 8.8×10^{15} L^{-1}, a value much smaller than that of the micelle ($N_{micelle}$).[26] In this regard, the primary nuclei significantly coalesce to decrease the particle concentration during stage I. We are carrying out further investigations to clarify the mechanisms for the micellar as well as emulsion copolymerizations using polymerizable surfactants and will report in the near future.

Fate of Micelles and Oligomer Radicals Formed in Water Phase. We present in Table 4 apparent weight-average molecular weights ($M_{w(app)}$) and *z*-average radius of gyration ($\langle S^2\rangle_z{}^{1/2}{}_{(app)}$), determined by SEC-MALLS measurements in DMF at 30 °C.

The graft copolymers with apparent molecular weights from 1.7×10^6 to 7.3×10^6 were found to be prepared by the present organized copolymerization. The molecular weight of the final graft copolymers increased, but the molecular weight distribution became to be slightly narrow with increasing alkylene chain length, irrespective of the type of initiator. This is in accord with the copolymerization behavior in Figure 5; that is, the rate of copolymerization increased, and the compositional heterogeneities decreased with alkylene chain length of the macromonomers.

Another interesting observation to be noted is based on the fact that the molecular weight of the final graft copolymers is much higher than the molecular weight of mixture of styrene and macromonomer per a micelle. For a mixture of C_1−PEO−C_7−S-18 and equimolar styrene, a graft copolymer formed is calculated to be composed of about 100 micelles in average. The detailed mechanism of the copolymerization is still open to question, but some points to be supposed include (1) that termination reactions will be highly limited between graft copolymer radicals because they are sterically stabilized by grafted PEO chains and somewhat buried inside of the amphiphilic graft copolymer particle, (2) that monomers will be fed by diffusion-controlled collision between monomer micelles and the graft copolymer particle containing a radical, and (3) the rate of radical generation from initiator in continuous phase ($2k_df$[I] $= 7.7 \times 10^{14}$ s^{-1} L^{-1} with $k_d = 6.0 \times 10^{-6}$ s^{-1},[18] $f = 1$, and [I] = 0.10_7 mmol/L) is too low compared to the number of micelles (2×10^{20} L^{-1} in Table 3) to allow frequent entry of oligomer radicals formed in the continuous phase into graft copolymer micelles containing a radical. The average time interval, τ, for an oliogomer radical in water phase to entry into a graft copolymer particle containing a radical may be 72 h as calculated from the ratio of $N_{micelle}$ to $2k_df$[I] at the beginning of copolymerization. This time is much longer than 1 h for the complete conversion of the monomers (Figure 5c). Near the end of the copolymerization, the value of τ is calculated to be reduced to 43 min. This estimation thus suggests that the probability of termi-

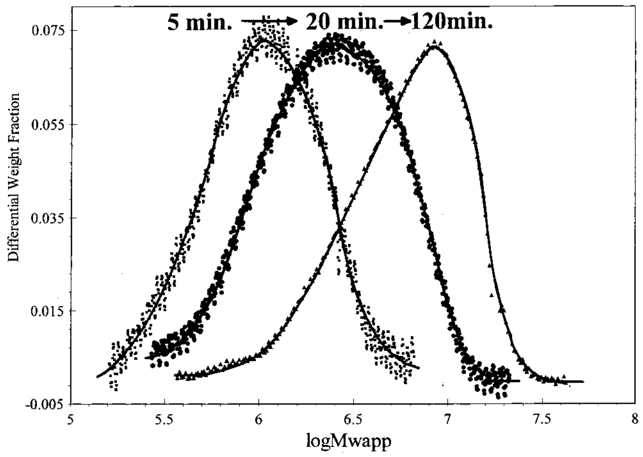


Figure 7. Differential weight fraction curves for the poly(styrene-*co*-C_1−PEO−C_7−S-18) obtained at different copolymerization times. The copolymers are the same as those in Figure 5c and Table 5.

nation by entry of an oligomer radical into a graft copolymer particle containing a radical may be extremely limited. The number of radicals generated during 1 h is calculated to be 2.8×10^{18} L^{-1}, which may be comparable to the number of the polymer chains formed ($N_p = 2 \times 10^{18}$ L^{-1}). An important conclusion drawn from the experimental results and calculation is that the oligomer radicals from C_1−PEO−C_7−S-18 formed in water phase exclusively enter into copolymerizable micelles to start copolymerization ($N_p \sim 2k_d f[I]t$) and that termination reactions between graft copolymer radicals and oligomer radicals from initiator in water are remarkably excluded, especially in the early stage of the polymerization.

The mechanism is, therefore, greatly different from those in the stage II of the conventional emulsion polymerization. According to a typical recipe of the emulsion polymerization, $N_{\text{particle}} = \sim 10^{18}$ L^{-1}, $2k_d f[\text{KPS}] = 2.7 \times 10^{17}$ L^{-1} with $k_d = 2.2 \times 10^{-5}$ s^{-1} at 70 °C, $f = 1$, and $[\text{KPS}] = 10^{-2}$ mol/L, the time τ is calculated to be 4 s. The particles as the polymerization sites are also considerably swollen (plasticized) by monomers during this stage. Therefore, for the emulsion polymerization the particle allows oligomer radicals to entry frequently.

The points we proposed above suggest that the radical in a graft copolymer particle from C_1−PEO−C_7−S-18 is forced to be isolated during the copolymerization time. In other words, the present copolymerization may follow a pseudo-living radical (controlled) copolymerization with remarkably limited termination due to organization. Figure 7 represents differential weight fraction curves at different copolymerization time, as determined by SEC-MALLS.

The most important experimental fact is that the apparent molecular weights of the graft copolymers increased with conversion. This clearly supports that our discussion as above is reasonable enough. To our best knowledge, this is first to prove the fact that it is possible to design a living-like radical copolymerization by using an organized system, without any particular additives as in the well-developed, living radical systems such as TEMPO-mediated polymerization[27] and ATRP.[28,29] Also important to be added, the living-like or pseudo-living polymerization here is conducted in normal conditions (at 60 °C) and in water.

Table 5. Characterization Results of Poly(styrene-*co*-C_1-PEO-C_7-S-18)[a]

copolymerization time (min)	conversions (%) styrene	conversions (%) macromonomer	$10^{-6}M_{w(app)}$[b]	$M_w/M_{n(app)}$[b]
5	30.3	25	1.3_2	1.6
10	47.2	45	2.4_2	1.8
15	59.3	57	2.9_5	2.0
20	72.9	68	3.1_2	1.9
25	82.5	80	3.1_7	1.7
30	84.4	87	3.6_0	2.5
40	91.9	90	2.2_3	2.3
50	94.8	98	5.5_5	2.0
60	98.1	100	6.2_8	1.4
120	100.0	100	7.2_8	1.7

[a] Copolymerizations were carried out for the solution of the macromonomer and equivalent amount of styrene at 60 °C. Copolymerization conditions are the same as in Figure 5. [b] Determined by SEC-MALLS at 30 °C.

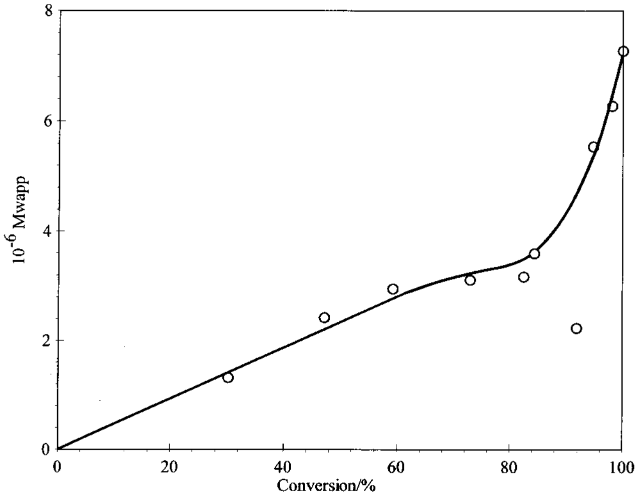


Figure 8. Plots of $M_{w(app)}$ vs conversion of styrene. The copolymers are the same as those in Figure 5c and Table 5.

The apparent molecular weights of the graft copolymers at each copolymerization time are summarized in Table 5, and the $M_{w(app)}$ is plotted against the conversion of styrene in Figure 8. Of course, as can be seen in this figure, the behavior is not so simple as an ideal living polymerization. The $M_{w(app)}$ increases linearly with styrene conversion up to 60% conversion and became almost constant to 85%, and above it increases steeply. The molecular weight distribution increases with styrene conversion up to 85% and decreases above it. The decrease in the slope in Figure 8 and the increase in the molecular weight distribution are thought to be due to the accumulation of the radicals and the terminations accompanied even rarely. The steep increase in $M_{w(app)}$ at the end of the copolymerization is supposedly due to the recombination terminations between graft copolymer radicals with depleted monomer-micelles. It should be emphasized that even at this stage the termination reactions between graft copolymer radical and newly formed oligomer radical in the water phase seem to be minor events, judging from τ as long as 43 min.

Solution Properties of Graft Copolymers. Finally, we present some of solution properties of the graft copolymers. We have reported previously that the homopolymer of C_1−PEO−C_4−S-50 was quantitatively characterized by perturbed semiflexible, cylindrical brush with persistence length of 17 nm and excluded-volume strength of 5.7_8 nm in water.[7] The persistence

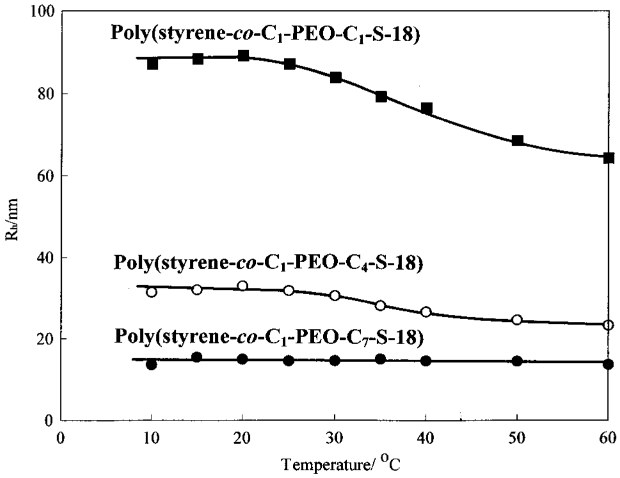


Figure 9. Hydrodynamic radius (R_h) of graft copolymers (in Figure 5) in water vs temperature: ploy(styrene-*co*-C_1−PEO−C_1−S-18) (■), poly(styrene-*co*-C_1−PEO−C_4−S 18) (○), and poly(styrene-*co*-C_1−PEO−C_7−S 18) (●).

length was also found to increase with PEO chain length.[30] Thus, it would be expected that the present graft copolymers of styrene with macromonomer, having lower PEO chain density than homopolymer, behave as a flexible polymer in a common solvent, DMF, but form intra- and/or intermolecular micelles in a selective solvent, water.

We begin with the solubility difference between the graft copolymers in water which is a selective solvent for branched chain. The aqueous solution of poly(styrene-*co*-C_1−PEO−C_1−S-18) with large compositional heterogeneities as suggested from the considerable difference in the conversion rates in Figure 5a changed reversibly from clear to turbid solution by changing temperature. This is due to the fact that the graft copolymer with styrene rich in the composition precipitates and/or forms intermolecular micelles, as shown later. In remarkable contrast, poly(styrene-*co*-C_1−PEO−C_7−S-18) never precipitates for the temperature change from 10 to 60 °C. The solution of poly(styrene-*co*-C_1−PEO−C_4−S-18) became a little turbid with decreasing temperature. Therefore, we conclude here that not only the average composition but also the exact structure in the amphiphilic graft copolymers is important to affect the aggregation behavior in a selective solvent for branch chains.

The hydrodynamic radius (R_h) for the graft copolymers was measured by dynamic light scattering in DMF at 20 °C and in water at 10−60 °C. We compare the hydrodynamic radius of the graft copolymers in DMF and water at 25 °C in Table 4. Also, the temperature dependence of the radius in water is shown in Figure 9. For the graft copolymers of poly(styrene-*co*-C_1−PEO−C_1−S-18), the value of R_h in water is 2 times higher than that in DMF, implying the intermolecular aggregation in water. In contrast, the value of R_h of poly(styrene-*co*-C_1−PEO−C_4−S-18) and poly(styrene-*co*-C_1−PEO−C_7−S-18) in water is remarkably smaller than that in DMF. Especially, the graft copolymers of poly(styrene-*co*-C_1−PEO−C_7−S-18) with AVA as an initiator have as small as ca. 15 nm in radius, almost independent of the temperature. When one assumes an ideal rigid sphere composed of polystyrene, the radius (R) of the sphere with molecular weight, M, may be given by the equation

$$R = \left(\frac{3M}{4\pi\rho N_A}\right)^{1/3} \tag{6}$$

where ρ is the density of the sphere (for polystyrene $\rho = 1.05$ g/cm^3). When one permits to use the $M_{w(app)}$ in Table 4, R is calculated to be 14 nm, which is consistent with that observed, implying a formation of unimolecular nanoparticles. A somewhat higher value (34 nm at 25 °C) of poly(styrene-*co*-C_1−PEO−C_4−S-18) graft copolymers than that of poly(styrene-*co*-C_1−PEO−C_7−S-18) in water may be due to intramolecular micelles with a lower density core and/or to intermolecular aggregation. Further characterizations of the unimolecular nanoparticles are in progress and will be reported in the near future.

The knowledge drawn from the characterization and solution properties of the resulting graft copolymers should be again correlated with the copolymerization behavior. That is, during the copolymerization, the graft copolymers of styrene with C_1−PEO−C_1−S-18 coalesce and/or form intermolecular micelles in water to decrease the number of particles and to increase the termination reaction between graft copolymer radicals. On the other hand, the graft copolymer radicals from C_1−PEO−C_7−S-18 (1:1 ratio) intramolecularly self-organize into a sterically stabilized unimolecular nanoparticle able to persist their lifetime with lower radical flux from the initiator decomposition than virgin micelles. This is an origin for the manner of pseudo-living radical copolymerization as was actually observed in the present organized, compartmentalized copolymerization.

Conclusions

The "micellar copolymerization" behavior of PEO macromonomers with a limited amount of styrene solubilized therein was characterized in detail. The copolymerization rates of styrene and macromonomers were found to be greatly enhanced by the presence of the counterparts. The micellar copolymerization considerably depends on the structure of the macromonomers, that is, the micelle structure. A feasible interpretation based on the compartmentalization effect qualitatively described the copolymerization behavior observed. A key is the fate of the graft copolymers formed in both phases, continuous and micelle phases. The characterization of the graft copolymers revealed that the organized copolymerization of styrene with C_1−PEO−C_7−S-18 proceeds in pseudo-living in that essentially all the radicals generated enter the virgin micelles and grow in size with highly limited terminations. In the micelles from C_1−PEO−C_7−S-18, the copolymerization proceeded very rapidly, azeotropically, and apparently transparently to afford a highly branched graft copolymer of poly(styrene-*graft*-PEO). The graft copolymers were revealed to form in water a "unimolecular nanoparticle" with 15 nm radius and $7.4_4 \times 10^6$ apparent molecular weight.

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References and Notes

(1) Ito, K. *Prog. Polym. Sci.* **1988**, *23*, 581.
(2) Ito, K.; Kawaguchi, S. *Adv. Polym. Sci.* **1999**, *142*, 129.
(3) Ito, K.; Tomi, Y.; Kawaguchi, S. *Macromolecules* **1992**, *25*, 1534.
(4) Tsukahara, Y. In *Macromolecular Design: Concept and Practice*; Mishra, M. K., Ed.; Polymer Frontiers International Inc.: New York, 1994; pp 161−227.
(5) Wintermantel, M.; Gerle, M.; Fischer, K.; Schmidt, M.; Wataoka, I.; Urakawa, H.; Kajiwara, K.; Tsukahara, Y. *Macromolecules* **1996**, *29*, 978.
(6) Nemoto, N.; Nagai, M.; Koike, A.; Okada, S. *Macromolecules* **1995**, *28*, 3854.
(7) Kawaguchi, S.; Akaike, K.; Zhang, Z.-M.; Matsumoto, H.; Ito, K. *Polym. J.* **1998**, *30*, 1004.
(8) Terao, K.; Nakarura, Y.; Norisuye, T. *Macromolecules* **1999**, *32*, 711.
(9) Siochi, E. J.; Desimone, J. M.; Hellstern, A. M.; McGrath, J. E.; Ward, T. C. *Macromolecules* **1990**, *23*, 4696.
(10) Gido, S. P.; Lee, C.; Pochan, D. J.; Pispas, S.; Mays, J. W.; Hadjichristidis, N. *Macromolecules* **1996**, *29*, 7022.
(11) Se, K.; Yamazaki, H.; Shibamoto, T.; Takano, A.; Fujimoto, T. *Macromolecules* **1997**, *30*, 1570.
(12) Hawker, C. J.; Mecerreyes, D.; Elec, E.; Dao, J.; Hedrick, J. L.; Barakat, I.; Dubois, P.; Jerome, R.; Volksen, W. *Macromol. Chem. Phys.* **1997**, *198*, 155.
(13) Heroguez, V.; Gnanou, Y.; Fontanille, M. *Macromol. Rapid Commun.* **1996**, *17*, 137.
(14) Ito, K.; Tanaka, K.; Tanaka, H.; Imai, G.; Kawaguchi, S.; Itsuno, S. *Macromolecules* **1991**, *24*, 2348.
(15) Ito, K.; Hashimura, K.; Itsuno, S.; Yamada, E. *Macromolecules* **1991**, *24*, 3977.
(16) Chao, D.; Itsuno, S.; Ito, K. *Polym. J.* **1991**, *23*, 1045.
(17) Furuhashi, H.; Kawaguchi, S.; Itsuno, S.; Ito, K. *Colloid Polym. Sci.* **1997**, *275*, 227.
(18) Nomura, E.; Ito, K.; Kajiwara, A.; Kamachi, M. *Macromolecules* **1997**, *30*, 2811.
(19) Candau, F. In *Polymeric Dispersions: Princile and Applications*; Asua, J. M., Ed.; NATO ASI Series E: Applied Science Vol. 325; Kluwer Academic Pub.: Dordrecht, The Netherlands, 1997; pp 127−140.
(20) Almgren, M.; Grieser, F.; Thomas, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 279.
(21) Pike, E. R.; Pomeroy, W. R. M.; Vaughan, M. *J. Chem. Phys.* **1975**, *62*, 3188.
(22) Kawaguchi, S.; Imai, G.; Suzuki, J.; Miyahara, A.; Kitano, T.; Ito, K. *Polymer* **1997**, *38*, 2885.
(23) Kawaguchi, S.; Soewito, D. P.; Ito, K. *Kobunshi Ronbunshu* **1997**, *54*, 923.
(24) Kawaguchi, S.; Yekta, A.; Duhamel, J.; Winnik, M. A.; Ito, K. *J. Phys. Chem.* **1994**, *98*, 7891.
(25) Gilbert, R. G. E*mulsion Polymerization, A Mechanistic Approach*; Academic Press: New York, 1995.
(26) Kawaguchi, S.; Tano, K.; Maniruzzaman, M.; Ito, K. *Macromol. Symp.*, in press.
(27) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Trends Polym. Sci.* **1994**, *2*, 66.
(28) Sawamoto, M.; Kamigaito, M. *Trends Polym. Sci.* **1996**, *4*, 371.
(29) Matyjaszewski, K. *Macromolecules* **1998**, *31*, 4710.
(30) Kawaguchi, S.; Matsumoto, H.; Katsuragi, K.; Iriany; Ito, K., manuscript in preparation.

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