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Vinyl Polymerization. 350. Polymerization of Methyl Methacrylate Initiated by the System Sodium Polyvinyl Sulfonate)/Ferric Chloride/Water

Minoru Imoto[a]; Hideki Suzuki[a]; Tatsuro Ouchi[a]

[a] Department of Applied Chemistry, Faculty of Engineering Kansai University Senriyama, Suita-shi, Osaka, Japan

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MINORU IMOTO, HIDEKI SUZUKI, and TATSURO OUCHI

Department of Applied Chemistry
Faculty of Engineering
Kansai University
Senriyama, Suita-shi
Osaka, Japan

ABSTRACT

In an aqueous medium, sodium poly(vinyl sulfonate)(PVS-Na) initiated radical polymerization of methyl methacrylate (MMA) in the presence of ferric chloride. The presence of water and Fe(III) ion was essential. The polymerization was concluded to take place in the aqueous phase. The effects of the amount of water, MMA, Fe(III) ion, and temperature on the polymerization were studied. The mechanism of the initiation is discussed.

INTRODUCTION

Recently, we reported that an aqueous solution of sodium poly(meth-allyl sulfonate) (PMAS-Na) [1] or the sodium salt of partially sulfonated polystyrene(PS-S-Na) [2] could polymerize some vinyl

monomers through a radical mechanism in the absence of any usual
initiator or metallic ion. In both cases, Michaelis-Menten relation-
ship was applicable.

In the present paper, we would like to report on the polymeriza-
tion of methyl methacrylate (MMA) by an aqueous solution of sodium
poly(vinyl sulfonate) (PVS-Na). Very interestingly, it was found that
the coexistence of some metallic ion was indispensable for the polym-
erization. Fe(III) ion was especially effective. In the necessity of
the metallic ion this system differs completely from the cases of
PMAS-Na and PS-S-Na.

The polymerization described in the present paper belongs to the
class of "uncatalyzed" polymerizations, and takes place by the re-
action of MMA with macromolecule and water. It was concluded
that the polymerization proceeded in the aqueous phase.

In order to verify that the initiating activity of PVS-Na was
afforded by the macromolecular effect, the reaction of the system
of MMA/FeCl$_3$/water was carried out under the same conditions
as those by PVS-Na, in the presence of sodium ethyl sulfonate(II)
which is considered a monomeric model compound of PVS-Na(I).

$$-\left(\!\!-CH_2-CH-\!\!\right)_n \quad\quad CH_3-CH_2$$
$$||$$
$$SO_3^-Na^+SO_3^-Na^+$$

$$III$$
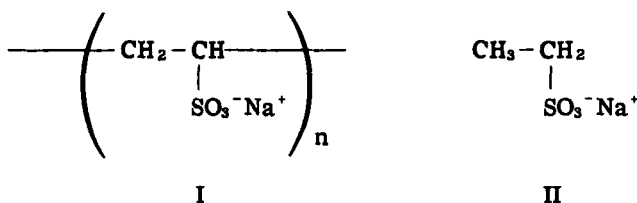
EXPERIMENTAL

Materials

Sodium vinyl sulfonate was prepared as described by Nagase and
Sakaguchi [3]. The scheme was as outlined in Eq. (1).

$$CH_3CH_2OH \xrightarrow{ClSO_3H} CH_3CH_2OSO_3H \xrightarrow{SO_3} HO_3S-CH_2CH_2-OSO_3H$$

$$\xrightarrow{NaOH} CH_2=CH-SO_3Na \quad\quad\quad\quad\quad (1)$$
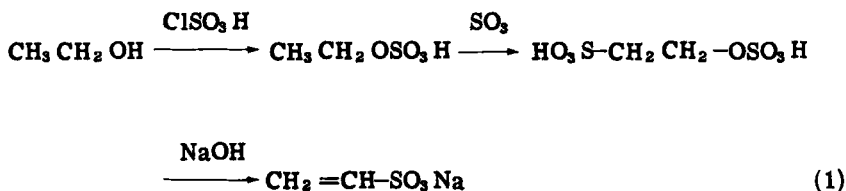
The aqueous solution finally obtained was evaporated to dryness under vacuum at $90°$ C. The polymerization of sodium vinyl sulfonate was as carried out by Breslow and Kutner [4].

A 75-g portion of the crude vinyl sulfonate obtained above was dissolved in 75 ml of water, and 0.8 g of ammonium persulfate, 1.5 g of sodium thiosulfite, and 1.5 g of sodium hydroxide were added. The solution was warmed at $40°$ C for 21 hr with stirring. During the polymerization, at each 7 hr, 0.38 g of ammonium persulfate was added. The total weight of persulfate fed was 1.14 g. The reaction mixture was poured into a large amount of methanol to separate out the poly(vinyl sulfonate). The collected polymer was purified twice by reprecipitation from its water solution with methanol. Sodium poly(vinyl sulfonate) (PVS-Na) thus obtained was white powder.

Analysis. Calcd. for $(C_2H_3SO_3Na \cdot H_2O)_n$: C, 16.21%; H, 3.40%. Found: C, 15.44%; H, 3.08%.

Breslow et al. [4] determined the relationship between $[\eta]$ ($30°$ C, H_2O) and the number-average degree of polymerization $\overline{P}_n$. According to the relationship, $\overline{P}_n$ of PVS-Na obtained here was estimated to be 87.

The content of peroxide groups in PVS-Na could not be detected by the KI method.

MMA, styrene(St), and acrylonitrile(AN) were purified by the usual method. Metallic chlorides were of special grade and used without further purification. Water was ion-exchanged and distilled.

Procedure

Vinyl monomer and an aqueous solution of PVS-Na were placed in a tube and sealed under vacuum after thawing with nitrogen. The tube was heated at $85°$ C under shaking. The contents were poured into a large amount of methanol, containing ferric chloride at a concentration of about 5% to precipitate the polymer. The collected polymer was washed thoroughly with water and methanol. After drying, the polymer was weighed. The conversion of MMA was calculated from the weight of polymer by dividing by the weight of MMA in the feed.

The number-average degree of polymerization $\overline{P}_n$ of PMMA, which was purified by reprecipitation using acetone and methanol, was determined from $[\eta]$ measured in benzene at $30°$ C, by the equation of Welch [5].

$$\log \overline{P}_n = 3.346 + 1.32 \log [\eta]$$

RESULTS AND DISCUSSION

Polymerization of MMA with Sodium Ethyl Sulfonate in Aqueous Ferric Chloride Solution

A 3-ml portion of MMA and 0.05 g of sodium ethyl sulfonate in 5 ml of water were heated under vacuum at 85°C for 3 hr in the absence or presence of 0.005 g of $FeCl_3 \cdot 6H_2O$. In neither case was polymerization of MMA observed. Accordingly, sodium ethyl sulfonate, which was used as a monomeric analog of PVS-Na, was concluded to have no initiating activity for the polymerization of MMA.

Indispensability of Metallic Ion for Polymerization

To a mixture of 3 ml of MMA, 0.05 g of PVS-Na, and 5 ml of water, was added 0.005 g of metallic chloride, and polymerization was carried out at 85°C for 3 hr. The results obtained are listed in Table 1. It was concluded that the presence of metallic ion was necessary for the polymerization of MMA. Fe(III) ion showed the most favorable effect. Therefore, Fe(III)-ion was used in all subsequent polymerizations.

TABLE 1. Effect of Various Metallic Chlorides on the Polymerization[a]

Metallic chloride	Conversion (%)
None	0.7
$CuCl_2 \cdot 2H_2O$	5.8
$FeCl_3 \cdot 6H_2O$	48.5
$FeCl_2 \cdot nH_2O$	2.3
CuCl	3.7
$NiCl_2 \cdot 6H_2O$	0.9
$SnCl_4 \cdot xH_2O$	0.8
$HgCl_2$	0.5

[a]Polymerization conditions: MMA = 3 ml; PVS-Na = 0.05 g; H_2O = 5 ml; metallic chloride = 5 mg; 85°C, 3 hr.
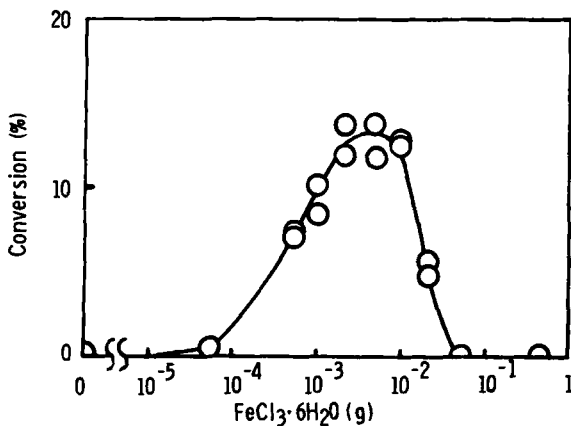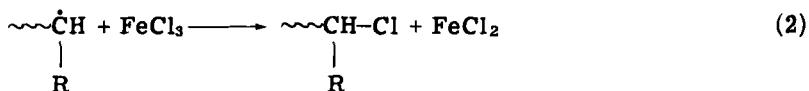
FIG. 1. Effect of the amount of ferric chloride on the polymeriza-
tion. MMA = 3 ml; PVS-Na = 0.05 g; H_2O = 3 ml; 85°C; 1.5 hr.

The effect of the amount of metallic ion on the rate of polymeriza-
tion was also studied. At constant amounts of MMA and PVS-Na (3
ml and 0.05 g, respectively), the amount of ferric chloride was
varied. The results obtained are shown in Fig. 1.

With 5 mg, Fe(III) ion, a maximum conversion of MMA was ob-
tained (Fig. 1). When metallic ion was used in excess, it became an
inhibitor [Eq. (2)].

$$\sim\sim\overset{\bullet}{C}H + FeCl_3 \longrightarrow \sim\sim CH-Cl + FeCl_2 \qquad (2)$$
$$\qquad\quad | \qquad\qquad\qquad\quad |$$
$$\qquad\quad R \qquad\qquad\qquad\quad R$$

Selectivity of Vinyl Monomer

A mixture of 3 ml of monomer, 0.05 g of PVS-Na, 3 ml of water
and 0.005 g of $FeCl_3 \cdot 6H_2O$ was heated under vacuum at 85°C for
1.5 hr.

For MMA, St, and AN the conversions were 48.5%, 1.0%, and
7.4%, respectively.

We have repeatedly written that MMA can be polymerized specifi-
cally easily [3], in the "uncatalyzed polymerization" carried out in
water in the presence of macromolecule and a small amount of cupric

ion. The macromolecules used were silk, cellulose, starch, nylon, and α-amylase. The results obtained in the present paper suggest that the reaction mechanism may resemble that in the case of the uncatalyzed polymerization.

On the contrary, when PMAS-Na or PS-S-Na was used, no metallic ion was necessary for polymerization. The mechanism, which differs from that of the uncatalyzed polymerization, was proposed previously by the present authors [1], i. e., vinyl monomer is adsorbed directly onto SO_3^- group. In the case of the uncatalyzed polymerization, vinyl monomer enters as a ligand into one site of a complex of metallic ion with macromolecule.

Proof of Radical Mechanism

Into a mixture of 3 ml of MMA and an aqueous solution of 0.05 g of PVS-Na and 0.005 g of $FeCl_3 \cdot 6H_2O$ in 5 ml of water, 0.1 g of diphenylpicrylhydrazyl, hydroquinone, or benzoquinone was added as a radical scavenger. Another polymerization was carried out in air. In no case did polymerization take place.

As further proof, copolymerization of MMA and St was carried out. This experiment gave the results shown in Fig. 2. These results show conclusively that the polymerization proceeded through a radical mechanism.

Effect of Water

At constant amounts of MMA (3 ml), PVS-Na (0.05 g), and metallic chloride (0.005 g), the effect of the amount of water on the conversion of MMA was studied. The results are shown in Fig. 3. As can be seen clearly, the presence of water is indispensable to the polymerization. However, with a small amount of water (about 1.5 ml), the maximum conversion was obtained. This is due to an especially high concentration of PVS-Na. As shall be stated in the later section, the polymerization proceeds in the aqueous phase [6-8]. Accordingly the concentration of MMA increases abnormally in the area surrounding PVS^-. After passing this point, this favored effect on the polymerization may vanish, and thereafter the polymerization proceeds normally.

Effect of Amount of PVS-Na

Various amounts of PVS-Na, 3 ml of MMA, and 5 ml of water were heated in the presence of 0.005 g of $FeCl_3 \cdot 6H_2O$ at 85°C for 3 hr. The results in Fig. 4 were obtained.
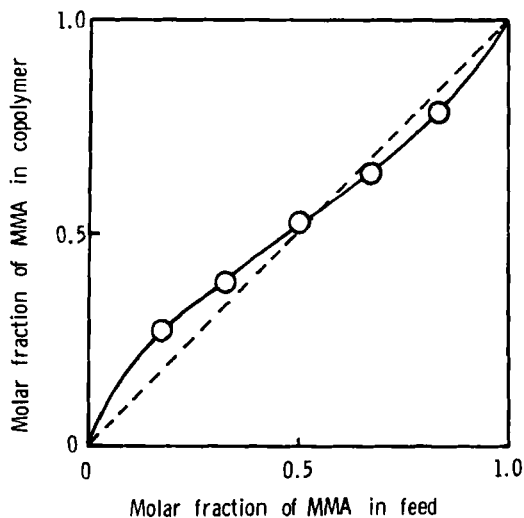
FIG. 2. Composition curve of copolymerization of MMA with St by PVS-Na/Fe(III) ion system. Monomer = 6 ml; PVS-Na = 0.05 g; H_2O = 3 ml; $FeCl_3 \cdot 6H_2O$ = 5 mg; $85°$ C; 1.5 hr.
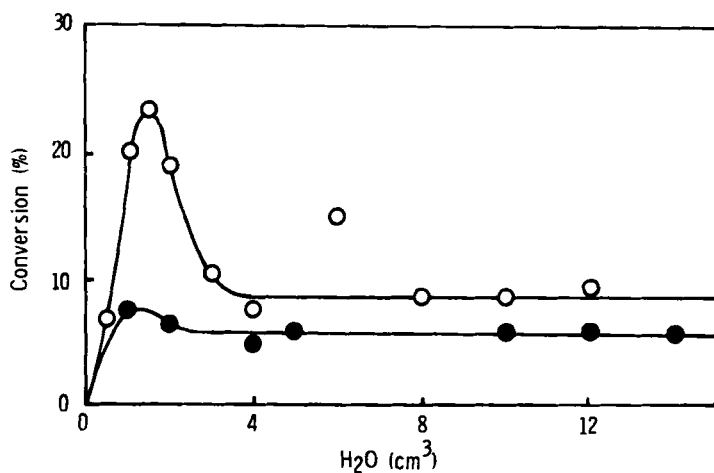

FIG. 3. Effect of the amount of H_2O on the polymerization: ($\circ$) $FeCl_3 \cdot 6H_2O$ = 5 mg, 1 hr; ($\bullet$) $CuCl_2 \cdot 2H_2O$ = 5 mg, 3 hr. MMA = 3 ml; PVS-Na = 0.05 g; $85°$ C.
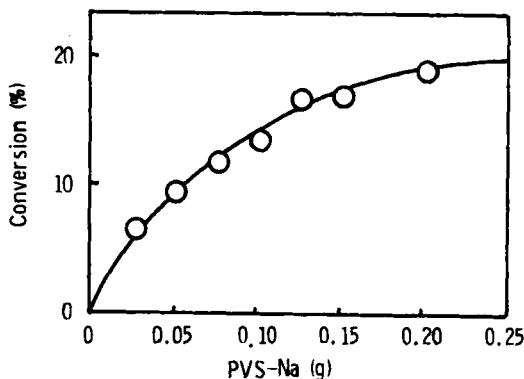
FIG. 4. Conversion of MMA vs. amount of PVS-Na in the feed.
MMA = 3 ml; H_2O = 10 ml; $FeCl_3 \cdot 6H_2O$ = 10 mg; 85° C; 1.5 hr.

When the concentration of PVS-Na in the water layer was not so
large, the rate of polymerization of MMA increased with the concen-
tration of PVS-Na, but gradually the rate became independent of the
concentration of PVS-Na. The reason is considered to be as follows.
The concentration of MMA in the aqueous layer is constant. How-
ever, as MMA polymerizes, monomeric MMA migrates into the
aqueous layer from the MMA phase which remains insoluble in
water. The rate of migration is too small to cover the polymeriza-
tion quantity of MMA in water. Accordingly, the concentration of
MMA in the water layer becomes lower than the approriate one
for the concentration of PVS-Na, i.e., the excess of PVS-Na becomes
ineffective.

Location of the Polymerization

In order to ascertain where the polymerization takes place, the
polymerization of MMA was carried out without shaking. A 3-ml
MMA and a solution of 0.05 g of PVS-Na and 5 mg of $FeCl_3 \cdot 6H_2O$
in 5 ml of water were sealed in a tube under vacuum as described
above and were allowed to stand at 85° C. After 1 hr, the upper
layer of MMA was clear, while the lower water layer became thickly
muddy. The MMA layer was pipetted out carefully and poured into
methanol to precipitate the PMMA. However, little PMMA was
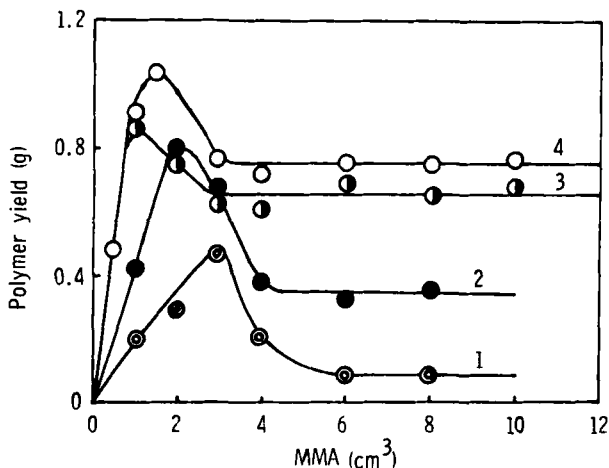obtained. On the contrary, the water layer gave PMMA in a yield
reaching 9.6%.

FIG. 5. Yield of PMMA vs. amount of MMA in the feed: (1) FeCl$_3$ ·6H$_2$O = 3 mg, H$_2$O = 3 ml, 1.0 hr; (2) FeCl$_3$ ·6H$_2$O = 5 mg, H$_2$O = 3 ml, 1.5 hr; (3) FeCl$_3$·6H$_2$O = 5 mg, H$_2$O = 5 ml, 2.0 hr; (4) FeCl$_3$·6H$_2$O = 5 mg, H$_2$O = 10 ml, 2.0 hr. All polymerizations at 85° C, PVS-Na = 0.05 g.

This result indicates that the polymerization proceeded in the aqueous phase. This conclusion agreed well with the observation obtained in the case of the polymerization of MMA initiated with the system of starch, water, and carbon tetrachloride [9].

Effect of Amount of MMA

Polymerization of various amounts of MMA in the presence of 0.05 g PVS-Na, 3, 5, or 10 cm^3 of water and 0.003 or 0.005 g of FeCl$_3$· 6H$_2$O was carried out at 85° C for 1-2 hr.

The relationship between the yield of MMA and MMA in the feed was unusual (Fig. 5). It showed the existence of a maximum at small MMA feed. At the present time, this unusual finding cannot be explained.

Effect of Temperature

The polymerization of a system of 3 ml MMA, 0.05 g PVS-Na, 5 ml water, and 0.005 g FeCl$_3$ ·6H$_2$O was carried out at 65-95°C for 2 hr (Fig. 6).
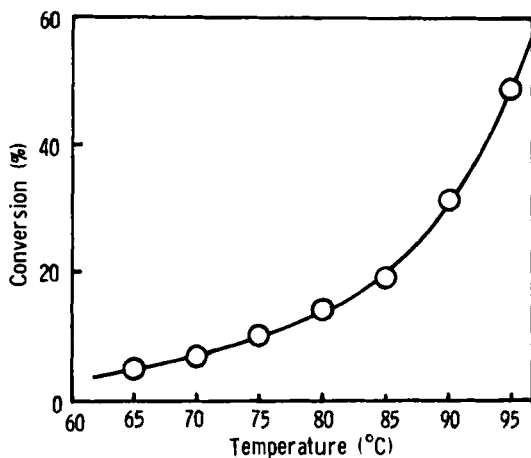
FIG. 6. Conversion of MMA vs. polymerization temperature. MMA = 3 ml; PVS-Na = 0.05 g; H_2O = 5 ml; $FeCl_3 \cdot 6H_2O$ = 5 mg; 2 hr.
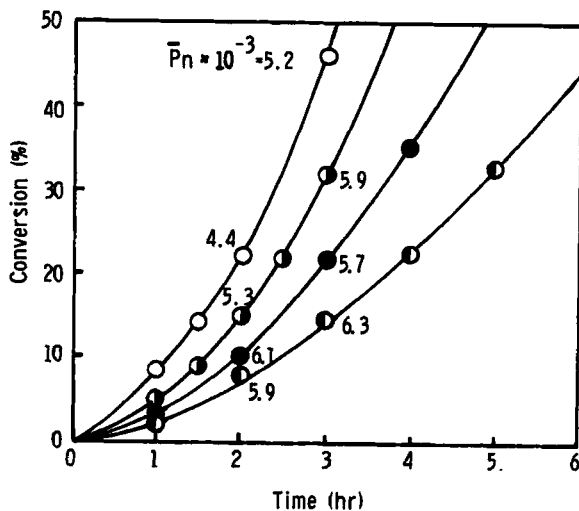

FIG. 7. Time-conversion curves and $\overline{P}_n$ of PMMA at several temperatures: (◐) 70° C; (●) 75° C; (◑) 80° C; (○) 85° C. MMA = 3 ml; PVS-Na = 0.05 g; H_2O = 5 ml; $FeCl_3 \cdot 6H_2O$ = 5 mg.

To determine the rate of polymerization of MMA, time-conversion curves were obtained at 70, 75, 80 and 85° C, as shown in Fig. 7. No straight relationships were obtained. This is attributed to the inhibiting effect of Fe(III) ion on the propagation reaction. Moreover, at conversion in excess of about 20%, the Trommsdorff effect enters into the polymerization. Accordingly, it was impossible to determine an exact rate of polymerization. However, to evaluate an approximate value of overall activation energy, tangents at zero time were drawn. From these lines, the approximate rates of polymerization were estimated and applied to the Arrhenius equation. The calculated activation energy was 22 kJ/mole.

$\overline{P}_n$ of PMMA obtained after 2 and 3 hr at every temperature were also shown in Fig. 7. $\overline{P}_n$ at 3 hr was larger than that at 2 hr. This fact is in good agreement with the above conclusion that the Trommsdorff effect participates in the polymerization. As mentioned in the experimental section, $\overline{P}_n$ of PVS-Na was 87. Accordingly, it could be concluded that the polymerization was not a matrix polymerization.

Effect of Sodium Sulfate and Urea

To a mixture of 3 ml MMA, 0.05 g PVS-Na, 5 ml of H_2O, and 5 mg of $FeCl_3 \cdot 6H_2O$, sodium sulfate or urea was added and heated at 85° C for 3 hr. As shown in Table 2, the conversion decreased remarkably.

TABLE 2. Effects of Sodium Sulfate and Urea on the Polymerization of MMA[a]

Added Substance		Conversion (%)
Type	Wt (g)	
None	—	48.5
Na_2SO_4	0.01	34.9
	0.1	6.6
	1.0	3.2
Urea	0.1	3.1

[a]MMA = 3 ml; PMAS-Na = 0.05 g; H_2O = 5 ml; $FeCl_3 \cdot 6H_2O$ = 5 mg; 85° C; 3 hr.

Clearly, SO_4^{2-} or NH_2CONH_2 occupies the complexing site of
Fe(III) ion, and it becomes more difficult for MMA, having a less basic
character, to approach to the Fe(III) ion. Furthermore, even if MMA
and H_2O can form a complex with Fe(III) ion, the macromolecular
effect of PVS-Na for the polymerization diminishes as a result of
participation of low molecular SO_4^{2-} ion or urea in the complex.

Mechanism of Initiation Reaction

Similar to the initiation mechanism for the usual uncatalyzed
polymerization, the mechanism shown in Eq. (3) can be considered.

$$(3)$$
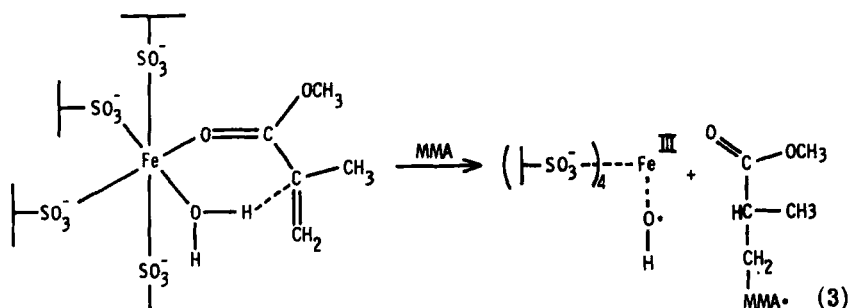
Difference between PMAS-Na and PVS-Na as Catalyst

The reason why PMAS-Na could initiate a radical polymerization
in the absence of metallic ion was discussed in a preceding paper [1].
Vinyl monomer having $\delta+$ charge on the $CH_2=$ group is adsorbed onto
the SO_3^- group of PMAS-Na. Two alternate SO_3^- groups are so con-
structed, that the two adsorbed vinyl monomers are situated almost
in parallel and in the range of van der Waals distance. The initiation
mechanism was concluded to consist of two steps: formation of a
charge-transfer complex between two monomers and migration of a
proton. The process may be represented as shown in Eq. (4).

PVS-Na could initiate radical polymerization only in the presence
of metallic ion. In order to explain the difference from the case of
PMAS⁻Na⁺, the following consideration was introduced. As in the
molecule of PMAS⁻Na⁺, the $-SO_3^-$ groups of PVS⁻Na⁺ repel each other
and are situated as apart as possible. By using five units of vinyl

$$(4)$$

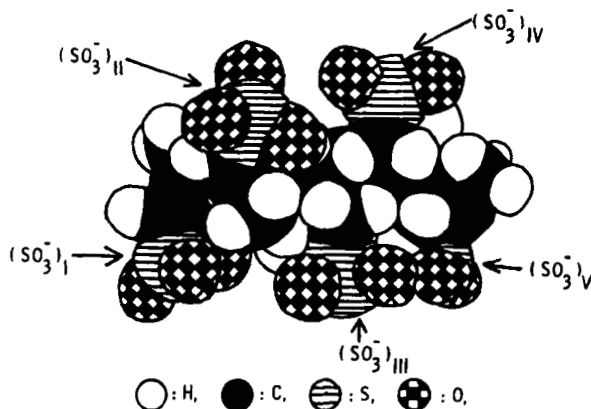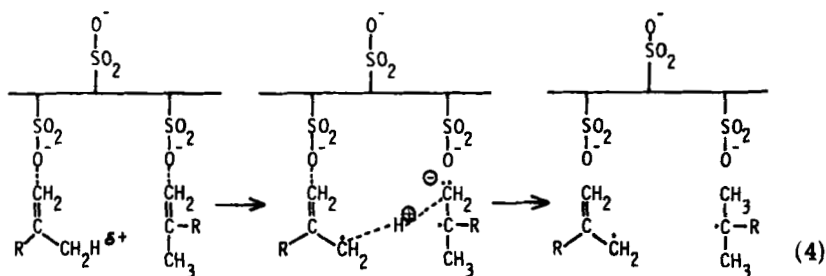$\bigcirc$: H, $\bullet$: C, $\ominus$: S, $\oplus$: O,

FIG. 8. Stewart model of five unit polymer of vinyl sulfonate.

sulfonate monomer, a probable Stewart model was constructed as shown in Fig. 8. From the models, the distances between two centers of the alternate sulfur atoms of PMAS⁻ and PVS⁻ were assumed to be about 0.55 nm and 0.50 nm, respectively. However, in the present case of PVS⁻, two vinyl monomers could not be arranged parallel, but in sideways. Accordingly, the two vinyl monomers adsorbed onto PVS⁻ could not be situated in an area of van der Waals distance.

The mechanisms of polymerization by the two catalysts differ. Initiation by PMAS⁻ takes place through hydrogen-atom transfer between two neighboring monomers by Flory's bimolecular reaction mechanism and that by PVS⁻ by complexing with metallic ion, water, and monomer.

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