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Vinyl Polymerization. 374. Radical Polymerization of Vinyl Monomer Initiated with Sodium Polystyrenesulfonate

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Vinyl Polymerization. 374.
Radical Polymerization of Vinyl Monomer Initiated with Sodium Polystyrenesulfonate

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ABSTRACT

The polymerization of vinyl monomer initiated by an aqueous solution of sodium polystyrenesulfonate (PSS-Na) was carried out at 85°C. Methyl methacrylate (MMA) and styrene were polymerized, while acrylonitrile was not. The rate of polymerization of MMA decreased with the increase of the degree of polymerization of PSS-Na. However, the polymerization was not initiated by sodium ethyl benzenesulfonate which was a unit molecule of PSS-Na. The polymerization proved to be a radical reaction. The polymerization was considered to commence with the formation of hydrophobic areas with PSS-Na in the aqueous phase. MMA is incorporated into these areas, and there the polymerization is initiated and proceeds. The hydrophobic areas were assumed to be similar to the micelles formed by anionic detergents such as sodium alkylbenzene sulfonate. An initiation mechanism is proposed.

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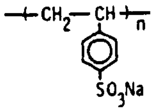
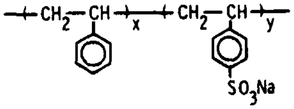
INTRODUCTION

Recently, we found that macromolecular sodium sulfonates such as poly(methallyl sulfonate) [1-2], poly(allyl sulfonate) [3], poly(vinyl sulfonate) [4], partially sulfonated polystyrene [5], ion-exchange resin (sodium crosslinked polystyrenesulfonate) [6] and chondroitin sulfate [7], could polymerize methyl methacrylate (MMA) in water through a radical mechanism.

The present paper deals with the radical polymerization of vinyl monomer initiated with sodium polystyrenesulfonate (PSS-Na). The effect of the average chain length of the molecule of PSS-Na was studied. Separately, in order to observe the effect of the concentration of sulfonate group on the conversion of MMA, the sodium salt of partially sulfonated polystyrene (PS-S-Na) was used as a macromolecule.



PSS-Na



PS-S-Na

EXPERIMENTAL

Materials

PSS-Na. PSS-Na was prepared from styrenesulfonic acid obtained from Tomoegawa Seishi Co. Ltd., according to the following method. Styrenesulfonic acid was dissolved in water, neutralized with sodium hydroxide, and polymerized by $Na_2S_2O_8$. The conditions were shown in Table 1. After a definite time, the reaction mixture was poured into a large amount of methanol to precipitate the polymer. The collected polymer was dialyzed overnight against water and then was evaporated to dryness under vacuum at 60-70°C. Three kinds of PSS-Na, No. 1, 2, and 3, were obtained. No. 1 PSS-Na was fractionated from water with acetone and two kinds of PSS-Na, No. 4 and 5, were obtained.

Measurement of Peroxide Group. The existence of peroxide group could not be observed by the KI method in any of the various types of PSS-Na.

PS-S-Na. PS-S-Na was prepared by the sulfonation of polystyrene (PSt). PSt obtained by the polymerization of styrene (St) initiated by 2,2-azobisisobutyronitrile in the presence of carbon

TABLE 1. Polymerization of Styrenesulfonate (95°C, in N_2)[a]

No.	$Na_2S_2O_8$ (wt % on monomer)	Time (hr)	$\overline{DP}_n$ of PSS-Na[b]
1	1.00	1	
2	0.10	1	870
3	0.04	3	3090
4	-	-	107
5	-	-	452

[a] As 30% aqueous solution.

[b] The number-average degree of polymerization ($\overline{DP}_n$) of PSS-Na was calculated by Kato's equation [8] from its viscosity in water.

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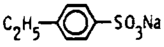
tetrachloride was purified twice by reprecipitation from the benzene-methanol system. $\overline{DP}_n$ of PSt was estimated to be 85 by Cesca's equation [9] from its viscosity.

Subsequently, into the solution of 2.5 g of PSt in 50 g of dichloroethane, a mixture of various amount of chlorosulfonic acid in 12 g of dichloroethane and 0.5 g of acetic acid (a preventor of gelation) was added dropwise during 10 min under vigorous stirring at room temperature; the solution was then allowed to stand for 1 hr to precipitate poly(styrenesulfonic acid). The precipitate collected was dissolved in water, dialyzed against water for 3 days, neutralized with the aqueous solution of sodium hydroxide, and then evaporated to dryness under vacuum at 60°C. The degree of sulfonation (DS) of PS-S-Na was estimated from the carbon percentage obtained by elemental analysis and then listed in Table 2. The KI method failed to detect the existence of peroxide groups in PS-S-Na. Sodium p-ethylbenzene sulfonate (p-EBS-Na) was a commercial product and used without further purification.



p-EBS-Na

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

TABLE 2. PS-S-Na of Different Degrees of Sulfonation[a]

No.	Elemental analysis[b] C (%)	H (%)	$\overline{DS}$ (%)
6	63.76	5.50	45
7	61.21	5.00	52
8	55.70	4.74	71
9	49.29	4.33	89
10	47.25	4.10	97

[a] $\overline{DP}_n$ = 85.

[b] Calcd for [$CH_2CH\ C_6H_4SO_3Na$]: C, 46.60%; H, 3.42%.

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Procedure

Vinyl monomer and an aqueous solution of PSS-Na or PS-S-Na were placed in a tube and sealed under vacuum, after thawing with nitrogen. The tube was heated at 85°C for definite time with shaking. The contents were poured into a large amount of methanol to precipitate the polymer produced. The collected polymer was washed repeatedly with methanol. After drying under vacuum, the conversion was calculated by the following equation:

$$\text{Conversion (\%)} = \frac{\text{Precipitate (g)} - \text{Sodium Polysulfonate (g)}}{\text{Monomer in Feed (g)}} \times 100$$

Isolation of MMA homopolymer was carried out as follows. The product above was extracted with chlorobenzene for 30 hr at boiling temperature. The extract was dropped into a large amount of n-hexane to precipitate the MMA homopolymer.

ANAL. Found, C, 59.32%; H, 8.00%. Calcd for $C_5H_8O_2$, C, 60.00%; H, 8.06%.

The number-average degree of polymerization $\overline{P}_n$ of homopoly-MMA was estimated from the intrinsic viscosity in benzene at 30°C by using Welch's equation [10].

TABLE 3. Effect of Degree of Polymerization of PSS-Na on the Vinyl Polymerization[a]

PSS-Na		Conversion (%)		
$\overline{DP}_n$	$[\eta]$[c]	MMA	AN	St
85[b]	-	41.0	0	20.2
107	0.0617	54.0	0	3.8
452	0.260	16.7	0	6.4
870	0.500	4.0	0	3.1
3090	1.779	1.7	0	1.8

[a] PSS-Na = 0.1 g, monomer = 3 cm^3, H_2O = 5 cm^3; 85°C, 3 hr.
[b] $\overline{DS}$ = 97% (PS-S-Na), cf. Table 4.
[c] Measured in 0.5 N NaCl aqueous solution at 30°C.

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RESULTS AND DISCUSSION

Selectivity of Vinyl Monomer and Effect of Degree of Polymerization of PSS-Na on the Rate of Polymerization

The polymerizations of three kinds of monomer were carried out in the presence of aqueous solution of PSS-Na at 85°C for 3 hr. The results obtained are shown in Table 3. As shown in Table 3, the polymerizations of MMA and St took place, while AN could not be polymerized at all. The reason for such monomer selectivity will be discussed in the last section of the present paper.

As can be seen in Table 3, the viscosity of the aqueous solution of PSS-Na increased rapidly with increasing of $\overline{DP}_n$, and the conversion of MMA decreased with $\overline{DP}_n$ of PSS-Na. This was explained as follows. When PSS-Na of larger $\overline{DP}_n$ is used, the molecules of PSS-Na become entangled with each other, and it becomes difficult for adequate hydrophobic areas to be formed. As reported previously [11-13], the incorporation of vinyl monomer in hydrophobic areas (or micelles) formed by PSS-Na is the first step of the polymerization. Therefore, when the formation of the hydrophobic areas becomes difficult, the quantity of MMA which can be incorporated become smaller. Thus, PSS-Na having too large $\overline{DP}_n$ is not appropriate for the polymerization.

TABLE 4. Effect of Degree of Sulfonation of PS-S-Na on the Vinyl Polymerization[a]

$\overline{DS}$ (%)	Conversion (%)		
	MMA	AN	St
46	18.1	0	2.1
52	16.7	0	7.3
71	28.1	0	16.4
89	31.9	0	23.4
97	41.0	0	20.2

[a] PS-S-Na = 0.1 g ($\overline{DP}_n$ = 85), monomer = 3 cm^3, H_2O = 5 cm^3; 85°C, 3 hr.

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Accordingly, PSS-Na No. 5 ($\overline{DP}_n$ = 452) was hereafter used as PSS-Na, except for the experiments shown in Fig. 9.

Effect of the Degree of Sulfonation of PSt on the Rate of Polymerization

As described above, $\overline{DP}_n$ of PSS-Na had a remarkable effect on the rate of polymerization. The second problem was the effect of the degree of sulfonation (DS) of PSt on the polymerization. Therefore, sodium salts of partially sulfonated PSt (PS-S-Na), having different degrees of sulfonation and a constant degree of polymerization were used.

The polymerizations of MMA, AN, and St were carried out at 85°C for 3 hr. The results are shown in Table 4.

Similarly to the cases initiated with PSS-Na, MMA and St were polymerized, while AN was not. It was found that the conversions of MMA and St tended to increase with $\overline{DS}$ of PS-S-Na; this suggests that the sulfonate group was an active center of polymerization.

Effect of the Amount of PSS-Na on the Rate of Polymerization of MMA

The dissolved amount of PSS-Na was varied, with the amounts of MMA and water being kept constant. The results obtained are shown

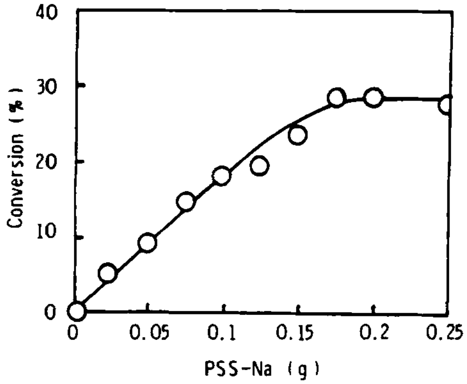

FIG. 1. Conversion of MMA vs. amount of PSS-Na in the feed. MMA = 3 cm^3, H_2O = 5 cm^3; 85°C, 3 hr.

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in Fig. 1. When the amount of PSS-Na was less than about 0.17 g, the rate of polymerization of MMA increased almost linearly with the amount of PSS-Na. However, with amounts of PSS-Na in excess of 0.17 g, the conversion became to independent of the amount of PSS-Na. Such results could be explained by the fact that the intermolecular entanglements of PSS-Na make incorporation of the monomer difficult.

Effect of the Amount of Water on the Rate of Polymerization of MMA

The effect of the amount of water on the conversion of MMA at constant amounts of MMA and PSS-Na (3 cm^3 and 0.1 g, respectively) was studied. The results obtained are shown in Fig. 2. As can be seen, a coexistence of water was indispensable for the polymerization initiated with PSS-Na. Moreover, the conversion of MMA increased with the amount of water and reached a constant value at 3 cm^3, i. e., the conversion became independent of the amount of water.

Effect of the Amount of MMA on the Polymer Yield

The polymerizations of various amounts of MMA in the presence of 0.1 g of PSS-Na and 5 cm^3 of water were carried out at 85°C for 3 hr with or without shaking, and the results in Fig. 3 were obtained. On standing, the polymer yield increased gradually (Fig. 3B). With

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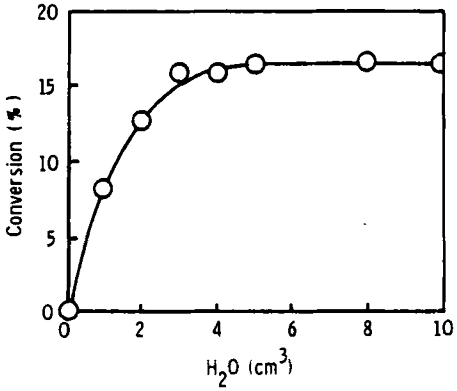

FIG. 2. Effect of the amount of H_2O on the polymerization of MMA. MMA = 3 cm^3, PSS-Na = 0.1 g; 85°C, 3 hr.

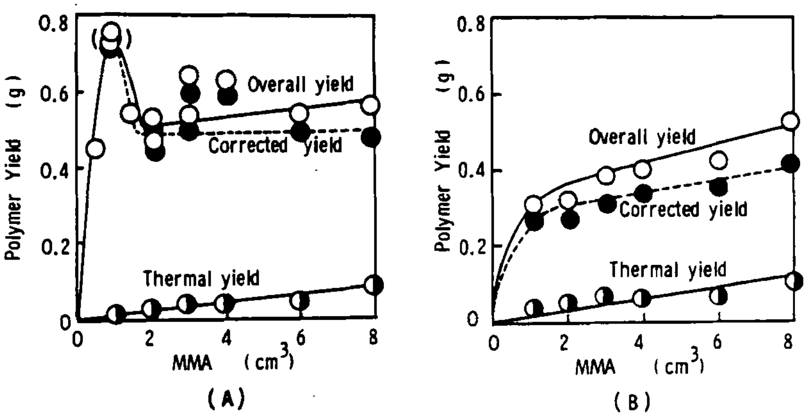

FIG. 3. Plots of (○) overall yield, (●) corrected yield, and (◑) thermal polymer yield vs. amount of MMA in the feed: (A) with shaking, (B) without shaking. H_2O = 5 cm^3; 85°C, 3 hr; PSS-Na (○, ●) 0.1 g, (◑) 0 g.

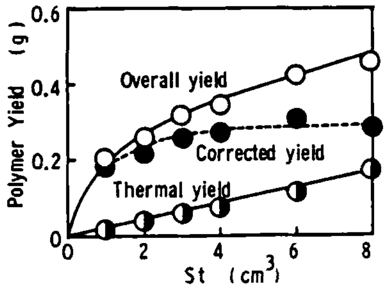

FIG. 4. Plots of (○) overall yield, (●) corrected yield, and (◑) thermal polymer yield vs. amount of St in the feed. PSS-Na = 0.1 g, H_2O = 5 cm^3; 85°C, 4 hr.

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shaking, a maximum polymer yield was obtained at 1 cm^3 of MMA (Fig. 3A). This phenomenon cannot be explained at the present time. By subtracting the thermal yield from the overall yield, the corrected yield was calculated. In excess of 1 cm^3 of MMA, the yield became independent of the amount of MMA. Except for the maximum, this behavior has been also observed in the polymerization of MMA initiated with other polysulfonates [1-7] and may be explained by the following consideration. As mentioned above, the first step of the polymerization is the incorporation of MMA into the hydrophobic areas. When a sufficient amount of MMA is added, the areas may be saturated with MMA. Thus, the excess of MMA becomes useless.

On the other hand, the effect of the amount of St on the polymerization with shaking was shown in Fig. 4. In this case, a maximum polymer yield was not observed.

Previously, Asahara et al. [14] reported that micelles of some detergents can initiate the radical polymerizations of MMA and St but not that of AN. The kinetic features of the polymerization are very similar to those described in the present paper. For example, Fig. 5 shows the results in the polymerization of MMA initiated with sodium tetrapropylenebenzene sulfonate (ABS). The filled points indicate the number of the polymer molecules produced in the polymerizations with varying initial concentration of ABS. Asahara et al. connected these points by the solid straight line. However, the present authors considered that the dotted line could also be applied. The open points indicate the relationship between the polymer yield and the initial concentration of MMA. The dotted line through the filled points and the line through the open points in Fig. 5 are similar to the lines in Figs. 1, 3, and 4. Thus, it can be considered

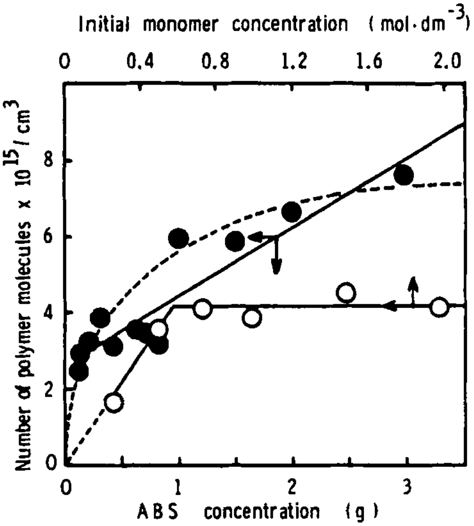

FIG. 5. Relationships between the quantities of polymer produced and initial MMA concentrations or ABS (detergent) concentrations (water 100 g; 80°C, 2 hr): (—) by Asahara et al. (----) by the present authors; (●) MMA 10 g, ABS varied; (○) MMA varied, ABS 0.3 g.

that the micelles formed with ABS detergent and the hydrophobic areas formed by PSS-Na are very much alike. The polymerizing activity of ABS differs from that of PSS-Na, i. e., ABS can initiate the polymerization of St more easily than MMA, while PSS-Na shows the opposite activity.

Structure of Polymerized System by Scanning Electron Microscopy

As mentioned above, the polymerization proceeds in the hydrophobic areas formed by PSS-Na. Therefore, the structure of the polymerized system was studied by JSM-35 type scanning electron microscopy (Nihon Denshi Co.). One drop of the reaction system was mounted on cylindrical brass support with nitrocellulose film, freeze-dried under vacuum, and rendered electrically conductive with a 20-30 nm coating of gold. Then it was viewed in a stereoscanning electron microscope operating at an accelerating voltage of 15 kV.

As shown in Fig. 6, PSS-Na (No. 4) dissolved in the water phase

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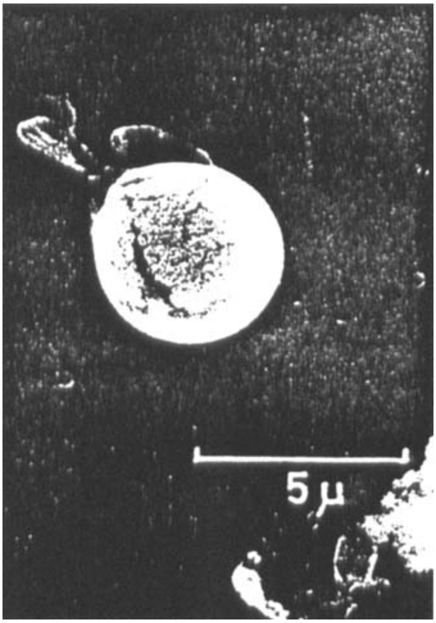

FIG. 6. Surface view of PSS-Na (0.1 g of PSS-Na No. 4) dissolved in 5 cm^3 of H_2O and diluted with water to 500 cm^3.

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was considered to have a possibility of forming micelles or hydrophobic areas. Figure 7 shows the structure of the polymerized system. Many particles, whose diameter was about 1×10^3 nm, can be seen. This structure suggests that the polymerization proceeded mainly at the interior of the hydrophobic areas. This observation agreed well with the results shown in Figs. 1, 3, and 4, i. e., PSS-Na in a higher concentration entangled with each other and could not form the sufficient and suitable hydrophobic areas to incorporate MMA.

Proof of Radical Mechanism

Into a mixture of 3 cm^3 of MMA and 0.1 g of PSS-Na in 5 cm^3 of water was added 0.1 g diphenylpicrylhydrazyl (DPPH), hydroquinone (HQ), or benzoquinone (BQ) and this mixture shaken at 85°C for 3 hr. The results obtained, listed in Table 5, show that addition of these reagents completely inhibited the polymerization. Thus, it was

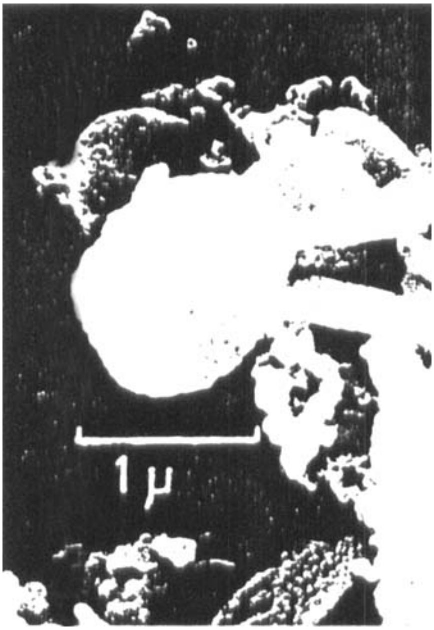

FIG. 7. Surface view of polymerized system. Polymerization of MMA (3 cm^3) was carried out in water (5 cm^3) containing 0.1 g of PSS-Na (No. 4) at 85°C for 3 hr on standing. The water layer was pipetted out and diluted with water to 500 cm^3.

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TABLE 5. Effects of Radical Scavenger on the Polymerization of MMA Initiated with PSS-Na[a]

Radical scavenger		
Type	Amt (g)	Conversion (%)
None	-	16.7
DPPH	0.1	0
BQ	0.1	0
HQ	0.1	0

[a] PSS-Na = 0.1 g, MMA = 3 cm^3, H_2O = 5 cm^3; 85°C, 3 hr.

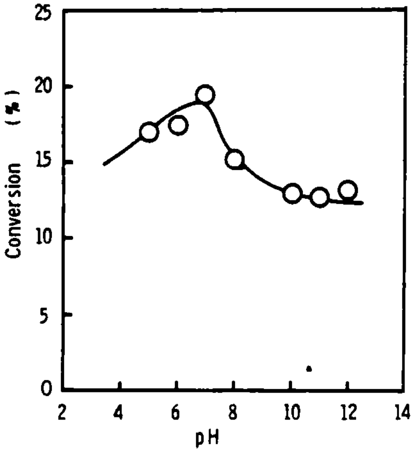

FIG. 8. Conversion of MMA vs. pH of the aqueous phase of the reaction system. MMA = 3 cm^3, PSS-Na = 0.1 g, H_2O = 5 cm^3; 85°C, 3 hr. Buffer solutions were prepared by the following systems: pH 5-6, M/10 citric acid-M/5 Na_2HPO_4; pH 7, M/10 HCl-M/20 $Na_2B_4O_7$; pH 8, M/15 Na_2HPO_4-M/15 KH_2PO_4; pH 9, M/15 KH_2PO_4-M/20 $Na_2B_4O_7$; pH 10, M/20 $Na_2B_4O_7$-M/10 NaOH; pH 11-12, M/10 NaOH-M/10 Na_2HPO_4.

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concluded that the polymerization proceeded through a radical mechanism.

Effect of pH of the Aqueous Phase on the Rate of Polymerization

The effect of pH of the aqueous phase on the conversion of MMA was observed (Fig. 8). The polymerization showed a maximum rate in approximately neutral medium. The same results were also obtained in the polymerizations with sodium poly(methallyl sulfonate) [2] and with sodium poly(allyl sulfonate) [3]. It is considered that, at such a pH, the sulfonate group can exist as a bare anion apart from the Na cation. In an acidic medium, the sulfonate anion is transformed un-ionized sulfonic acid and is able to take on a positively charged vinyl group only with difficulty. On the other hand, in an alkaline medium, the hydroxide ion surrounds the positive part of the vinyl monomer to separate it from the sulfonate ion.

In order to confirm that this view is correct, the effect of potassium fluoride on the rate of polymerization was investigated. The results

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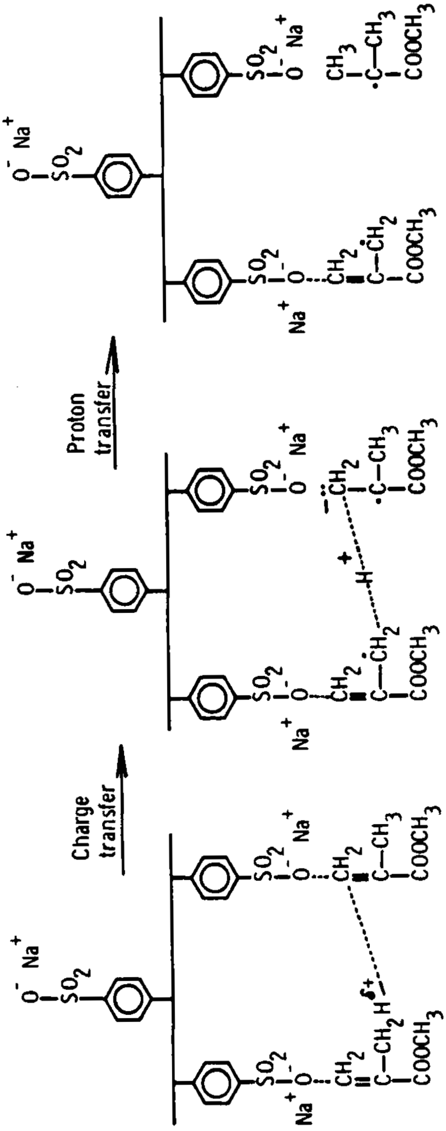

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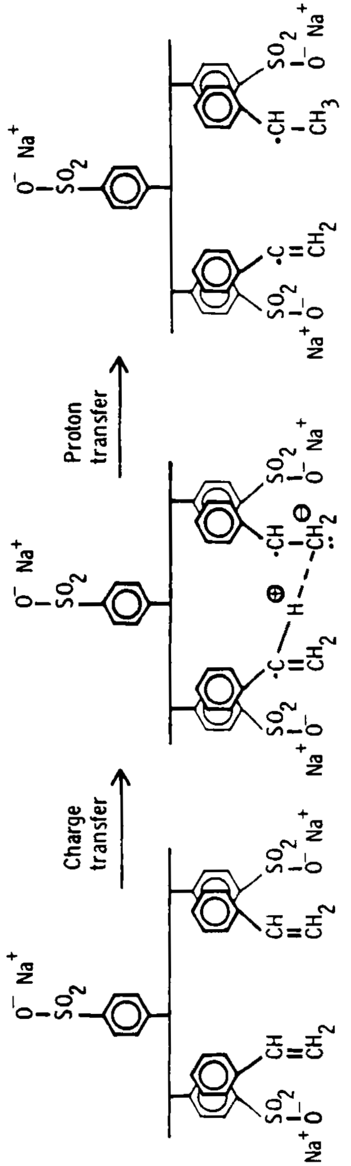

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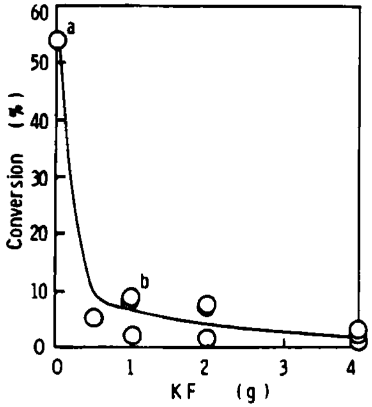

FIG. 9. Effect of F^- ion on the conversion of MMA PSS-Na: (a) $\overline{P}_n$ of poly-MMA = 2.52 × 10^4; (b) $\overline{P}_n$ of poly-MMA = 1.69 × 10^4. PSS-Na ($\overline{DP}_n$ = 107, No. 4 in Table 1) = 0.1 g, MMA = 3 cm^3, H_2O = 5 cm^3, 85°C, 3 hr.

shown in Fig. 9 were obtained. Potassium fluoride can give the strong anion F^-. The fluoride anion surrounds the positively charged part of MMA, and MMA cannot approach to the active SO_3^- anion part of PSS^-. Therefore, the polymerization of MMA could not be initiated. Figure 9 clearly shows this.

Initiation Mechanism

As discussed previously [2, 3], the vinyl group of monomer is considered to be adsorbed first on the SO_3^- group of the macromolecule. Thus, only the monomer having positively charged vinyl group can be polymerized. Between two adsorbed monomers, a charge transfer, followed by a proton transfer, takes place. These considerations explain the polymerization of MMA with PSS-Na. The mechanism is expressed by Eq. (1).

In the case of St, the initiation mechanism shown in Eq. (2) was assumed, concluding in a π-complex formation between the phenyl groups of phenyl sulfonate and those of St.

AN is somewhat hydrophilic. Therefore, AN can hardly be incorporated into the hydrophobic area formed by PSS-Na in water, and AN was thus not polymerized.

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