Vinyl Polymerization. 431. Vinyl Polymerizations Initiated by Block and Random Poly(Styrene-co-Sodium Methacrylate)

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ABSTRACT

The polymerization of some kinds of vinyl monomer was found to occur without an ordinary initiator in aqueous solutions of AB-type block or random copolymers of sodium methacrylate with styrene as a so-called "uncatalyzed polymerization." Although the spin trapping technique showed that the initiation mechanism by the block copolymer was the same as that by the random copolymer, the initiating ability of the block copolymer was lower than that of the random copolymer. Such results are attributable to the difference in the incorporating ability of monomer into the micelles formed by the block copolymer and into the hydrophobic areas formed by the random copolymer.

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INTRODUCTION

We previously found that the copolymer of styrene (St) and sodium acrylate (poly(St-co-AA-Na)) and the copolymer of methyl methacrylate (MMA) and sodium methacrylate (poly(MMA-co-MAA-Na)) can polymerize vinyl monomers in aqueous solution through radical mechanisms [1]. Such polymerizations initiated by hydrophilic macromolecules have been described as "uncatalyzed polymerization" since they can be initiated without the addition of any ordinary free-radical initiator [2, 3]. It has been shown that the polymerization proceeds as follows: 1) the hydrophilic macromolecules form hydrophobic areas (HA) in the aqueous phase, 2) the vinyl monomer dissolves in the aqueous phase and then is incorporated into the HA, and 3) radical polymerization commences in the HA.
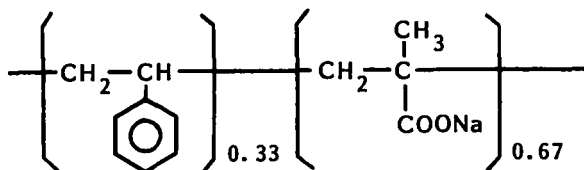
The HA are called "harder" when the interior of the HA is more hydrophobic; "softer" when it is more hydrophilic. Monomers can also be classified into "hard and soft monomers" according to their solubilities in water [4]. As a matter of course, the hydrophobicities of HA and monomers differ from each other.

We have proposed a concept of "hard and soft HA and monomers," which means that the hard HA prefers to incorporate the hard monomer, while the soft HA prefers to incorporate the soft monomer [4]. This concept has been confirmed experimentally by two methods, i.e., by the copolymerization of St and MMA and by the selectivity of the monomer initiated into parent copolymers of different compositions [1]. This monomer selectivity has been explained by considering that the ease of incorporation of the monomer can be controlled by changing the hydrophobicity of the HA by changing the composition of the parent copolymer. It was presumed that the amount of monomer incorporated into the HA was controlled by the additive effect of the size of the HA and of its hydrophobicity.

From the standpoint of the difference in the amount of monomer incorporated into the HA, the present paper deals with the ease of polymerization in "uncatalyzed polymerizations" initiated by the block and random copolymers of sodium methacrylate and St (poly(St-co-MAA-Na)).

Furthermore, the spin trapping technique has been used to investigate whether the initiating radical species generated for AB-type block copolymer (poly(St_1-b-MAA-Na_2)) are the same as for random copolymer (poly(St_1-r-MAA-Na_2)).

It should be noted that the block copolymer is a kind of detergent. Accordingly, the HA formed by the block copolymer are micelles (MC) just like those formed by such ordinary detergents as dodecylbenzenesulfonate [5]. The MC formed by block copolymer are tighter than the HA formed by random copolymer. Accordingly, the interior of MC consists of an aggregate of hydrocarbon units and is very hard.

$$-\left(CH_2-CH\left\langle\bigcirc\right\rangle\right)_{0.33}\left(CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle COONa}{|}}{C}}\right)_{0.67}-$$

Poly(St_1-co-MAA-Na_2)

EXPERIMENTAL

Materials

MMA, St, MAA, ethyl methacrylate (EMA), n-, i-, t-butyl meth-acrylate (n-, i-, t-BMA), and n-hexyl methacrylate (n-HMA) were purified by the conventional methods and distilled under vacuum before use. Sodium 2,4-dimethyl-3-nitrosobenzene sulfonate-d_8 (DMNS-d_8), used as a water-soluble nitroso spin-trapping agent, was prepared by the method of Konaka and Sakata [6]. Water was ion exchanged and distilled.
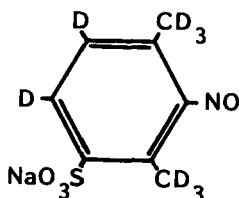
DMNS-d_8

Preparation of Poly(St_1-b-MAA-Na_2)

AB-type block copolymer (poly(St_1-b-MAA_2)), composed of 0.33 (mole fraction) of St and 0.67 of MAA, was prepared by means of living anionic polymerization by the research group of Professors Nozakura and Morishima of Osaka University. St was polymerized by lithium naphthalene in tetrahydrofuran to yield a living polymer solution, to which trimethylsilyl methacrylate was added to allow block copolymerization. The trimethylsilyl ester groups in the block copolymer were quantitatively hydrolyzed by treatment with aqueous methanol at room

temperature, yielding MAA sequences. The N,N-dimethylformamide (DMF) solution of poly(St_1-b-MAA_2) was added dropwise to a calculated amount of 1 N NaOH aqueous solution, and the resulting solution was dialyzed to remove DMF completely, adjusted to pH 9.5, and then freeze-dried to give poly(St_1-b-MAA-Na_2).

Preparation of Poly(St_1-r-MAA-Na_2)

The random copolymer poly(St_1-r-MAA_2), which was composed of 0.33 (mole fraction) of St and 0.67 of MAA, was prepared by the method of Hastings [7] and then twice reprecipitated from ethanol and n-hexane. The solution of copolymer dissolved in a small amount of ethanol was neutralized to pH 9.5 and then freeze-dried to give poly(St_1-r-MAA-Na_2).

Application of the KI and x-ray fluorescence techniques revealed neither the peroxide moiety nor metallic impurities in poly(St_1-b-MAA-Na_2) and poly(St_1-r-MAA-Na_2). Moreover, it was confirmed by ESR that the free-radical content was not measurable in these parent polymers. Intrinsic viscosity measurements gave

$$\text{Poly}(St_1\text{-b-MAA-}Na_2): \quad [\eta]_{0.5N\text{-NaCl aq}}^{25°C} = 0.67, \quad \overline{P}_n = 300$$

$$\text{Poly}(St_1\text{-r-MAA-}Na_2): \quad [\eta]_{0.5N\text{-NaCl aq}}^{25°C} = 0.54$$

Polymerization Procedure

The polymerizations were carried out in sealed tubes at 85°C with or without shaking. The reaction mixture was poured into a large amount of methanol to precipitate the polymer produced. Here, the isolation of polymer from the reaction mixture was done by additionally using the salting-out technique. The conversion of monomer was calculated from the weight of polymer.

The number-average degree of polymerization ($\overline{P}_n$) of poly(MMA) and poly(i-BMA) produced were calculated by Welch's equation [8] from the intrinsic viscosity measured in benzene at 30°C and by Valles' equation [9] from that measured in acetone at 25°C.

Observation by Transmission Electron Microscopy

The polymerization systems were observed by transmission electron microscopy (TEM) according to the method of Kunitake and Okahata [10].

Identification of the Initiating Radical Species

The determination of the initiating radical species was done by means of the spin trapping technique described in a previous paper [11]. The reaction of poly(St_1-co-MAA-Na_2) and monomer in water was carried out at 60°C without shaking in the presence of DMNS-d_8 in a flat-type ESR cell which was rinsed with a stream of argon. After a given time the ESR spectrum of the reaction mixture was taken at 60°C by using a JES-FE-1X spectrometer with 100 kHz field modulation.

RESULTS AND DISCUSSION

Polymerization of Vinyl Monomers

The results of the polymerization of eight kinds of vinyl monomers by poly(St_1-b-MAA-Na_2) or poly(St_1-r-MAA-Na_2) are summarized in Fig. 1. It was evident that these parent copolymers had initiating ability for vinyl polymerizations. By subtracting the thermal conversion from the overall conversion, the corrected conversion could be obtained as follows:

Corrected conversion = [conversion in the presence of poly(St_1-co-MAA-Na_2)] - [conversion in the absence of poly(St_1-co-MAA-Na)]

(1)

It was clear that the initiating ability of the block copolymer was lower than that of the random copolymer for polymerizations of the vinyl monomers used and that the selectivities of monomer in both systems differed from each other.

Table 1 shows the values of the corrected degree of polymerization [12] of poly(MMA) and poly(i-BMA) obtained by using poly(St_1-b-MAA-Na_2) or poly(St_1-r-MAA-Na_2). The $\overline{P}_{nc}$ of poly(MMA) and poly(i-BMA) produced by using the block copolymer as a parent polymer were found to be smaller than those produced by using the random copolymer. However, the end group in the polymers produced was not detectable within the sensitivity of ^{1}H- or ^{13}C-NMR.

Moreover, the tacticities of poly(MMA) produced by using poly(St_1-b-MAA-Na_2) and poly(St_1-r-MAA-Na_2) were almost equal to the tacticity of poly(MMA) obtained in ordinary radical polymerization, as shown in Table 1.
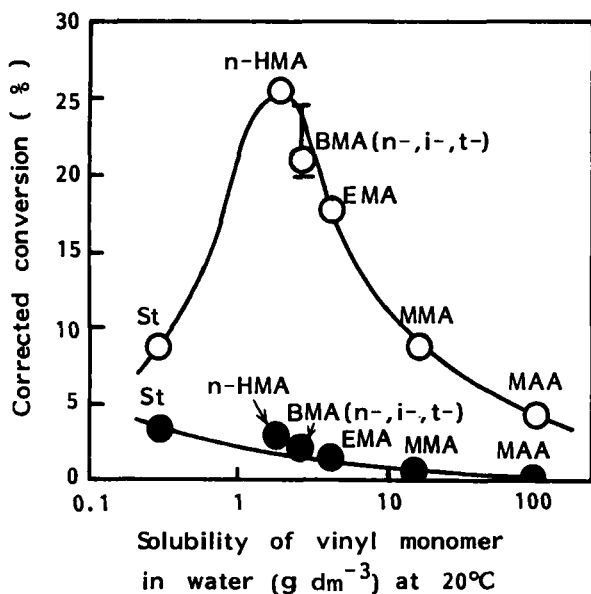
FIG. 1. The polymerization of various kinds of monomer initiated by poly(St_1-co-MAA-Na_2). Monomer, 1 mL; poly(St_1-co-MAA-Na_2), 0.01 g; H_2O, 10 mL; 85°C; 3 h; with shaking. ($\bullet$) Poly(St_1-b-MAA-Na_2), ($\circ$) poly(St_1-r-MAA-Na_2).

Initiation Mechanism

The initiation mechanism was studied by means of the spin trapping technique.

Figure 2 shows the ESR spectra of the reaction mixtures obtained when MMA was allowed to react with poly(St_1-b-MAA-Na_2) and poly-(St_1-r-MAA-Na_2) aqueous solutions in the presence of DMNS-d_8 under the same fed conditions. The same spectrum patterns were observed in both systems. The nonary signals were assigned to the adduct $\underset{\sim}{5}$ (R = CH_3) of 2-methoxycarbonyl allyl radical $\underset{\sim}{1}$ (R = CH_3) to DMNS-d_8 (g = 2.0057, a_N = 14.8 G, $a_{H-\beta}$ = 12.2 G) (Eq. 4). The triplet equivalent signals were assigned to the adduct $\underset{\sim}{6}$ (R = CH_3) of 1-methoxycarbonyl-1-methylethyl radical $\underset{\sim}{2}$ to DMNS-d_8 (g = 2.0060, a_N = 14.1 G) (Eq. 5).

TABLE 1. Polymerizations of MMA and i-BMA Initiated by Poly(St$_1$-b-MAA-Na$_2$) or Poly(St$_1$-r-MAA-Na$_2$)[a]

Monomer, mL	(Poly(St$_1$-co-MAA-Na$_2$), g	Corrected conversion, %	$\overline{P}_{nc}$	Produced polymer		
				I,[b] %	H,[b] %	S,[b] %
MMA 1	Poly(St$_1$-b-MAA-Na$_2$) 0.01	0.36	5.3×10^3	7	34	59
MMA 1	Poly(St$_1$-r-MAA-Na$_2$) 0.01	8.81	3.6×10^4	6	36	58
i-BMA 1	Poly(St$_1$-b-MAA-Na$_2$) 0.01	20.20	5.9×10^2	-	-	-
i-BMA 1	Poly(St$_1$-r-MAA-Na$_2$) 0.01	1.74	10.8×10^2	-	-	-

[a]H$_2$O, 10 mL; 85°C; 5 h; with shaking.

[b]These tacticity values were estimated by analyses of the triad due to the α-methyl group of poly(MMA) by means of ^{1}H-NMR.
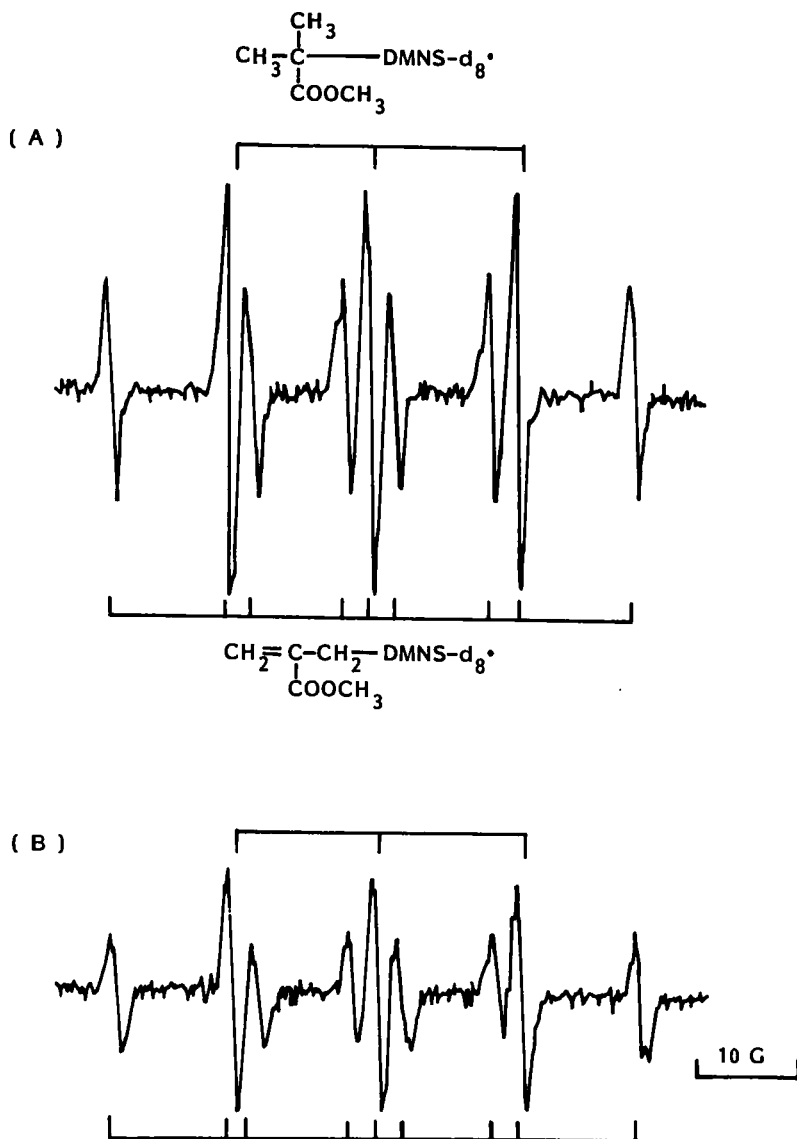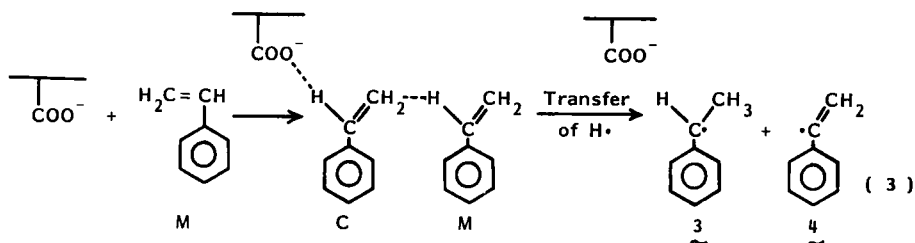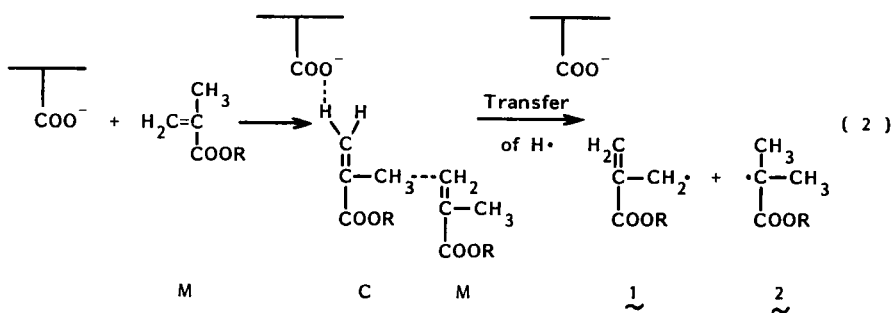
FIG. 2. ESR spectra of the system MMA/poly(St_1-co-MAA-Na_2)/ DMNS-d_8 in aqueous solution at 60°C after 1 h. MMA, 2.8 mmol; poly(St_1-co-MAA-Na_2), 1.0 mg; DMNS-d_8, 4.1 μmol; H_2O, 1.0 mL. (A) Poly(St_1-b-MAA-Na_2), (B) poly(St_1-r-MAA-Na_2).
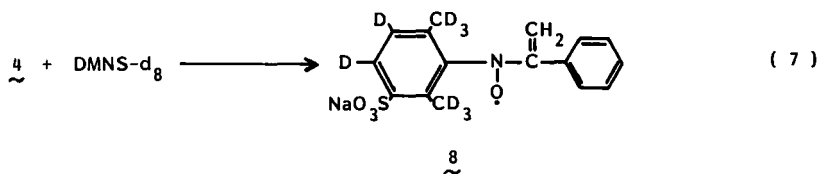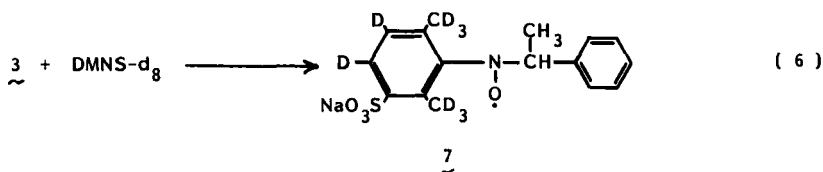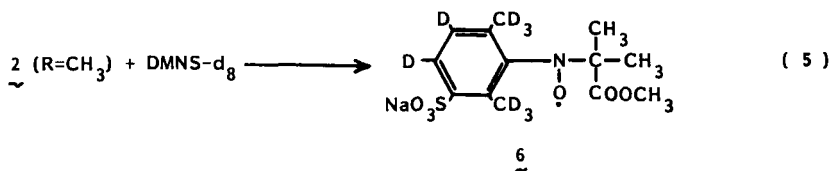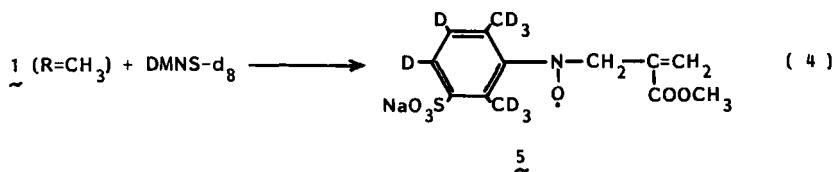
On the other hand, the ESR spectra consisted of the nonary signals and the triplet signals were also obtained in the i-BMA/poly(St$_1$-b-MAA-Na$_2$)/H$_2$O/DMNS-d$_8$ and i-BMA/poly(St$_1$-r-MAA-Na$_2$)/H$_2$O/DMNS-d$_8$ systems.

Accordingly, the initiation mechanism for the polymerization of methacrylates expressed by Eq. (2) was confirmed by means of the spin trapping technique. This mechanism includes hydrogen transfer between molecules of the methacrylate monomer. Although Flory's initiation mechanism of hydrogen transfer between two free monomers has been ruled out from the standpoint of reaction energy (the energy required for the opening of a double bond) [13], we have explained by the Frontier Electron Molecular Orbital method that initiation by hydrogen transfer is possible in the uncatalyzed polymerization [14].

Figure 3 shows ESR spectra of the reaction mixtures observed in the poly(St$_1$-b-MAA-Na$_2$)/H$_2$O/DMNS-d$_8$ and poly(St$_1$-r-MAA-Na$_2$)/H$_2$O/DMNS-d$_8$ systems when St was used as a monomer. The sextet signals were assigned to the adduct 7 of 1-phenylethyl radical 3 to DMNS-d$_8$ (g = 2.0053, a$_N$ = 14.7 G, a$_{H-\beta}$ = 7.2 G) (Eq. 6). The triplet signals were assigned to the adduct 8 of 1-phenylvinyl radical 4 to DMNS-d$_8$ (g = 2.0053, a$_N$ = 14.6 G) (Eq. 7).

Therefore, the primary radical species of 3 and 4 are considered to be generated by hydrogen atom transfer from free St monomer to the complexed St monomer, as shown by Eq. (3).

1 (R=CH$_3$) + DMNS-d$_8$ $\longrightarrow$

[structure]

5

$$(4)$$

2 (R=CH$_3$) + DMNS-d$_8$ $\longrightarrow$

[structure]

6

$$(5)$$

3 + DMNS-d$_8$ $\longrightarrow$

[structure]

7

$$(6)$$

4 + DMNS-d$_8$ $\longrightarrow$

[structure]

8

$$(7)$$

Estimation of Overall Activation Energy

On applying the Arrhenius equation to the polymerization rate of i-BMA, the good linear relations in Fig. 4 were obtained. From the slopes, overall activation energies for poly(St$_1$-b-MAA-Na$_2$) and for poly(St$_1$-r-MAA-Na$_2$) were both calculated to be 37 kJ/mol.

This result supports the conclusion that the initiation mechanism in the polymerization initiated by block copolymer is the same as that initiated by random copolymer.

Observation of HA by TEM

In order to visualize the polymerization system, the aggregates of poly(St$_1$-b-MAA-Na$_2$) and poly(St$_1$-r-MAA-Na$_2$) in water were observed by TEM (Fig. 5). It was clear from these pictures that both

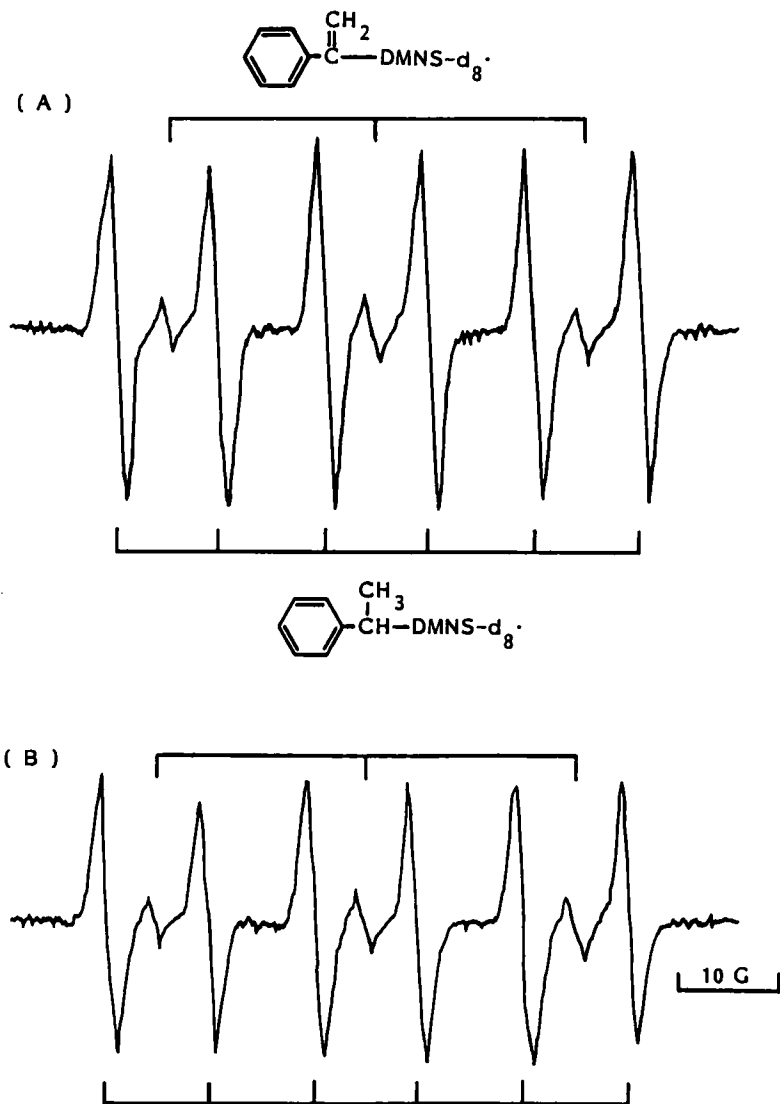FIG. 3. ESR spectra of the system of $St/poly(St_1-co-MAA-Na_2)/$
$DMNS-d_8$ in aqueous solution at 60°C after 5 h. St, 0.26 mmol; poly-
$(St_1-co-MAA-Na_2)$, 1.0 mg; $DMNS-d_8$, 12 μmol; H_2O, 1.0 mL. (A)
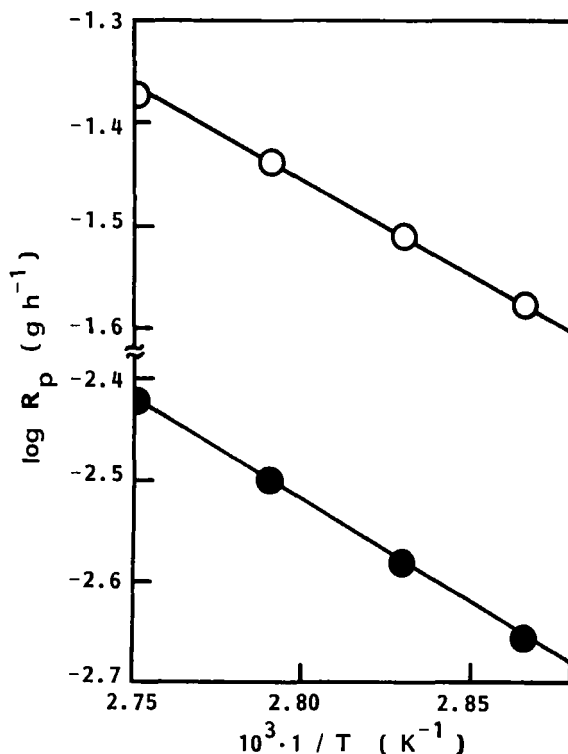$Poly(St_1-b-MAA-Na_2)$, (B) $poly(St_1-r-MAA-Na_2)$.

FIG. 4. Arrhenius plots for the polymerizations of i-BMA initiated by poly(St_1-co-MAA-Na_2). i-BMA, 1 mL; poly(St_1-co-MAA-Na_2), 0.01 g; H_2O, 10 mL; with shaking. (•) Poly(St_1-r-MAA-Na_2), (○) poly(St_1-r-MAA-Na_2).

macromolecular electrolytes dissolved in water by forming aggregates without formation of lamellar or vesicular structures. We have called these aggregates "HA" and "MC," where the polymerization commences, respectively. As expected, the block copolymer formed the MC, which is of very small size, while the HA formed by the random copolymer is of larger size.

Difference in Initiating Ability between Block and Random Copolymers

Consider the difference in the initiating abilities of poly(St_1-b-MAA-Na_2) and poly(St_1-r-MAA-Na_2). As described above, the initiating
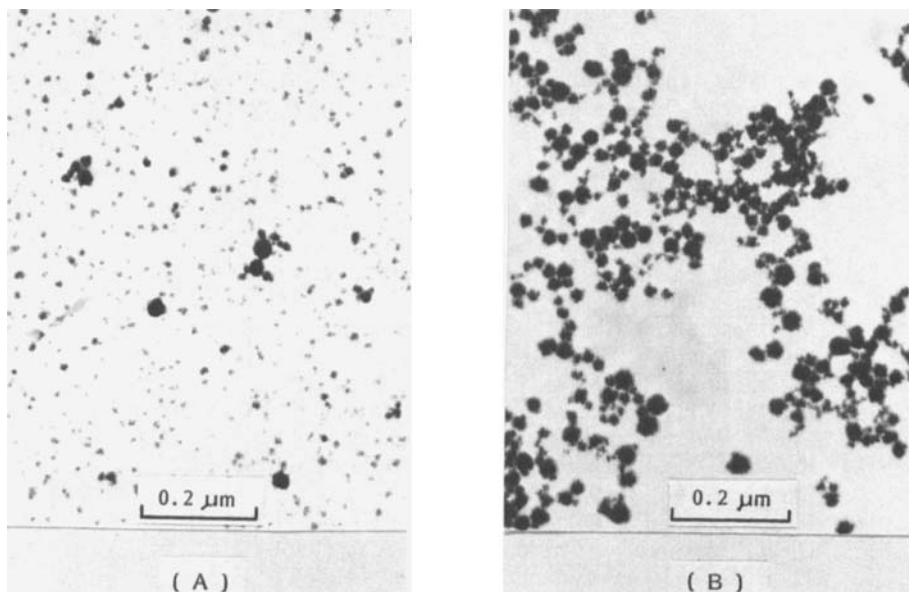
FIG. 5. Surface views of poly(St_1-b-MAA-Na_2) (A) and poly(St_1-r-MAA-Na_2) (B) in the water phase.

ability of poly(St_1-b-MAA-Na_2) is lower than that of poly(St_1-r-MAA-Na_2). This result can be explained by considering that the interior of the MC formed by the block copolymer is similar to an aggregate of hydrocarbon molecules and is very hard. By "the concept of hard and soft HA and monomers" [4], the monomers used can be considered to be barely incorporated into the MC.

The conversions of St in the MC and the HA were found to be 3.5 and 8.5%, respectively, possibly due to the difference of the thickness of MC and HA; that is, the MC is structured much more tightly than the HA.

On the other hand, it was also found that the conversion of monomer increased with increasing hydrophobicity of monomer in the polymerization by poly(St_1-b-MAA-Na_2) aqueous solution, and n-HMA showed a maximum conversion in the polymerization by poly(St_1-r-MAA-Na_2) aqueous solution. Such monomer selectivities can be easily explained by "the concept of hard and soft HA and monomers."

Thus, it is concluded that the difference in the apparent initiating abilities of poly(St_1-b-MAA-Na_2) and poly(St_1-r-MAA-Na_2) results in the amount of monomer incorporated into the MC and the HA.

ACKNOWLEDGMENT

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