

NOTES

**Spontaneous Polymerization of Amphiphilic Vinyl Monomers V.  
Effect of Sodium Chloride on Spontaneous Polymerization of  
Sodium Dodecyl 2-Hydroxy-3-methacryloyloxypropyl Phosphate**

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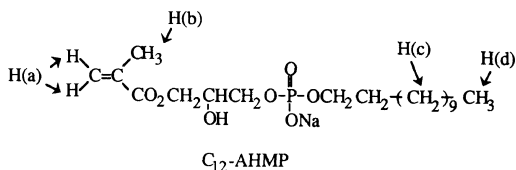
In the previous papers of this series,<sup>1-4</sup> we have reported on the spontaneous polymerization of some amphiphilic vinyl monomers, such as sodium alkyl 2-hydroxy-3-methacryloyloxypropyl phosphate (C<sub>n</sub>-AHMP) and alkyl-2-methacryloyloxyethyltrimethylammonium bromide, in which the polymerization takes place under the formation of monomer aggregates, *e.g.*, micelles or inverse micelles, through radical mechanism in the absence of conventional initiators. The aggregation state of monomer is a dominant factor to control the spontaneous polymerizability, *i.e.*, the generation of initiating radical species. The measurement of <sup>1</sup>H spin-lattice relaxation time (*T*<sub>1</sub>) of amphiphilic monomers in D<sub>2</sub>O provides the information of their molecular motion related to the monomer aggregation state.<sup>2,3</sup> Addition of an inorganic electrolyte, sodium chloride, to the micellar solution of low-reactive C<sub>8</sub>-AHMP increased the spontaneous polymerizability to produce the polymer quantitatively at 35°C, and this behavior was related to the decrease of *T*<sub>1</sub> values with increasing amount of NaCl added.<sup>3</sup>

In connection with elucidation of the relation between monomer aggregation state and

spontaneous polymerizability, the present report deals with the modification of micellar state of sodium dodecyl 2-hydroxy-3-methacryloyloxypropyl phosphate (C<sub>12</sub>-AHMP), having the highest spontaneous polymerizability among C<sub>n</sub>-AHMP,<sup>2</sup> by adding NaCl.

EXPERIMENTAL

The monomer, C<sub>12</sub>-AHMP, prepared and characterized previously,<sup>1</sup> was used. Measurement of *T*<sub>1</sub> and polymerization experiments were carried out in the same manner as previously described.<sup>1,2</sup>



RESULTS AND DISCUSSION

Table I shows the effect of NaCl on the polymerization of C<sub>12</sub>-AHMP without initiator in water. Without adding NaCl, the monomer polymerized spontaneously as has

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**Table I.** Effect of sodium chloride on the polymerization of C<sub>12</sub>-AHMP in water without initiator:  
[C<sub>12</sub>-AHMP] = 50 mmol l<sup>-1</sup>

NaCl	Temp <sup>a</sup>	Time	Polymer yield <sup>b</sup>
mmol l <sup>-1</sup>	°C	h	%
0	r.t.	21	72
	80	2.5	100
0.1	r.t.	21	0
	80	2.5	19
0.3	r.t.	21	0
		720	88
	80	2.5	50
0.5	r.t.	21	0
	80	2.5	0
1.0	r.t.	21	0
	80	2.5	0

<sup>a</sup> r.t., room temperature (25–30°C).

<sup>b</sup> Determined by UV-method.<sup>1</sup>

**Table II.** Effect of sodium chloride on the <sup>1</sup>H spine-lattice relaxation time (*T*<sub>1</sub>) of C<sub>12</sub>-AHMP in D<sub>2</sub>O at 30°C<sup>a</sup>

NaCl	<i>T</i> <sub>1</sub>			
	ms			
mmol l <sup>-1</sup>	H(a)	H(b)	H(c)	H(d)
	δ: 6.12	1.93	1.28	0.88 in ppm
0	659	1078	748	1598
0.1	633	1038	738	1551
0.3	617	997	732	1485
0.5	586	1020	703	1404
1.0	583	820	744	1094

<sup>a</sup> [C<sub>12</sub>-AHMP] = 50 mmol l<sup>-1</sup> in the presence of *p*-benzoquinone 1000 ppm.

been reported.<sup>1</sup> Addition of NaCl in the concentration range from 0.1 to 0.3 mmol l<sup>-1</sup> inhibited the polymerization at a room temperature, though long time standing produced the polymer at last, and suppressed the formation of polymer at a higher temperature, 80°C. Further increase of added NaCl inhibited the polymerization even at

**Table III.** Relation between the *T*<sub>1</sub> values of terminal methyl protons and the spontaneous polymerizability of C<sub>*n*</sub>-AHMP in water

C <sub><i>n</i></sub> -AHMP	[NaCl]	<i>T</i> <sub>1</sub> <sup>a</sup>	Spontaneous polymerizability <sup>b</sup>		
			35°C	60°C	80°C
mmol l <sup>-1</sup>	mmol l <sup>-1</sup>	ms			
C <sub>8</sub> : 100	0	1882	×	○	
	100	1619	○		
C <sub>12</sub> : 5	0	1608	○		
	50	1598	○		
	50	1404			×
: 100	0	1391	○		
	5	1285		×	○
C <sub>14</sub> : 5	0	1242			×
C <sub>16</sub> : 5	5 <sup>c</sup>	1600		○	

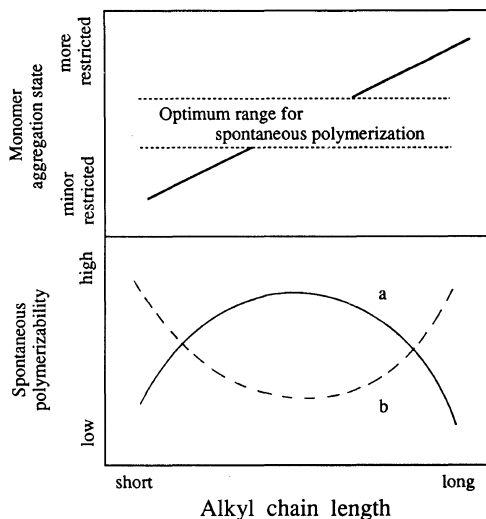
<sup>a</sup> Determined in D<sub>2</sub>O at 30°C.

<sup>b</sup> Polymerization activity without initiator in water.<sup>1–3</sup>

<sup>c</sup> Sodium dodecylglyceryl phosphate was added instead of NaCl.

80°C. These results suggested that the presence of NaCl modified the monomer aggregation state to check the generation of initiating radical species, contrary to the case of C<sub>8</sub>-AHMP.<sup>3</sup> As shown in Table II, the increase of NaCl added decreased the *T*<sub>1</sub> values, especially those of terminal methyl protons in long chain alkyl.

Table III shows the comparison of the *T*<sub>1</sub> values of C<sub>*n*</sub>-AHMP, having different alkyl chain, with the spontaneous polymerizabilities in the absence and presence of NaCl. The *T*<sub>1</sub> values decreased with increasing alkyl chain length and adding NaCl at the same monomer concentration, indicating that the molecular motion of the monomer was suppressed in the micelle. The spontaneous polymerizability of C<sub>*n*</sub>-AHMP is governed by alkyl chain length, and dodecyl group gives the highest polymerizability, *i.e.*, the highest activity in the generation of initiating radical species. Thus, the occurrence of spontaneous polymerization requires an appropriate freedom of molecular motion in the monomer aggregates, in which longer alkyl chain gives more tightly packed state, and the presence of inorganic electrolyte,



**Figure 1.** Conceptual illustration of the spontaneous polymerization of amphiphilic monomers in the micellar solution: a, original reactivity; b, modified reactivity with additives.

NaCl, leads to more restricted state of the monomer aggregation to change the monomer reactivity. Another way to change the monomer aggregation state is the addition of a surfactant being able to form a mixed-micelle. Addition of equimolar amount of sodium dodecylglyceryl phosphate to the micellar solution of non-reactive  $C_{16}$ -AHMP increased the  $T_1$  value of terminal methyl protons and

converted it to be high reactive.<sup>3</sup>

The discussion described above is summarized in Figure 1, as conceptual illustration.

Lingnau and Meyerhoff have proposed the thermal initiation mechanism of methyl methacrylate, in which the dimer diradical is formed spontaneously from the monomer molecules followed by chain-transfer reaction giving the dimer monoradical as initiating species.<sup>5-7</sup> The present polymerization system is assumed to follow the similar mechanism, and the suitable monomer aggregation state is considered to facilitate the reaction step giving diradical and/or monoradical. Further discussion will be presented in a future publication.

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