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ABSTRACT

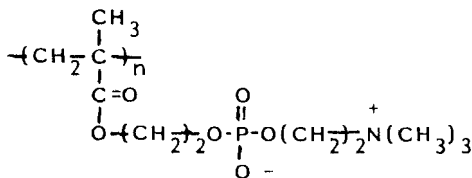
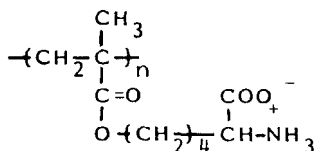
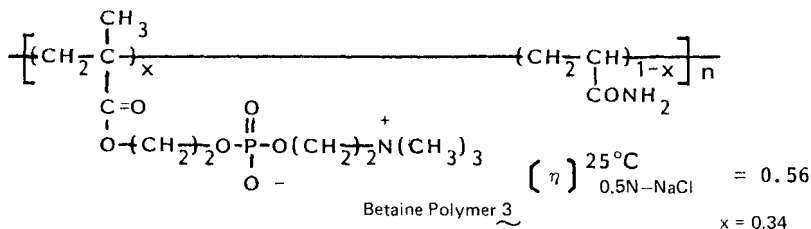
Three kinds of betaine-type polymers, which are macromolecular amphoteric electrolytes, were found to be able to polymerize vinyl monomers in aqueous solution through a radical mechanism without any further initiator. Betain-type polymers form hydrophobic areas

(HA) in water. Vinyl polymerization commenced in the HA. The effect of the pH of the aqueous solution on polymerization was investigated.

INTRODUCTION

In recent years we have found some anion-type macromolecular electrolytes (such as sodium poly(2-methyl-2-propene-1-sulfonate) [1], sodium poly(2-propene-1-sulfonate) [2], sodium polystyrene-sulfonate [3], sodium polyethylenephosphate [4], sodium poly-p-vinylphenolate [5], poly(styrene-co-sodium acrylate) [6], poly(methyl methacrylate-co-sodium methacrylate) [6], and poly(styrene-alternative-disodium maleate) [7]) and some cation-type macromolecular electrolytes (such as poly(vinylbenzyltrimethyl)ammonium chloride [8] and poly-(N,N,N-trimethyl-N-2-methacryloxyethyl)ammonium chloride [9]) can polymerize vinyl monomers in water through a radical mechanism without an ordinary initiator. This simple polymerization has been named "uncatalyzed polymerization." The polymerization proceeds as follows: 1) the macromolecules form hydrophobic areas (HA) in water phase, 2) the vinyl monomer dissolves in the water phase and is then incorporated into the HA, and 3) radical polymerization commences in the HA.

This paper is concerned with polymerizations of vinyl monomer where the following three kinds of betaine-type polymers are used as the initiating macromolecular electrolytes.

Betaine Polymer 1; $n = 300$ Betaine Polymer 2; $n = 1100$ 

The effect of the pH of the aqueous solution on the polymerization of MMA was then studied.

EXPERIMENTAL

Materials

Betaine Polymer 1 and Betaine Polymer 3 were synthesized through the homopolymerization and the copolymerization of 2-(methacryloyloxy)ethyl-2-(trimethylammonium)ethyl phosphate [10] with acrylamide by Nakaya's group, respectively. Betaine Polymer 2 was prepared by the homopolymerization of ϵ -methacryloyl lysine by Nakaya's group, according to the method of Morawetz et al. [11].

Methyl methacrylate (MMA), styrene (St), and acrylonitrile (AN) were purified by the usual methods. Water was ion-exchanged and distilled.

Procedure

Polymerization was carried out in a sealed tube at 85°C with or without shaking. The reaction mixture was poured into a large amount of 2-propanol to precipitate the polymerized product. After drying the product at 80°C in vacuo, conversion of monomer was obtained by

$$\text{Conversion (\%)} = \frac{(\text{wt of product}) - (\text{wt of fed betaine polymer})}{(\text{wt of fed monomer})} \times 100 \quad (1)$$

The efficiencies of grafting (EG) of MMA, St, and AN onto betaine polymer were calculated according to following equation, after the extraction of homopolymers for 50 h using a Soxhlet with benzene and N,N-dimethylformamide, respectively:

$$\text{EG (\%)} = \frac{(\text{wt of produced polymer}) - (\text{wt of homopoly (MMA)})}{(\text{wt of produced polymer})} \times 100 \quad (2)$$

The number-average degrees of polymerization (\bar{P}_n) of homopoly-(MMA), homopoly(St), and homopoly(AN) were calculated by the equations of Welch [12], Flory [13], and Stockmayer [14] from the intrinsic viscosities measured in benzene at 30°C, in benzene at 25°C, and in N,N-dimethylformamide at 25°C, respectively.

The polymerization systems were observed by transmission electron microscopy (TEM) according to the method of Kunitake and Okahata [15]: 5.0 mg of Betaine Polymer 1 was dissolved in 1.0 cm³ of water. The solution was mixed with 1.0 cm³ of 2% aqueous uranyl

acetate (a staining reagent) and sonicated for 20 s. The mixture was applied to carbon-coated grids. A Hitachi electron microscope (Hitachi-HS-9) was used for the measurement.

RESULTS AND DISCUSSION

Polymerization of Vinyl Polymers

The results of the polymerizations of MMA, St, and AN by the three kinds of betaine-type polymer in aqueous solution are summarized in Table 1. It is clear that these betaine polymers have initiating abilities for the vinyl polymerizations. Here, conversions in the absence of betaine polymer mean thermal polymerization. Such a selectivity of vinyl monomer can be explained by "the concept on hard and soft hydrophobic areas (HA) and monomers" as proposed by our group [6-9]. According to this concept, a hard HA prefers to incorporate a hard monomer and a soft HA prefers to incorporate a soft monomer. Therefore, it is concluded that the HA formed by the three betaine polymers used is softer.

Subsequent experiments employed polymerization initiated by Betaine Polymer 1.

Proof of Radical Mechanism

Into a mixture of 1.5 cm³ of MMA, 0.050 g of Betaine Polymer 1, and 5.0 cm³ of water, 0.050 g of 1,3,5-triphenylverdazyl (TPV) was added and then the system was shaken at 85°C for 3 h. The results,

TABLE 1. Polymerizations of Vinyl Monomers Initiated by Betaine Polymers^a

Betaine Polymer	Conversion (%)		
	AN	MMA	St
None	0	1.0	2.0
1	10.2	8.8	7.0
2	1.3	2.5	2.2
3	2.3	3.3	2.8

^aMonomer, 1.5 cm³; betaine polymer, 0.050 g; H₂O, 5.0 cm³; 85°C; 3 h; with shaking.

TABLE 2. Effect of Radical Scavenger on the Polymerization of MMA^a

Radical scavenger	Conversion (%)
None	8.8
TPV, 0.050 g	0

^aMMA, 1.5 cm³; betaine polymer 1, 0.050 g; H₂O, 5.0 cm³; 85°C; 3h; with shaking.

listed in Table 2, show that TPV (a typical radical scavenger) inhibits polymerization. Thus, polymerization was concluded to proceed through a radical mechanism.

Estimations of the Efficiency of Grafting and the Degree of Polymerization of Homopolymer Produced

The efficiencies of grafting (EG) and the degree of polymerization (\bar{P}_n) of homopolymers produced in the polymerization of vinyl monomers initiated by Betaine Polymer 1 were estimated. The results obtained are listed in Table 3.

Phase Where Polymerization Takes Place

In order to observe the locale where polymerization proceeds, the polymerizations of MMA, St, and AN were carried out without shaking. The reaction tubes were allowed to stand at 85°C for 3 h. After the

TABLE 3. Polymerizations of Vinyl Monomers Initiated by Betaine Polymer 1^a

Monomer	Conversion (%)	EG (%)	\bar{P}_n of homopolymer
AN	10.2	29	3.3×10^3
MMA	8.8	28	3.3×10^4
St	7.0	35	1.8×10^4

^aMonomer, 1.5 cm³; betaine polymer 1, 0.050 g; H₂O, 5.0 cm³; 85°C; 3 h; with shaking.

TABLE 4. Polymerizations of Vinyl Monomers Initiated by Betaine Polymer 1 without Shaking^a

Monomer	Conversion (%)	
	Water layer	Monomer layer
AN	11.6	0
MMA	9.0	1.0
St	5.0	1.9

^aMonomer, 1.5 cm³; betaine polymer 1, 0.050 g; H₂O, 5.0 cm³; 85°C; 3 h.

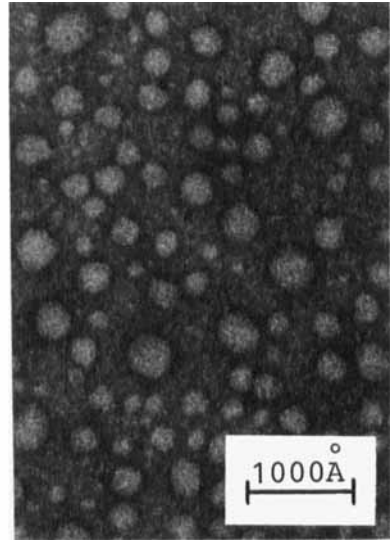
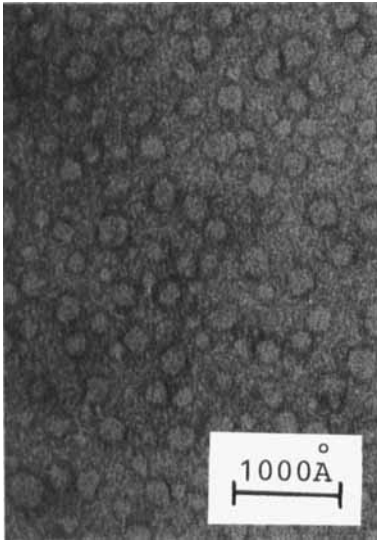
polymerizations the upper, clear layers were pipetted out and poured into 2-propanol. The muddy, aqueous layers were poured into methanol. The results are listed in Table 4. Conversions in the monomer layers were due to thermal polymerizations. Accordingly, it was concluded that polymerization by a betaine-type polymer was initiated, propagated, and terminated in the water layer.

Confirmation of the Formation of Hydrophobic Areas

In order to view the polymerization system, the modes of aggregates of Betaine Polymer 1 before and after the polymerization of MMA were measured by TEM. The results obtained are shown in Figs. 1(a) and (b). Many kinds of ammonium amphiphile have been reported to form lamellar or vesicle structures which were composed of stable bilayer assemblies in a dilute aqueous solution by Kunitate and Okahata et al. [15-17]. However, a stable bilayer could not be observed for the betaine polymer, as shown in Fig. 1(a). This may be attributed to its chemical structure. It was concluded that Betaine Polymer 1 dissolved in water by forming loose aggregates. We call these aggregates hydrophobic areas (HA), and we have explained the polymerization processes in uncatalyzed polymerization as follows: 1) vinyl monomer is incorporated into the HA, and 2) polymerization commences. The results of electron micrograph shown by Fig. 1(b) can be explained in this way.

Effect of pH of the Aqueous Solution on the Conversion of MMA

Polymerizations of MMA by Betaine Polymer 1 were carried out at various pH values of the aqueous solution. The results obtained are shown in Fig. 2. The maximum conversion of MMA was obtained



(a)

(b)

FIG. 1. Surface views of betaine polymer. (a): MMA-untreated Betaine Polymer 1. (b): Betaine Polymer 1 after polymerization.

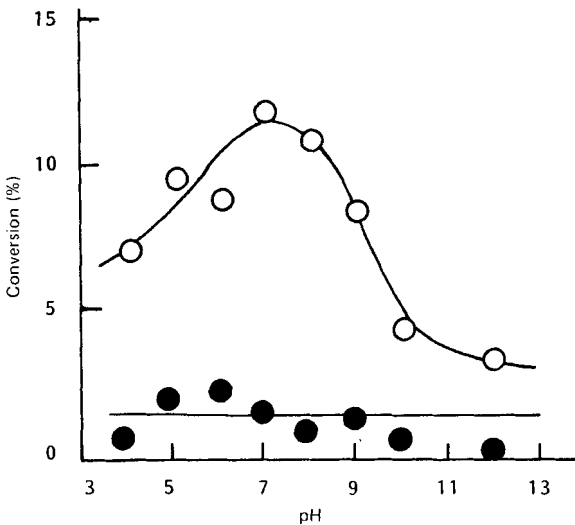


FIG. 2. Conversion of MMA vs pH of the aqueous solution. MMA, 1.5 cm³; Betaine Polymer 1, 0.050 g (○), 0 g (●); buffered solution, 5.0 cm³; 85°C; 3 h with shaking. Buffered solutions were prepared with the following systems: pH 4, M/10 sodium citrate-M/10 HCl; pH 6, M/10 sodium citrate-M/10 NaOH; pH 7-8, M/10 KH₂PO₄-M/20 Na₂B₄O₇; pH 10-12, M/5 Na₂B₄O₇-M/10 NaOH.

at pH 7. The HA formed became harder when the reaction system was acidic or basic because the cationic and anionic parts of the parent polymer could be neutralized. The hardness of the HA may correspond to the hardness of MMA.

The initiation mechanism of polymerization by a betaine-type polymer can be considered to be like that of an anionic [6] or cationic type [8] macromolecular electrolyte.

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