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### Vinyl Polymerization. 436. Effect of Magnetic Field on Uncatalyzed Polymerization

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## VINYL POLYMERIZATION. 436. EFFECT OF MAGNETIC FIELD ON UNCATALYZED POLYMERIZATION

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### ABSTRACT

The radical polymerization of vinyl monomers initiated with several kinds of hydrophilic macromolecule was carried out in a magnetic field. The magnetic field promoted the polymerization; the conversion of monomers and the molecular weight of the polymers obtained increased with increasing field strength in the range of 0-0.1 T. The dependence of the composition and tacticity of the mother polymer on the magnitude of the magnetic field was studied. Using graft or block copolymers, which consisted of hard and soft segments, the effect of a magnetic field was further investigated. The degree of hardness and tightness of the hydrophobic areas (reaction areas) formed by the mother polymer in the aqueous solution was found to affect the magnetic field effect on the uncatalyzed polymerization. The overall activation energy obtained in the magnetic field was almost equal to that obtained without a magnetic field.

### INTRODUCTION

We have found that many kinds of water-soluble or hydrophilic macromolecule can polymerize vinyl monomers in water through radical mechanisms.

Such a polymerization was named "uncatalyzed polymerization" since it could be initiated without an ordinary initiator [1, 2].

Such effective macromolecules were divided into two groups: Those in Group I required a metal ion for polymerization; those in Group II did not require a metal ion. 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 occurs in the HA.

When the interior of the HA is more hydrophobic, the HA is called "harder," and when it is more hydrophilic, the HA is called "softer." Monomers can also be classified into "hard" and "soft" monomers according to their solubilities in water.

We have proposed "a concept of hard and soft HA and monomers," which means that the hard HA prefers to incorporate hard monomer, while the soft HA prefers to incorporate soft monomer, and applied it as a criterion of incorporation of monomer into the HA [3].

Recently, Turro et al. reported the noteworthy results of an external magnetic field effect on photoinduced emulsion polymerization of styrene (St) initiated with dibenzyl ketone in sodium dodecylsulfate micelles [4, 5]. The conversions of St during photoirradiation for 3 h at 0 and 0.025 T were about 30 and 90%, respectively. The molecular weights of the poly(St) produced at 0 and 0.10 T were about  $1 \times 10^5$  and  $5 \times 10^5$ , respectively.

These results were explained by cage reactions of triplet (T) radical pairs in micelles (Fig. 1). They appear to originate from Zeeman splitting of the  $T_{\pm}$  triplet levels from the singlet (S) level, which causes the magnetic field effect by decreasing  $T_{\pm} \rightarrow S$  intersystem crossing and, thereby, allows for an increase in the efficiency of radical escape [6]. A decrease in the efficiency of cage destruction of radicals simultaneously allows more efficient initiation of polymerization, more efficient overall initiation, and less efficient termination by inhibiting the extent of combination of propagating radicals and initiator radicals.

Consequently, the increases of monomer conversion and molecular weight of the polymer produced can be understood as due to a decreased recombination of radicals formed in micelles.

As mentioned above, although the mechanism of uncatalyzed polymerization differs essentially from that of emulsion polymerization since there is no initiator, the polymerization behavior in the two cases is analogous. Accordingly, the magnetic field effect can be expected to occur for uncatalyzed polymerization. In a preliminary experiment we investigated the effect of a magnetic field on the polymerization of methyl methacrylate (MMA) initiated

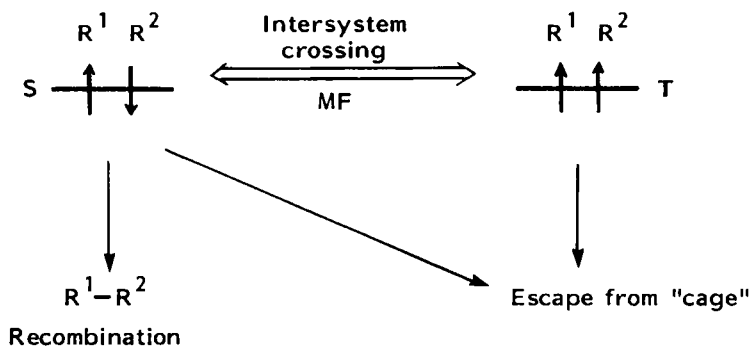


FIG. 1. Schematic representation of the influence of MF on the efficiency of the cage reaction of a geminated triplet radical pair.

with poly(2-hydroxyethyl methacrylate) (PHEMA;  $\bar{N}$  1 800) in water at room temperature and noted that the polymerization was enhanced by application of a magnetic field [7].

The present paper is concerned with the detailed effect of an external magnetic field on uncatalyzed polymerization in the absence of metal ion by the various kinds of "mother" polymers shown on the next page.

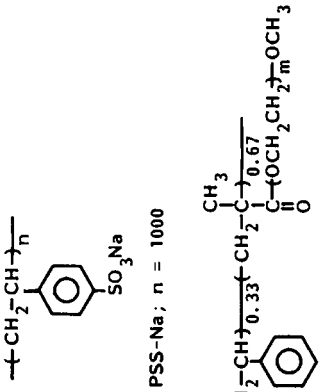
## EXPERIMENTAL

### Materials

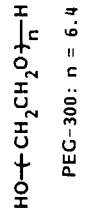
Water-soluble macromolecules used as mother polymers were prepared or purified by the following methods.

PHEMA ( $\bar{N}$  1 040, 1 310) [8], sodium polystyrenesulfonate (PSS-Na;  $\bar{N}$  1 000) [9], and betain polymer ( $\bar{N}$  300) [10] were prepared as reported previously.

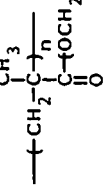
Highly isotactic poly(methacrylic acid) (PMAA;  $I = 92.3\%$ ) was obtained by means of concentrated sulfuric acid hydrolysis [11] of the corresponding poly(MMA) synthesized by anionic polymerization initiated with  $\text{LiAlH}_4$  in ethyl ether at  $-70^\circ\text{C}$  for 24 h [12]. Isotactic-rich PMAA ( $I = 68.3\%$ ) was obtained from the corresponding poly(MMA) prepared by anionic polymerization initiated with  $n\text{-BuLi}$  in toluene at  $30^\circ\text{C}$  for 30 min [13]. Heterotactic poly(MAA) ( $I = 5.2\%$ ) was synthesized by thermal polymerization of meth-



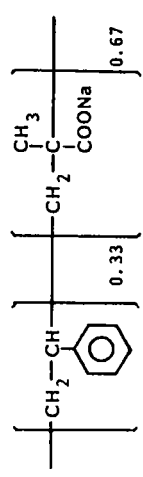
Poly( $\text{St}_1$ -co-MEO $_2$ ):  $m = 4.0$   
 $[\eta]_{30^\circ\text{C}}^{\text{Benzene}} = 0.25$



Poly(Oligoethylene Methacrylate)  
 PMEO;  $m = 4.0$   $[\eta]_{30^\circ\text{C}}^{\text{Benzene}} = 0.23$

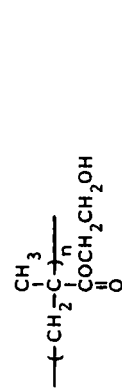


or  $[\eta]_{30^\circ\text{C}}^{\text{Benzene}} = 0.13$

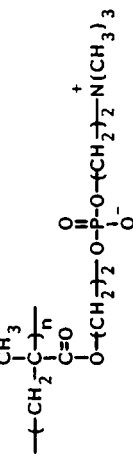


Poly( $\text{St}_1$ -b-MAA- $\text{Na}_2$ ):  $[\eta]_{25^\circ\text{C}}^{\text{aq.}} = 0.67$ ,  $\bar{P}_n = 300$   
 Poly( $\text{St}_1$ -r-MAA- $\text{Na}_2$ ):  $[\eta]_{25^\circ\text{C}}^{\text{aq.}} = 0.54$

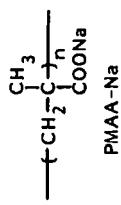
Polymer Structures



PHEMA  
 $n = 1040, 1310$



BetaIn Polymer ;  $n = 300$



$I = 92.3$  % ( $n = 1480$ )  
 $68.3$  % ( $n = 810$ )  
 $5.2$  % ( $n = 8420$ )

acrylic acid in benzene at 80°C for 24 h. The poly(MAA) samples produced in this manner were neutralized to pH 9.5 by 1 *N* aqueous NaOH and then freeze dried to give the corresponding PMAA-Na.

Poly(oligoethylene oxide methacrylates) (PMEO;  $m = 4.0, 8.7$ ) were synthesized by radical polymerization of the corresponding oligoethylene oxide methacrylates (MEO) initiated by *N,N'*-azobisisobutyronitrile (AIBN) in tetrahydrofuran (THF) at 60°C for 13 h. The products were reprecipitated 3 times by the benzene-ethyl ether system.

Copolymer of St with MEO ( $m = 4.0$ ) [Poly(St<sub>1</sub>-*co*-MEO<sub>2</sub>)], 0.33/0.67 (mol/mol) St/MEO, was synthesized by copolymerization of St with MEO initiated by AIBN in THF at 60°C for 5 h. The copolymer produced was reprecipitated 3 times with the benzene-*n*-hexane system.

AB-type block copolymer of St with sodium methacrylate [Poly(St<sub>1</sub>-*b*-MAA-Na<sub>2</sub>)], 0.33/0.67 (mol/mol) St/NaMAA, was prepared by living anionic polymerization (by the research group of Prof. Nozakura and Prof. Morishima of Osaka University). The random copolymer [Poly(St<sub>1</sub>-*r*-MAA-Na<sub>2</sub>)] was prepared by the method reported in a previous paper [14].

Poly(ethylene glycol), MW 300 (PEG-300;  $n = 6.4$ ), was purified before use by bulk passage through a column filled with activated alumina in a stream of N<sub>2</sub>.

So far as KI and x-ray fluorescence techniques were applied, no peroxide moiety and metallic impurities were detected in these mother polymers. Moreover, it was confirmed that there was no free-radical content detectable by ESR in these mother polymers.

Monomers were purified by conventional methods. Water was ion exchanged and distilled.

## Procedure

Polymerization in the dark or photopolymerization was performed in a magnetic field.

A Pyrex tube (10 mm diameter) was charged with measured amounts of each component. After the mixture was degassed several times with a Hg-diffusion pump, the tube was sealed off under vacuum. The tube was allowed to stand at 40-70°C between two magnets having variable-field strength.

A high-pressure mercury lamp (Ushio Co. Ltd., 500 W Hg lamp) was used as a light source for the photopolymerization.

After a given time, the reaction mixture was poured into a large amount of methanol to precipitate the polymer obtained.

The number-average degree of polymerization ( $\bar{N}_n$ ) of the poly(MMA) pro-

duced was estimated by Welch's equation [15] from the intrinsic viscosity measured in benzene at 30°C.

The determination of initiating radical species in the polymerization of MMA with PHEMA was done by the spin-trapping technique reported in previous papers [16, 17]. Sodium 2,4-dimethyl-3-nitrosobenzenesulfonate- $d_8$  (DMNS- $d_8$ ) and 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO), used as the water-soluble nitroso and nitron spin-trapping agents, were prepared by Konaka and Sakata [18] and obtained from Aldrich Chemical Co., respectively.

## RESULTS AND DISCUSSION

### Effect of Magnetic Field on Polymerization of MMA Initiated with PHEMA

As mentioned above, we found preliminarily that the rate of polymerization of MMA initiated with PHEMA in water was accelerated by the application of a magnetic field (1.41 T). However, we did not study the effect in detail. In the present paper we deal with the effect of a magnetic field on this system from various standpoints.

*Initiation Mechanism of the System of PHEMA/MMA/H<sub>2</sub>O.* In a previous paper [8] we found that the polymerization of MMA could be initiated with PHEMA in water and speculated about the initiation mechanism. However, we did not have the evidence to establish this mechanism. Therefore, the initiation mechanism in this system was first investigated by means of the spin-trapping technique.

The ESR spectrum shown in Fig. 2 was obtained with DMNS- $d_8$  as a trapping agent. The nonet signals are assigned to the adduct of 2-methoxycarbonylallyl radical to DMNS- $d_8$  ( $g = 2.0057$ ,  $a_N = 14.8$  G,  $a_H \cdot \beta = 12.2$  G). The triplet equivalent signals are assigned to the adduct of 1-methoxycarbonyl-1-methylethyl radical to DMNS- $d_8$  ( $g = 2.0060$ ,  $a_N = 14.1$  G). However, the characteristic quartet signals with peak ratio 1:2:2:1 assigned to the adduct of hydroxyl radical and DMPO were not observed.

From these results we would like to rescind the initiation mechanism proposed previously [8] and propose the mechanism shown in Scheme 1. This mechanism means that the initiation of MMA polymerization takes place through a hydrogen atom transfer from the monomer complexed at the OH groups of PHEMA to the free monomer. This is the same as the typical initiation mechanism offered previously for the uncatalyzed polymerization requiring no metal ion [1, 16].

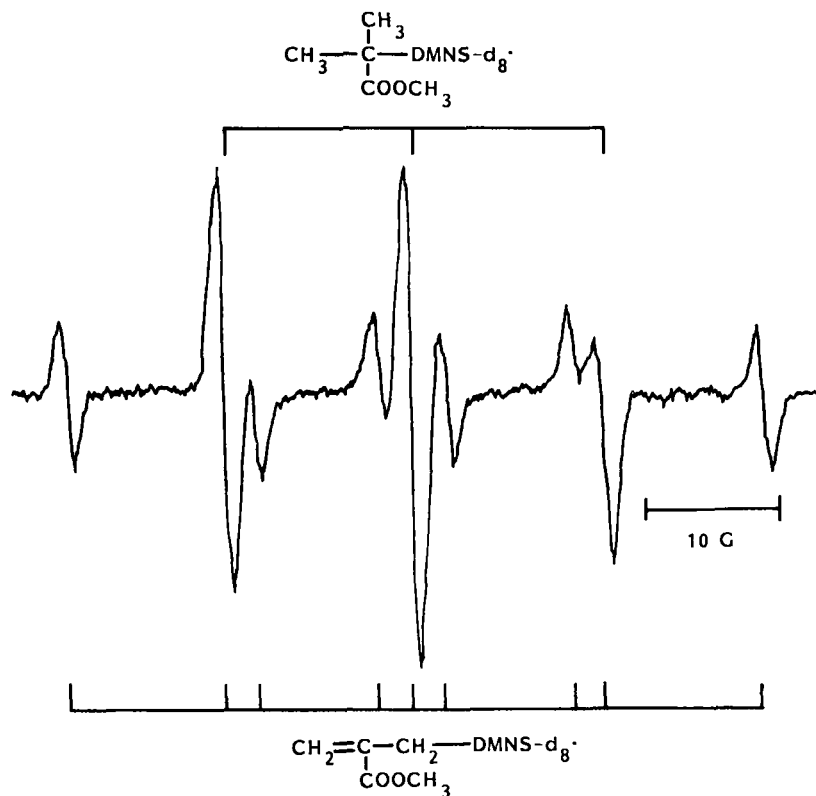
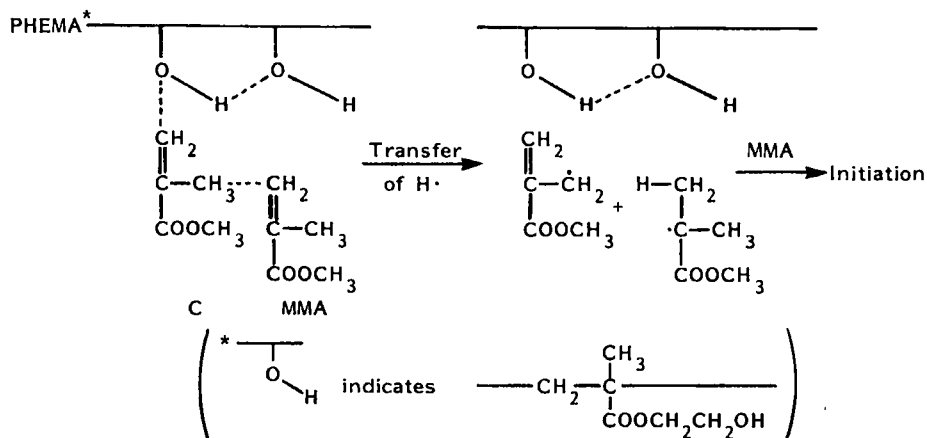


FIG. 2. ESR spectrum of the system MMA/PHEMA/DMNS- $d_8$  in aqueous solution at 60°C after 10 min. MMA, 0.939 mmol; PHEMA ( $n = 1\ 040$ ), 76.8 unit  $\mu\text{mol}$ ; DMNS- $d_8$ , 0.408 mmol;  $\text{H}_2\text{O}$ , 0.2  $\text{cm}^3$ .

*Effect of Magnetic Field Intensity.* Figure 3 shows the effect of magnetic field intensity on the polymerization of MMA initiated by PHEMA ( $n = 1\ 310$ ) in water. As shown in this figure, the conversion of MMA by PHEMA increased with increasing magnetic field up to 0.1 T. However, there was a tendency for the conversion to saturate beyond 0.1 T.

On the other hand, the efficiencies of grafting of MMA onto PHEMA were remarkably high, 90% or above, regardless of the intensity of the magnetic field. The efficiency of grafting was estimated by extracting homopoly(MMA) with benzene for 50 h in a Soxhlet extractor.





SCHEME 1. Initiation mechanism of the radical polymerization of MMA by PHEMA.

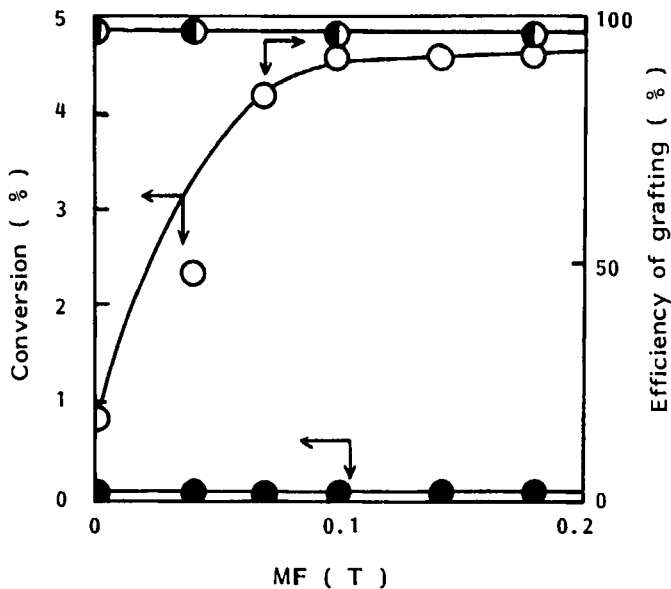


FIG. 3. Effect of magnetic field intensity on the polymerization of MMA initiated by PHEMA. MMA, 1.5 cm<sup>3</sup>; H<sub>2</sub>O, 5 cm<sup>3</sup>; time irradiated by MF, 12 h; reaction time, 26 h. (○, ●) PHEMA ( $n = 1.310$ ), 0.05 g; (●) PHEMA, 0 g.

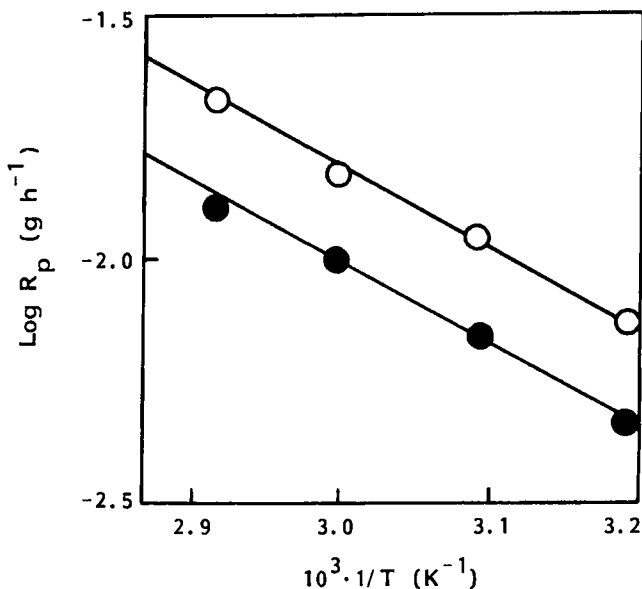


FIG. 4. Arrhenius plots for the polymerization of MMA initiated by PHEMA. MMA, 1.5 cm<sup>3</sup>; PHEMA ( $n = 1\ 040$ ), 0.5 g; H<sub>2</sub>O, 5 cm<sup>3</sup>; reaction time, 5 h; (○) MF, 0.18 T; (●) MF, 0 T.

*Effect of Polymerization Temperature.* The polymerizations of MMA with PHEMA ( $n = 1\ 040$ ) and H<sub>2</sub>O were carried out at 40–70°C in and out of the magnetic field. The overall activation energies in and out of the magnetic field were determined to be 29.5 and 30.3 kJ/mol, respectively by the Arrhenius equation (Fig. 4) from the rates of polymerization ( $R_p$ ) calculated by the method described in a previous paper [8]. These results suggest that the polymerization mechanism in a magnetic field is the same as that without one. Therefore, the magnetic field effect can be attributed to the stoichiometrical advantage conferred by the magnetic field.

*Effect of Magnetic Field on Polymerization of Other Methacrylates.* The promotion of polymerization by a magnetic field was also found for ethyl, iso-propyl, and *n*-butyl methacrylates.

### Effect of Magnetic Field on Uncatalyzed Polymerization Initiated with Various Kinds of Mother Polymer

Tables 1 and 2 show the results of a magnetic field on the uncatalyzed polymerization of MMA initiated with various kinds of mother polymers. It can be seen that polymerizations initiated by these water-soluble macromolecules other than PHEMA were also enhanced by a magnetic field. The monomer conversion and the molecular weight of poly(MMA) obtained increased on application of a magnetic field.

Table 2 also shows that PMEO and Poly( $St_1$ -*co*-MEO<sub>2</sub>) have initiating ability for the polymerization of MMA under no magnetic field.

Moreover, it was found that the rate of MMA polymerization initiated with PMAA-Na was affected by the tacticity of PMAA-Na under no magnetic field, and the extent of the magnetic field effect was influenced by the tacticity of the mother polymer. Since the degree of hardness and tightness of HA formed by PMAA-Na in aqueous solution varies with its tacticity, such results are not unexpected. However, we cannot discuss this in detail at the present time in view of these limited data.

TABLE 1. Effect of Magnetic Field on Uncatalyzed Polymerization of MMA<sup>a</sup>

Parent polymer	Conversion, %	
	No MF	MF <sup>b</sup>
PHEMA <sup>c</sup> (0.05 g)	6.6	11.0
PEG-300 (0.5 g)	6.2 <sup>d</sup>	8.2 <sup>e</sup>
PSS-Na (0.02 g)	3.8	6.2
Betain polymer (0.05 g)	13.0	15.8
PMAA-Na (I = 92.3%) (0.05 g)	0.4	1.3
PMAA-Na (I = 68.3%) (0.05 g)	9.2	14.7
PMAA-Na (I = 5.2%) (0.05 g)	1.4	4.3

<sup>a</sup>MMA, 1.5 cm<sup>3</sup>; H<sub>2</sub>O, 5.0 cm<sup>3</sup>; 60°C; 10 h.

<sup>b</sup>MF, 0.18 T.

<sup>c</sup> $n = 1\ 040$ .

<sup>d</sup> $P_n$  of produced poly(MMA) =  $4.24 \times 10^4$ .

<sup>e</sup> $P_n$  of produced poly(MMA) =  $5.41 \times 10^4$ .

TABLE 2. Effect of Magnetic Field on Uncatalyzed Polymerization of MMA by Graft and Block Copolymers<sup>a</sup>

Parent polymer	Conversion, %	
	No MF	MF <sup>c</sup>
PMEO/4.0 (0.2 g)	5.7	9.7
PMEO/8.7 (0.3 g)	8.8 <sup>d</sup>	19.3 <sup>e</sup>
Poly(St <sub>1-co</sub> -MEO <sub>2</sub> ) (0.1 g)	4.7	12.5
Poly(St <sub>1-b</sub> -MAA-Na <sub>2</sub> ) (0.0002 g) <sup>b</sup>	0.9 <sup>f</sup>	9.7 <sup>g</sup>
Poly(St <sub>1-r</sub> -MAA-Na <sub>2</sub> ) (0.0002 g) <sup>b</sup>	6.4	13.8

<sup>a</sup>MMA, 1.5 cm<sup>3</sup>; H<sub>2</sub>O, 5.0 cm<sup>3</sup>; 60°C; 10 h.

<sup>b</sup>MMA, 0.5 cm<sup>3</sup>.

<sup>c</sup>MF, 0.18 T.

<sup>d</sup> $P_n$  of produced poly(MMA) =  $3.46 \times 10^4$ .

<sup>e</sup> $P_n$  of produced poly(MMA) =  $5.71 \times 10^4$ .

<sup>f</sup> $P_n$  of produced poly(MMA) =  $4.07 \times 10^4$ .

<sup>g</sup> $P_n$  of produced poly(MMA) =  $10.08 \times 10^4$ .

The order of the promotion effect on polymerization by a magnetic field was as follows: PEG-300 < PHEMA < PME0/4.0 < PME0/8.7 < Poly(St<sub>1-co</sub>-MEO<sub>2</sub>), and then Poly(St<sub>1-r</sub>-MAA-Na<sub>2</sub>) < Poly(St<sub>1-b</sub>-MAA-Na<sub>2</sub>). Since the graft and block copolymers consisting of hard and soft segments form tight HA in the aqueous solution, the T<sub>±</sub>→S intersystem crossing is depressed by the magnetic field in these uncatalyzed polymerizations, and the extent of combination of primary radicals and propagation radicals formed in HA is inhibited. Thus there appears to be a remarkable enhancement of polymerization.

### Effect of Magnetic Field on Uncatalyzed Photopolymerization

For comparison with the magnetic field effect in the photoinduced emulsion polymerization of St initiated with dibenzyl ketone in sodium dodecyl sulfate micelles [4, 5], the magnetic field effect on the uncatalyzed photopolymerization of St by Poly(St<sub>1-b</sub>-MAA-Na<sub>2</sub>) or Poly(St<sub>1-r</sub>-MAA-Na<sub>2</sub>) in aqueous solution was investigated at room temperature. The results obtained are shown in Table 3. The photopolymerization of St by Poly(St<sub>1-co</sub>-MAA-

TABLE 3. Effect of Magnetic Field on Uncatalyzed Photopolymerization<sup>a</sup>

Poly( <i>St</i> <sub>1</sub> - <i>co</i> -MAA-Na <sub>2</sub> )	Conversion, %			
	0 T	0.18 T	0 T + <i>hν</i> <sup>b</sup>	0.18 T + <i>hν</i> <sup>b</sup>
None	0	0	1.2	1.4
Poly( <i>St</i> <sub>1</sub> - <i>b</i> -MAA-Na <sub>2</sub> )	Trace	Trace	2.3	5.6
Poly( <i>St</i> <sub>1</sub> - <i>r</i> -MAA-Na <sub>2</sub> )	Trace	Trace	2.4	4.4

<sup>a</sup>St, 0.2 cm<sup>3</sup>; Poly(*St*<sub>1</sub>-*co*-MAA-Na<sub>2</sub>), 0.8 mg; H<sub>2</sub>O, 2 cm<sup>3</sup>; room temperature; 10 h.

<sup>b</sup>Light source, 500 W high-pressure Hg lamp; length, 20 cm.

Na<sub>2</sub>) was found to be enhanced by the magnetic field. The effect of the magnetic field on photopolymerization initiated by block mother copolymer was small but larger than that initiated by random mother copolymer. That the effects of the magnetic field in the uncatalyzed photopolymerization are so small might be because the polymerization proceeded heterogeneously, causing shielding of light.

Accordingly, the enhancement of uncatalyzed polymerization without initiator by magnetic fields could be generally explained by the following reasoning: a radical pair in the S-state generated in the HA formed by the mother polymer is converted into the T-state. The T<sub>±</sub> → S intersystem crossing is depressed by the magnetic field. The radical pair of the T-state cannot recombine, and therefore the conversion of monomer and the molecular weight of polymer produced in the HA increase with application of a magnetic field.

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