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Effect of location of polymerizable double bond on the polymerization of micelle-forming monomers

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Summary

The polymerizability of micelle-forming quaternary ammonium monomers, which were derived from a methacrylic ester and styrene, carrying a polymerizable double bond close to the head group (Type H) or at the alkyl chain end (Type T) including a new monomer, 5-(*p*-vinylphenyl)pentyltrimethylammonium bromide, has been investigated above their critical micelle concentrations in water. The results are explained on the basis of the structure of the obtained polymers as well as the micelle structure of the monomers in water. The Type H monomers were able to thermally polymerize, while the Type T monomers could not.

Introduction

Ionic micelle-forming monomers show characteristic polymerization behavior in a micellar solution, which is markedly different from that in an isotropic solution [1,2]. The polymerizability of the monomers in the micellar solutions is governed by reactivities based on not only the chemical structure of the monomer, which can be estimated in isotropic solution, but also the structure of the micelle as reaction locus. Basically, the micelle formation facilitates the polymerization to produce a higher molecular weight polymer at a higher reaction rate. These effects would be varied by the location of the polymerizable double bond in the monomer molecule; the double bond is either attached close to the head group (Type H), or the double bond is attached to the hydrophobic chain end (Type T).
The polymerization of 2-methacryloyloxyethyldodecyldimethylammonium bromide (**1**) as a Type H monomer by γ–irradiation above its critical micelle concentration (cmc) in water required 2 h to complete, while the polymerization of 11-methacryloyloxyundecyltrimethylammonium bromide (**2**) as a Type T monomer was completed within ca. 5 min under similar conditions [3]. The reason for the exceptionally high reactivity of monomer **2** has been postulated to be due to the concentration effect by the aggregation of the double bond in the micelle core [3]. Fast polymerization of 11-acryloyloxyundecyldimethylammonio acetate (**3**), being a Type T monomer, in the presence of potassium persulfate in water was similarly explained [4]. Although sodium 11-acrylamidoundecanoate (**4**) has a high polymerizability [5], the double bond is reported to be located close to the micelle surface due to the hydrophilicity of the amido group in spite of the Type T monomer. The fast polymerization was accounted for by the slow termination [6,7]. The structures of the monomer micelles are schematically represented in Figure 1.

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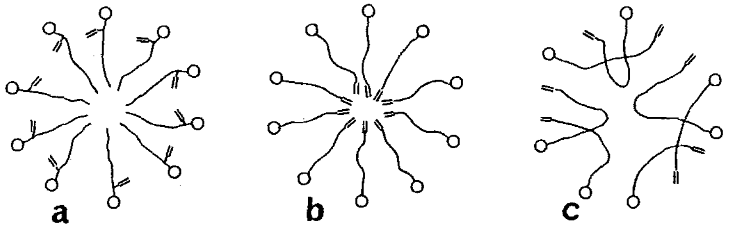

Figure 1. Schematic representation of monomer micelles. **a**: Type H, **b**: Type T with non-polar polymerizable group, **c**: Type T with polar polymerizable group.

Although the micelle structure of monomer **4** is distinguished from that of monomers **2** and **3** in the above description, Hamid and Sherrington have reported that the double bond of monomer **2** is located close to the micelle surface by forming the loop-like conformation of the hydrophobic alkyl chain [8]. This is in conflict with the explanation of such high polymerizability of this monomer as previously mentioned. Since monomers **2**, **3**, and **4** have equal (meth)acrylic double bonds and high polymerizability in their aqueous micellar solutions, the adaptable reason for their fast polymerizations may be the same. To avoid the complexity due to polarity of the (meth)acrylic group, the polymerization of amphiphilic monomers with a non-polar double bond, e.g. styrene derivatives, should be investigated. Although the results of an investigation concerning the phase behavior and polymerization of allyldodecyldimethylammonium bromide belonging to the Type H category and 10-undecenyltrimethylammonium bromide belonging to the Type T category have recently been reported [9], these monomers are not necessarily appropriate for comparing the polymerizabilities because of substantial activity for degradative chain-transfer.

The object of this work is to compare the polymerizability of the different types of methacryl and styryl monomers in their micellar solutions, as an approach to elucidate the micellar polymerization mechanism. The spontaneous polymerization [2,10] of these monomers are also investigated in connection with their micelle structures.

Experimental

Materials

p-Chloromethylstyrene was provided by Hokko Chemical Industry, Tokyo. Dilithium tetrachlorocuprate (Li_2CuCl_4) as a Grignard coupling reagent was purchased from Aldrich Chemical Co. as the 0.1M tetrahydrofuran solution. All other chemicals of reagent grade were obtained commercially and purified when necessary.

Oil-soluble and water-soluble azo initiators were recrystallized from appropriate solvents; 2,2'-azobisisobutyronitrile (AIBN) from methanol, dimethyl 2,2'-azobisisobutyrate (MAIB) from hexane, and 2,2'-azobis[2-methyl-N-(2-hydroxyethyl)propionamide] (AHPA) from methanol.

Water was distilled after being ion-exchanged. Deuterium oxide (Aldrich 99atom%D) was used as received.

Monomers

11-Methacryloyloxyundecyltrimethylammonium bromide (**2**)

Methacryloyl chloride (0.04 mol in 30 ml benzene) was added dropwise to a benzene solution (70 ml) of 11-bromoundecan-1-ol (0.02 mol) and triethylamine (0.02 mol) at 0°C, and the mixture was stirred for 4 h. After standing overnight at room temperature, the precipitate formed was removed by filtration. Benzene and unreacted methacryloyl chloride were distilled off *in vacuo* in the presence of a small amount of *p*-tert-butylcatechol as a radical inhibitor to leave 11-bromoundecyl methacrylate. The crude product obtained above was reacted with excess amounts of trimethylamine in acetone under continuous stirring at room temperature in the dark for 4 days. The resulting white precipitate was filtered off, washed with acetone, and recrystallized twice from acetone/methanol (20/1 by v/v) to obtain colorless crystals (yield 62%). The structure and purity of the product, 11-methacryloyloxyundecyltrimethylammonium bromide (**2**), were confirmed by ^{1}H-NMR spectrum [8] and elemental analyses: Found C 57.06%, H 9.45%, N 3.64%; Calcd. for $C_{16}H_{36}NO_2Br$, C 57.16%, H 9.95%, N 3.70%. The cmc was determined to be 2.0 x 10^{-2}mol/L.

5-(p-Vinylphenyl)pentyltrimethylammonium bromide (**5**)

p-Chlorostyrene (0.083 mol) was reacted with an equimolar amount of magnesium turnings in tetrahydrofuran (100 ml) to obtain *p*-vinylbenzylmagnesium bromide solution. To the tetrahydrofuran solution (150 ml) containing 1,5-dibromopentane (0.15 mol) and Li_2CuCl_4 solution (10 ml), the Grignard reagent obtained above was added dropwise for 1 h under a nitrogen atmosphere in an ice-bath, followed by stirring for one day at room temperature. After the addition of methanol to stop the reaction, the solvents were distilled off *in vacuo*, and the residual products were dissolved in benzene and washed with water. After drying the benzene solution over anhydrous sodium sulfate, benzene and the unreacted raw materials were removed under reduced pressure at 60°C. The mixture (3.30 g) of *p*-(5-bromopentyl)styrene and 1,5-dibromopentane, in ca. 5:2 molar ratio determined by its ^{1}H-NMR spectrum, was obtained as a methanol-soluble fraction.

The reaction of *p*-chlorostyrene (0.17 mol) with 1,5-dibromopentane (0.11 mol) using the same procedure mentioned above, except for the removal of unreacted dibromopentane under reduced pressure, gave the mixture (7.95 g) of *p*-(5-bromopentyl)styrene and 1,5-dibromopentane in ca.1:2 molar ratio.

The combined products obtained above were added to an acetone solution (150 ml) containing 10.1 g of trimethylamine and stirred for 5 days at room temperature in the dark. The resulting precipitate was separated by filtration and dried *in vacuo*. After removal of the chloroform-insoluble fraction, which seemed to be a bisquaternary ammonium salt

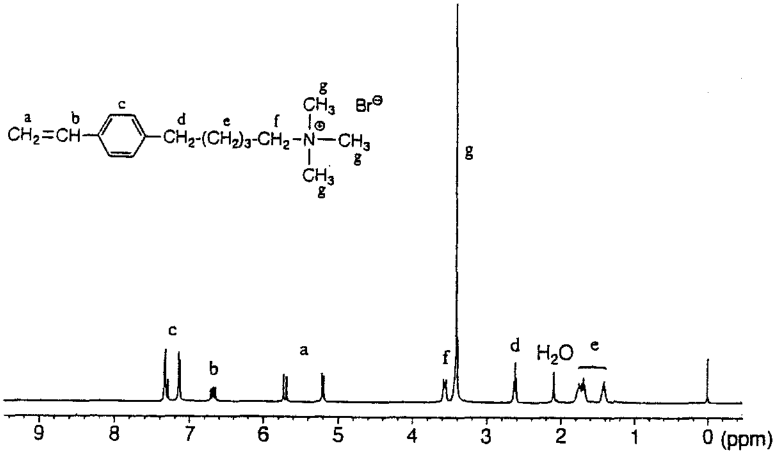

Figure 2. ^{1}H-NMR spectrum of 5-(*p*-vinylphenyl)pentyltrimethylammonium bromide in $CDCl_3$

derived from 1,5-dibromopentane, the product was reprecipitated twice using the ethanol-ethyl acetate system; yield 3.68 g (colorless solid). The structure was confirmed by its ^1H-NMR spectrum (Figure 2) and elementary analyses: found C 59.47%, H 8.27%, N 4.34%; calcd. for $C_{16}H_{26}NBr \cdot 0.58H_2O$ C 59.56%, H 8.43%, N 4.34%. This monomer contained ca. 3% water which was similar to the other styryl ammonium monomers of Type H alkyldimethyl-4-vinylbenzylammonium chlorides [11,12]. The cmc was determined to be 7.5 x 10^{-3} mol/L.

Measurement

^1H-NMR spectra were recorded in $CDCl_3$ using a JEOL JNM-A400 spectrometer. The determination of the cmc was carried out using surface tension measurements with a du Noüy tensiometer at room temperature.

Polymerization

The polymerization was carried out in a sealed glass tube in the dark after removal of dissolved oxygen by repeated freeze-thaw cycles using purified nitrogen. D_2O was used as the polymerization solvent. An oil-soluble initiator was solubilized in the micellar solution of the monomer by warming the solution just above its melting point and treating by ultrasonic vibration. The solubilization of benzene was carried out in a similar manner.

The polymerization proceeded homogeneously. The conversion was monitored by the decrease in absorption peaks (5.5~6.0ppm for **2** and 5.1~5.6ppm for **6**) based on the vinyl double bond in the ^1H-NMR spectra. Methanol, when it was used as a polymerization solvent, was evaporated under reduced pressure and the residue was dissolved in D_2O for the ^1H-NMR measurement.

Results and discussion

Polymerization of monomer 2

Azo-initiated polymerization: The polymerization of **2** in the presence of oil-soluble MAIB or water-soluble AHPA above the cmc in D_2O at 60°C was completed within a very short time, producing a clear gel, hence the time course of the reaction could not be followed and the difference between initiators was not observed. On the other hand, the polymerization with AIBN in methanol, in which the isotropic solution would be formed, gave the polymer in only 17% yield after 5 h ([**2**] = 5.0 x 10^{-2} mol/L, [AIBN] = 2.5 x 10^{-2} mol/L). These results indicate the great acceleration effect of the micellar aggregation on the polymerization. When benzene was solubilized in the monomer micelle ([benzene]/ [monomer] = 2/5), the rate of polymerization was appreciably reduced and the reaction time course was able to be followed (Figure 3). This was possibly due to dilution of the polymerizable double bond in the micelle core.

Thermally initiated polymerization: 2-Methacryloyloxyethylalkyldimethylammonium bromides, such as monomer **1**, belonging to the Type H category, are thermally polymerizable in their micellar solutions [13]. On the other hand, despite the very high polymerizability of monomer **2** as stated above, the thermal polymerization of this monomer has never been reported. The results of the attempted thermal polymerization of **2** performed above the cmc in D_2O at 60 and 80°C are shown in Figure 4.

After an abnormally long induction period, the polymerization proceeded very fast, especially at 80°C. When benzene was solubilized in the monomer micelle, the induction period was extended ca. ten times more, while the rate of polymerization was still high after

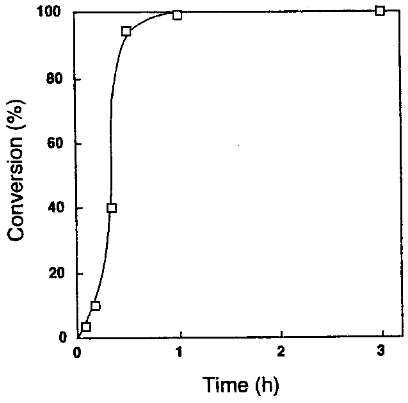

Figure 3. Polymerization of **2** with AHPA in the presence of benzene in D_2O at 60°C. [**2**] = 5.0 x 10^{-2} mol/L, [AHPA] = 1.0 X 10^{-3} mol/L, [Benzene] = 2.0 x 10^{-2} mol/L.

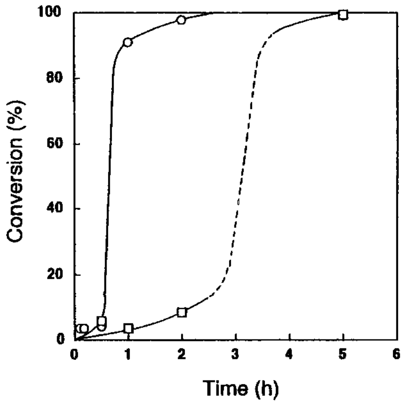

Figure 4. Polymerization of **2** without added initiator in D_2O at 60°C (□) and 80°C (○). [**2**] = 5.0 x 10^{-2} mol/L

the induction period. No polymerization occurred at 60°C even after 20 h, as shown in Figure 5.

In order to confirm the possibility of a peroxide contaminant as a radical source, the effect of addition of a reducing agent was examined. In the presence of 5 mol% sodium sulfite toward the monomer, the polymerization did not occur even after 2 h at 60°C, to contradict the peroxide initiation. We could not obtain evidence for the radical formation by monomer-monomer interaction, because the long induction period was not able to be reasonably explained.

Polymerization of monomer ***5***

The monomer **5** was polymerized above its cmc in D_2O at 60°C in the presence of the

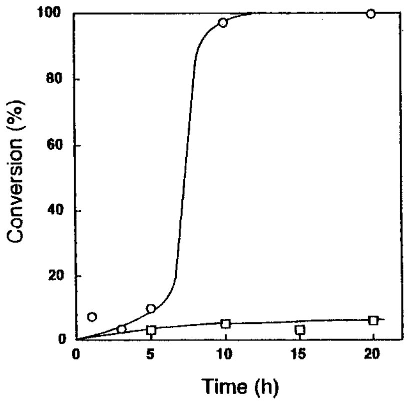

Figure 5. Polymerization of **2** without added initiator in the presence of benzene in D_2O at 60°C (□) and 80°C (○). [**2**] = 5.0 x 10^{-2} mol/L, [Benzene] = 2.0 x 10^{-2} mol/L.

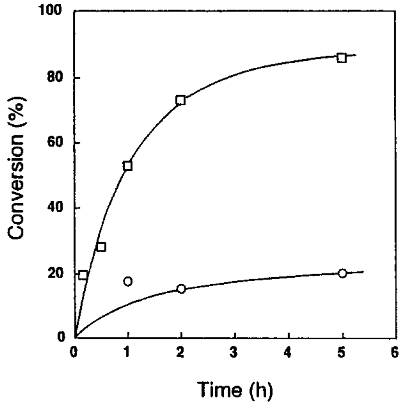

Figure 6. Polymerization of **5** with MAIB (□) and AHPA (○) in D_2O at 60°C. [**5**] = 5.0 x 10^{-2} mol/L, [Initiator] = 1.0 X 10^{-3} mol/L.

MAIB or AHPA initiator and gave the soluble polymer, while the thermal polymerization did not occur even by heating at 80°C for 20 h. An obvious difference between initiators used was observed in the time-conversion curves, as shown in Figure 6. The oil-soluble MAIB initiator brought about higher conversion, indicating the importance of the locus of radical production.

The polymerizability of this monomer was found to be significantly lower than that of **2** and also than that of hexadecyldimethyl-*p*-vinylbenzylammonium chloride (**6**) being a styryl ammonium Type H monomer, which the polymerization in water was completed even without added initiator within 4 h at 60°C [12].

Mechanism

The polymerizability of the micelle-forming monomers observed in the presence of a radical source are qualitatively summarized as follows:

Polymerizability in micellar solution

methacryl monomer   Type H < Type T
V
styryl monomer   Type H > Type T

The high polymerization rate is resulted from (*a*) fast initiation, (*b*) fast propagation and/or (*c*) slow termination. In comparison between the parent monomers, the overall rate of polymerization of methyl methacrylate is 5.2 times greater than that of styrene under the following conditions: [monomer] = 1.0 M, [AIBN] = 1 x 10^{-3} M, in benzene at 60°C [14]. Because the propagation rate constants are reported to be 340-350 L/mol · sec for styrene [15] and 500-700L/mol · sec for methyl methacrylate [16], the difference in the overall rate of polymerization is mostly accounted for by the difference in termination rate constants. The polymerization of methyl methacrylate is highly susceptible to the *gel-effect* [17], and this further magnifies the rate difference. Similarly, the methacryl monomer may have a larger polymerizability than the styryl monomer in the present case.

On the basis of the micelle structure of the monomers shown in Figure 1, Paleos et al. have

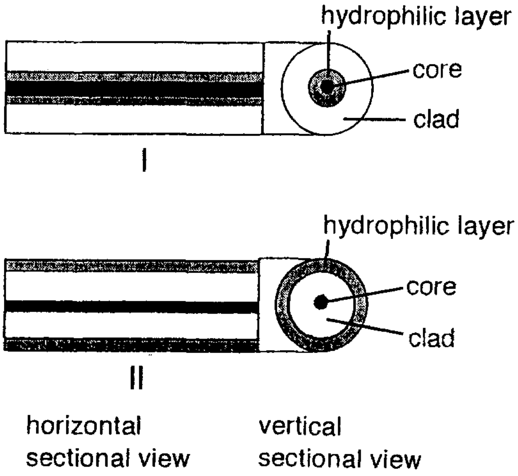

Figure 7. Geometrical structure of polymers from surface active monomers.
I : from Type H monomers, II : from Type T monomers

described that the fast polymerization of **2** is based on *b* [3], whereas Gan et al. have concluded that the fast polymerization of **4** is due to *c* [6,7]. However, the structure of the growing polymer chain in water must also be important as well as the structure of the monomer micelles. Although the monomer of Type T can form the micelle of **b** or **c** in Figure 1 reflecting the polarity of the polymerizable group, the geometrical structure of the resulting polymer would be the same based on the structural limitations.

As illustrated in Figure 7, the polymer derived from the surfactant monomer seems to have a structure of core/clad combination, in which the polymer main chain (core) contributes as a hydrophobic function. The long alkyl moieties of the monomer units constitute the hydrophobic clad. The head groups of the monomer units form the middle layer between the core and clad in the polymer from the Type H monomer and the outer layer of the clad in the polymer from the Type T monomer. Thus, the polymers from the former structure such as **1** and **6** become finally insoluble in water [11-13] due to the absence of an effective hydrophilic function, whereas the polymers from the latter structure such as **2** and **5** are soluble in water due to the surrounding hydrophilic layer. Laschewsky and Zerbe have explained these phenomena based on the concept of 'skin-controlled' solubility [18].

The terminal radicals of the growing polymer chain derived from the Type H monomer may exist at the interface between the hydrophobic domain and the continuous phase, because of the short distance between the double bond and head group in the monomer. On the other hand, the growing polymer radicals from the Type T monomer would be surrounded by the hydrophobic moieties to confine them. The reactivities of both radicals must be significantly lowered sterically in the propagation and termination steps. The radicals from the Type T monomer are seemingly much harder to react with other polymer radicals to terminate the reaction, leading to acceleration of the polymerization, especially in the polymerization of **2**, as observed.

As another reason to facilitate the polymerization of Type T monomer, the Coulombic repulsion between the growing chain end and the monomer is reduced in comparison with the Type H monomer, because the head group is separated from the double bond [9].

The Type H monomer spontaneously polymerized, but the Type T monomer did not. According to our concept for the spontaneous polymerization [2,9], this difference must be accounted for by the structural difference in the monomer micelles (Figure 1), because the productivity of initiating radical species in the thermal reaction of monomer molecules is strongly governed by the aggregation state of the monomers. The micelle structure of **5** is supposed to be **b** in Figure 1, in which the double bonds are concentrated and oriented in a rather tightly packed state in the core of the micelle, and may not be appropriate for the radical formation. The solubilization of benzene in the micellar solution to release it from the restriction of monomer molecules did not facilitate the radical formation. In the case of **2**, the reason that the radical formation did not take place could not be made clear as well as the micelle structure.

The spontaneous (thermal) polymerizability of the micelle-forming monomers is governed by the formation of initiating radicals as the dominant factor, while the general polymerizability of these monomers estimated by the overall rate of polymerization in the presence of a radical initiator is mainly controlled by the propagation and termination reactions. Thus both apparent reactivities are not necessarily in agreement with each other.

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