

NOTES

## Spontaneous Polymerization of Micelle-Forming Styryl Ammonium Derivatives in Water

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We have recently found that some amphiphilic methacrylate monomers such as sodium alkyl 2-hydroxy-3-methacryloyloxypropyl phosphates and alkyl-2-methacryloyloxyethyl-dimethylammonium bromides spontaneously polymerize in the aqueous micellar solution, and the micelle formation is indispensable for the initiation of reaction.<sup>1,2</sup> The initiating radical species has been assumed to be produced by the thermal reaction of two monomer molecules giving the dimer diradical (1,4-diradical) followed by a chain-transfer to result the dimer monoradical, just like the thermal polymerization of methyl methacrylate,<sup>3</sup> which would be promoted by the micelle formation.

Although styrene is the most well known thermally polymerizable monomer, spontaneous polymerization of the micelle-forming monomer having styryl group has never been reported. This paper concerns with the spontaneous polymerization of alkyldimethyl-*p*-vinylbenzylammonium chlorides ( $C_n$ -VBAC) as the styrene derivatives capable of forming micelles,<sup>4</sup> so that the micellar organization would make possible to facilitate the spontaneous polymerization of these monomers like the methacrylic ester derivatives.<sup>1,2</sup>

### EXPERIMENTAL

#### Monomers

Reagent grade 2-phenylethyl bromide and alkyl amines as starting materials for preparation of the monomers were purchased from Tokyo Kasei Co. and Kishida Chemicals Co. and were used without further purification.

*p*-Vinylbenzyl chloride, which was prepared by chloromethylation of 2-phenylethyl bromide followed by dehydrobromination and was purified by recrystallization from hexane to remove its ortho isomer,<sup>5</sup> was reacted with corresponding alkyldimethylamine as described by Cochin *et al.*<sup>4</sup>

The resulted crude monomers were thoroughly purified by repeated recrystallizations from ethyl acetate containing a small quantity of water for  $C_{16}$ - and  $C_{12}$ -VBAC and by reprecipitation using water/acetone system for  $C_1$ -VBAC. The structure and purity of the monomers were confirmed by <sup>1</sup>H NMR spectra<sup>4</sup> recorded in CDCl<sub>3</sub> using a JEOL JNM-A400 spectrometer. Although the monomers contained a small quantity of water (*ca.* 2%) as already reported,<sup>4</sup> they were used for the polymeriza-

tion experiments without further drying.

Critical micelle concentration (cmc) of the monomers in aqueous solution was determined by surface tension measurement using a du Noüy tensiometer at room temperature.

#### Polymerization

The polymerization was carried out in a sealed glass tube in the dark after removing dissolved oxygen by repeated freeze-thaw cycles using a purified nitrogen. Water as polymerization solvent was distilled after ion-exchanged. In the case of  $C_{16}$ - and  $C_{12}$ -VBAC, after heating in a thermostated water bath for a given time, the polymerizing solution was freeze-dried. The resulted monomer-polymer mixture was washed to separate each other by acetone which is a solvent for the monomer and a non-solvent for the polymer. The absence of vinyl double bond in the remaining solid was confirmed from the <sup>1</sup>H NMR and the IR spectra. The conversion was determined gravimetrically. For the  $C_1$  monomer, the polymerization was carried out in D<sub>2</sub>O (Aldrich 99 atom%D) and the conversion was determined from the decrease of absorption peaks based on the vinyl double bond (5.3 and 5.8 ppm) in the <sup>1</sup>H NMR spectra.

The polymerization in organic solvents, which were freshly distilled, was performed in a similar manner as above.

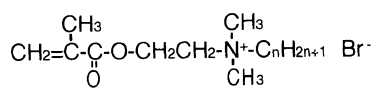
### RESULTS AND DISCUSSION

The cmc values of the monomers were determined to be  $7.0 \times 10^{-5}$  and  $3.2 \times 10^{-3} \text{ mol l}^{-1}$  for  $C_{16}$ - and  $C_{12}$ -VBAC, respectively.  $C_1$ -VBAC which does not carry a long chain alkyl also showed the inflection point at *ca.*  $0.6 \text{ mol l}^{-1}$  corresponding to its cmc in the plot of surface tension vs. log(concentration), as shown in Figure 1.

The polymerization of  $C_{16}$ -VBAC performed at the concentration above its cmc proceeded spontaneously without added initiator at 60 and 80°C in water. The appearance of the polymerizing system changed from clear solution at initial stage to turbid solution with progress of the polymerization. Although Cochin *et al.* did not detect the spontaneous polymerizability of this monomer below 30°C,<sup>6</sup> in the present study the polymerization, however, occurred rather easily even at such low temperature. The time-conversion curves are given in Figure 2. In the presence of *p*-benzoquinone or air as a

radical inhibitor, no polymerization was observed in support of a radical mechanism.

The requisite of micelle formation was proved from the result obtained in acetonitrile giving an isotropic solution, in which the polymerization was not observed at 60 and 80°C even after 24 h. In benzene the spontaneous polymerization occurred at 60°C. This would be due to the reverse micelle formation. The results mentioned above were quite similar to those obtained in the case of quaternary ammonium amphiphiles derived from a methacrylic ester (DMAEMA-RBr).<sup>7</sup>



DMAEMA-RBr

The monomer C<sub>12</sub>-VBAC also polymerized in the similar conditions. The results are shown in Table I.

The monomer C<sub>1</sub>-VBAC, having high cmc value 0.6 mol l<sup>-1</sup> was attempted to polymerize thermally in D<sub>2</sub>O at concentrations above and below its cmc. As shown in Table II, at the concentration 1.0 mol l<sup>-1</sup> this monomer also polymerized spontaneously, while at the concentration 0.1 mol l<sup>-1</sup> no polymerization was observed indicating the indispensable role of the micelle formation.<sup>1,2</sup>

The time-conversion curve at [C<sub>1</sub>-VBAC]=1.0 mol l<sup>-1</sup> 80°C in Figure 3 shows the limit of the conversion after

prolonged heating. This is explicable by the presence of significant amounts of dissolved monomer (unmicellized monomer) in bulk phase, because of the high cmc which is close to the monomer concentration in the polymerization recipe.<sup>8</sup>

The fact that the polymerization of styryl ammonium derivatives took place without added initiator in the micellar solution is quite similar to the behavior observed for amphiphilic methacrylic ester derivatives.<sup>1,2</sup> The possibility of formation of radical species through the thermal or redox decomposition of quaternary ammonium surfactants including benzyl ammonium derivatives<sup>9,10</sup> was contradicted by the experimental facts obtained in aqueous polymerization of methyl methacrylate in our previous work, and it was concluded that the micelle formation of the surfactants facilitates the radical production by monomer-monomer interaction.<sup>11</sup> Consequently, in the present case, it is speculated that the thermal reaction between monomer molecules in the micelle produces radical species for the initiation of polymerization.<sup>12</sup>

The initiation mechanism involving Diels-Alder dimerization of monomer molecules followed by a hydrogen transfer from the dimer to a monomer molecule has

Table I. Polymerization of C<sub>12</sub>-VBAC without initiator at [monomer]=0.05 mol l<sup>-1</sup>

Solvent	Temp/°C	Time/h	Convsn/%
Water	80	24	53.4
Water	60	24	35.2
Benzene	80	20	11.6
Acetonitrile	60	20	0

Table II. Polymerization of C<sub>1</sub>-VBAC without initiator in water

Concn/mol l <sup>-1</sup>	Temp/°C	Time/h	Convsn/%
(below cmc)			
0.1	60	24	0
0.1	80	24	0
(above cmc)			
1.0	60	24	30
1.0	80	24	72

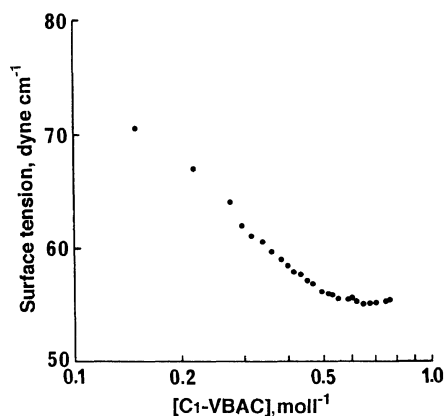


Figure 1. Plot of surface tension vs. log[C<sub>1</sub>-VBAC].

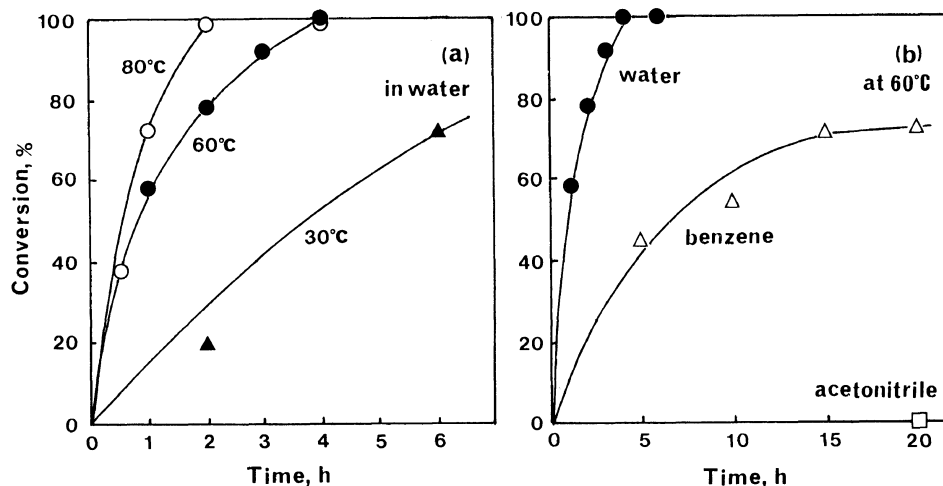


Figure 2. Time-conversion curves in thermal polymerization of C<sub>16</sub>-VBAC, [monomer]=0.01 mol l<sup>-1</sup>. (a) at different temperature in water; (b) at 60°C in various solvents.

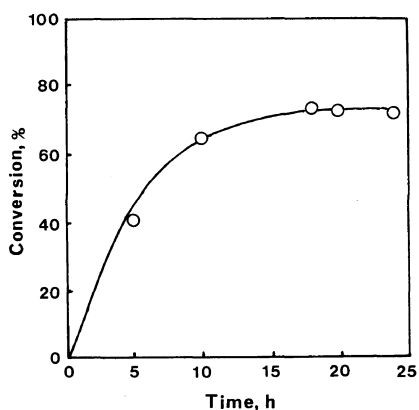
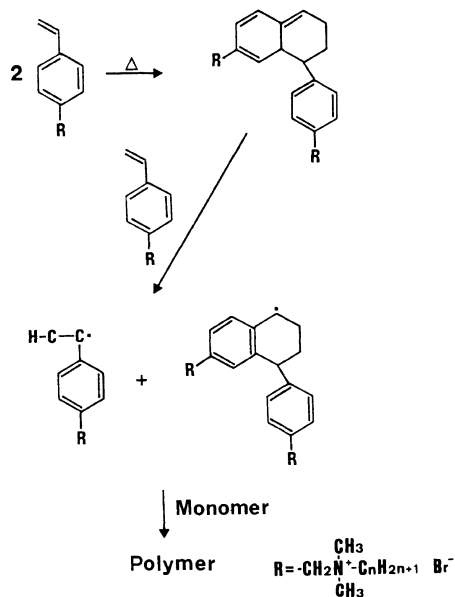
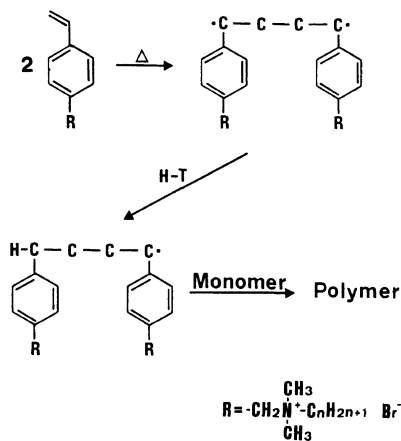


Figure 3. Time-conversion curve in thermal polymerization of  $C_1$ -VBAC, [monomer] =  $0.1 \text{ mol l}^{-1}$  in  $D_2O$  at  $80^\circ\text{C}$ .



Scheme 1.



Scheme 2.

been generally accepted for the spontaneous polymerization of styrene (Scheme 1).<sup>13</sup> However, in the case of pentafluorostyrene, the 1,4-diradical is believed to be formed at first and then converted to monoradical as the initiating species (Scheme 2),<sup>14</sup> similarly to the case of methyl methacrylate.<sup>3</sup> In the present case, if the alkyl

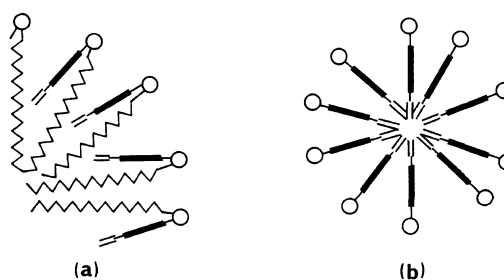


Figure 4. Speculated structure of monomer micelles. (a)  $C_n$ -VBAC with a long chain alkyl; (b)  $C_1$ -VBAC.

ammonium substituent at *para* position of styryl group interferes the Diels-Alder dimerization due to the formation of organized structure of monomer molecules with hydrophobic interaction between the long chain alkyls in the micelle, the 1,4-diradical mechanism could become plausible. In the case of  $C_1$ -VBAC, because this monomer does not have a long alkyl hydrophobic moiety, 4-vinylbenzyl group must behave alone as lipophile. The micelle structure would be different from other  $C_n$ -VBAC with long chain alkyl as illustrated in Figure 4, and the mutual interaction between the molecules will become weaker as indicated by its higher cmc value. The spontaneous polymerizability of  $C_1$ -VBAC above cmc indicates that its micelle structure is also suited for the thermal initiation in spite of rather loose aggregation state.<sup>1</sup> Thus the clear conclusion did not be obtained yet on the thermal initiation mechanism of the micelle-forming styryl monomers.

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