BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49 (5), 1342—1345 (1976)

Vinyl Polymerization. 341.[1] A Proposal of a Mechanism for Radical Polymerization of Vinyl Monomers with Sodium Polymethallylsulfonate

Minoru Imoto, Yoshiaki Nakamura, and Tatsuro Ouchi

Department of Applied Chemistry, Faculty of Engineering, Kansai University, Suita-shi, Osaka 564

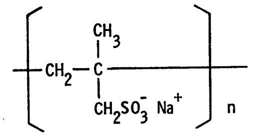
(Received October 1, 1975)

In aqueous solution, sodium polymethallylsulfonate (PMAS-Na) can initiate a radical polymerization of vinyl monomer which has positively charged vinyl group. In the polymerization of MMA, Michaelis-Menten equation was applicable. From the results obtained, a bimolecular initiation mechanism, involving hydrogen atom transfer, was concluded to be reasonable. The relationships between pH of the aqueous layer and conversion and between polymerization temperature and conversion were of downward bell type. By Stewart model, it was found that PMAS-Na has a very rigid conformation. This structure can be compared with a rigid tertiary structure of enzyme, and the reaction appearances of enzyme and PMAS-Na can be considered to resemble very much each other.

Recently we reported[2] that an aqueous solution of sodium polymethallylsulfonate (PMAS-Na) could polymerize some vinyl monomers in the absence of any usual initiator. In the present paper, we would like to propose a probable mechanism for the generation of an initiating radical species by the reaction of sulfonate group with vinyl monomer, *i.e.* a generation by the interaction of two molecules of vinyl monomer through the Flory's mechanism.[3]

Experimental

Materials. PMAS-Na was prepared by the polymerization of sodium methallylsulfonate with ammonium peroxodisulfate in water, as described in the former report[2]: [η] 0.08 dl/g (30 °C, in water). Peroxide group and metallic ion in PMAS-Na were hardly detected by KI-method and atomic absorption spectrometry technique, respectively.



$$\left[-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_2SO_3^- Na^+}{C}}- \right]_n$$

PMAS-Na

Styrene (St), methyl methacrylate (MMA) and acrylonitrile (AN) were of commercial and purified by usual method. *p*-Nitrostyrene (*p*-NO_2-St)[4] and *p*-methoxystyrene (*p*-CH_3O-St)[5] were synthesized according to the literatures. Water was ion-exchanged.

Procedure. Vinyl monomer and an aqueous solution of PMAS-Na were placed in a tube and seald under vacuum after thawing with nitrogen. The tube was heated at 85 °C for 1 h under shaking. The content was poured into a large amount of methanol to precipitate the polymer. The collected polymer was washed throughly with water and the polymer of vinyl monomer was separated. After drying, the polymer was weighed.

Results and Discussion

Proof of Radical Mechanism. In a mixture of 3 ml of MMA and an aqueous solution of 0.05 g of PMAS-Na in 5 ml of water, diphenylpicrylhydrazyl, hydroquinone or benzoquinone was added in an amount of 0.1 g, as radical scavenger. Another polymerization without radical scavenger was carried out in air. In all cases, formation of poly-MMA was not observed. Thus, it was concluded that the polymerization proceeded through a radical mechanism.

Efficiency of Grafting. In the polymerization of MMA, the efficiency of grafting was measured by extracting the polymer obtained with benzene. The results showed that the grafting reaction did not take place.

Selectivity of Vinyl Monomer. A solution of 0.05 g of PMAS-Na in 5 ml of water and 3 ml of vinyl monomer were reacted as described in a former section. Five kinds of monomer were used. The conversions observed were drawn in Fig. 1. Here, "e" is the Alfey-Price's polymerization factor.[6] The conversion was found to be linearly proportional to the "+*e*"-value of the monomer. The "*e*"-value of —0.3 is considered to be the point at which a vinyl monomer behaves as a non-polarized molecule.

From the results, it was confirmed that only the vinyl monomer having plus-charged vinyl group could be polymerized by PMAS-Na. This conclusion agrees well with the consideration in which the plus-charged vinyl group is adsorbed on the minus-charged sulfonate group.

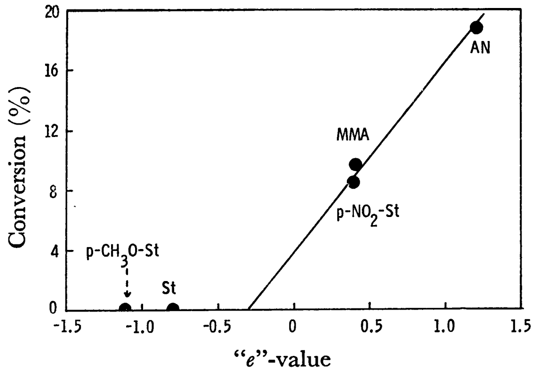


Fig. 1. Conversions of vinyl monomers *vs.* their "*e*"-values.

Relationship between Amounts of PMAS-Na and Polymer Yield. Using various amounts of MMA, the polymerization was carried out at 85 °C for 1 h to obtain the results shown in Fig. 2. The yield of polymer increased with the added amount of MMA and reached a constant yield at a certain point of the amount of MMA. Beyond the point, the yield became to be independent of the amount of MMA. This relationship between the polymer yield and the feeded amount of MMA resembles well to the relationship between the rate of reaction and the amount of substrate in enzymatic reaction.

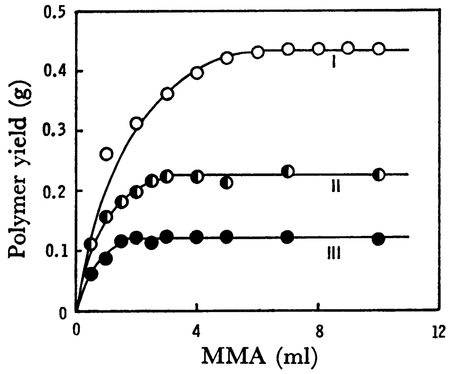


Fig. 2. Polymer yield *vs.* feeded amount of MMA.
H_2O: ○ 10 ml, ◐ 5 ml, ● 2.5 ml.
[PMAS-Na]=0.01 g per 1 ml of water. 85°C, 1 h.

Application of Michaelis-Menten Equation to the Polymerization of MMA. The results obtained in Fig. 2 were found to fit in Michaelis-Menten Equation (1);

$$E + S \underset{k_2}{\overset{k_1}{\rightleftharpoons}} ES \xrightarrow{k_3} E + P \qquad (1)$$

where E is PMAS-ion, S is MMA, ES is a adsorbed complex of MMA on PMAS-ion and P is a radical initiator. From Eq. 1, Lineweaver-Burk's Equation (2) is obtained.

$$\frac{1}{R_p} = \frac{K_a}{k_3[E]} \times \frac{1}{[S]} + \frac{1}{k_3[E]}$$

$$K_a = (k_2+k_3)/k_1 \qquad (2)$$

Here, as "P", we adopted poly-MMA instead of radical initiator. Accordingly, R_p in Eq. 2 is the rate of polymerization. By application of Eq. 2, the reciprocals of R_p were coordinated with those of the feeded amounts of MMA, as shown in Fig. 3. Straight lines were obtained. From the intercepts of the ordinate at the zero point and from the inclinations of the lines, $k_3[E]$ and Michaelis-Constant, K_a, were calculated as shown in Table 1.

As can be seen, K_a was obtained as a constant value of 1.06 ± 0.09, and $k_3[E]$ was almost proportional to [E]. Thus it was confirmed that Michaelis-Menten Equation fits in the present polymerization.

TABLE 1. VALUES OF K_a AND K_3 [E]
(PMAS-Na 0.01 g/ml H_2O; 85 °C, 1 h)

Case	H_2O (ml)	K_a (g)	$k_3[E]$ g/h
III	2.5	1.15	0.222
II	5	0.98	0.285
I	10	1.05	0.500

Effect of pH of the Aqueous Phase on the Rate of Polymerization of MMA. The effect of pH of the aqueous phase on the conversion of MMA was observed as shown in Fig. 4. It was very interesting that this radical polymerization showed the most rapid rate at the pH near to 6. It is considered that at such pH the PMAS-ion can exist in a bare state as sulfate anion apart from Na^+ cation. At acidic area, sulfate anion of PMAS-Na becomes to unionized sulfonic acid and to be difficult to adsorb a positively charged vinyl group. On the other hand, in alkaline area, hydroxide ion surrounds a positive part of vinyl monomer to put it apart from sulfate ion.

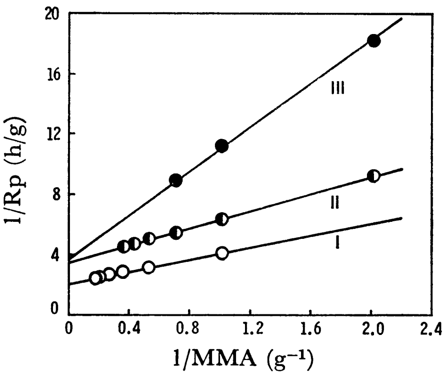


Fig. 3. Application of Eq. 2 to the results obtained in Fig. 2.

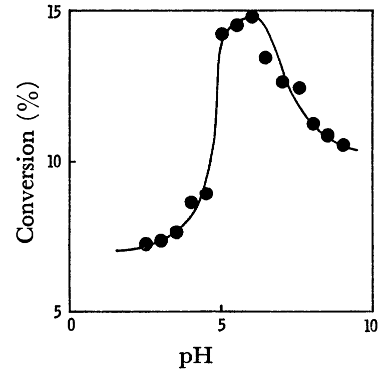


Fig. 4. Conversion of MMA *vs.* pH of the aqueous layer of the reaction system.
(MMA 3 ml, PMAS-Na 0.05 g, buffered water 5 ml; 85 °C, 1 hr. Buffer solutions were prepared by the following systems; pH 2.5—6.0, M/10 citric acid-M/5 Na_2HPO_4; pH 6.5—7.5, M/10 HCl-M/20 $Na_2B_4O_7$; pH 7.5—9.5, M/15 Na_2HPO_4-M/15 KH_2PO_4)

Effect of Reaction Temperature on the Rate of Reaction. The polymerization of MMA initiated with an aqueous solution of PMAS-Na was carried out at the temperature between 55 and 120 °C. The result can be seen in Fig. 5. The maximum conversion was obtained at 90 °C. Over this temperature, the degree of adsorption of MMA by $PMAS^{n-}$ is concluded to decrease.

From three points of A, B and C in Fig. 5, an overall activation energy, E, was calculated to be 12.8 kcal/mole, as shown in Fig. 6. Granting that $(2E_p - E_t)$ is 9.0 kcal/mol,[7] the activation energy of initiation, E_i, was calculated to be 16.6 kcal/mol from the equation, $2E = E_i + 2E_p - E_t$. Here E_p and E_t are activation energies of propagation and termination reactions, respectively.

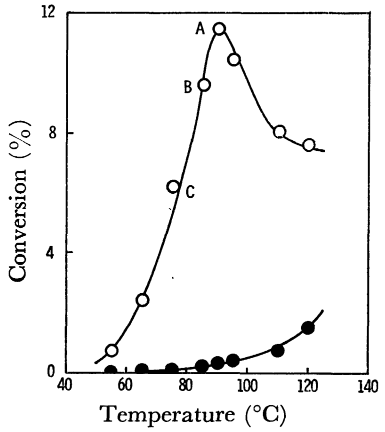


Fig. 5. Conversion of MMA *vs.* polymerization temperature. (MMA 3 ml, H_2O 5 ml, PMAS-Na 0.0 g (●) or 0.05 g (○); 1 h)

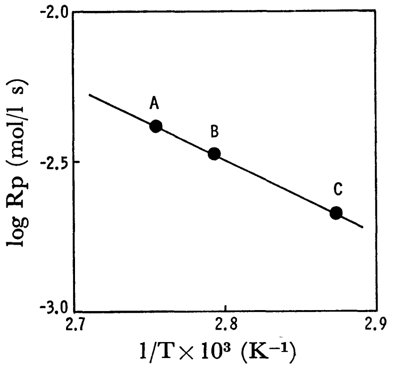


Fig. 6. Arrhenius plot of three points of A, B, and C in the former figure.

Mechanism of the Initiation Reaction. Figure 1 indicates that a mechanism which accomodates the results is one in which the plus-charged methylene of vinyl monomer is adsorbed to the SO_3^- group of $PMAS^{n-}$ and goes into reaction. The formula of polarized vinyl monomer having "$+e$"-value on CH_2 group is expressed as the formula (3).

$$\overset{\delta+}{CH_2}=CH-\overset{\delta-}{R} \qquad (3)$$

On the other hand, $-SO_3^-$ groups of $PMAS^{n-}$ repel each other and situate separately as far as they can. Thus, it is a reasonable consideration that the macromolecule of $PMAS^{n-}$ has a structure near to syndiotactic configuration. A probable Stewart's model of $PMAS^{n-}$ is shown in Fig. 7. In this model, only three units were taken. However, the structure of $PMAS^{n-}$ was found to be very rigid. In Fig. 7, furthermore, two adsorbed molecule of acrylonitrile were also shown. From the model it was concluded that the two vinyl monomers could exist within a van der Waals distance.

The rigid structure of $PMAS^{n-}$ is considered to correspond to a rigid tertiary structure of enzyme by which an enzyme can afford a specificitic reactivity to substrate.

As usually known, in enzymatic reaction, a relationship between rate of reaction and reaction temperature or pH of the reaction system is of downward bell type. Michaelis-Menten Equation was verified to be applicable. Thus, the observations obtained in the present paper agreed very well with enzymatic reaction figures.

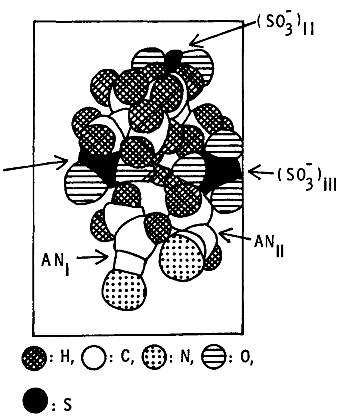
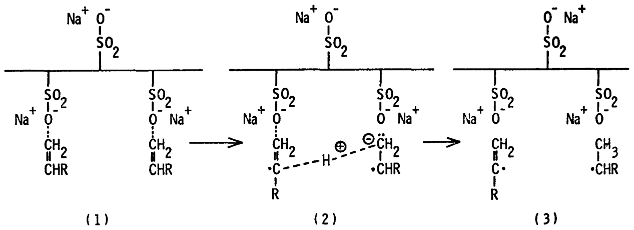


Fig. 7. Stewart's model of 3 units in $PMAS^{n-}$.

From the results obtained above, the mechanism of the initiation reaction was concluded to be as shown in the following Scheme 1.

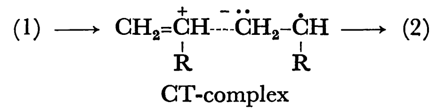


Scheme 1. Initiation mechanism of vinyl monomer by PMAS-Na.

By complexing of $-SO_3^-$ anion with positively charged $CH_2=$ group of the monomer, a following partial electron transfer may proceed.

$$-\overline{O}|^{-}\cdots\overset{\delta+}{CH_2}=CH-R \qquad (4)$$

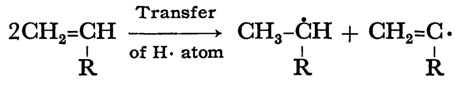
Thus, electron density around the carbon atom of $=CH-$ increases and becomes easier to donate its electron. In other words, a charge-transfer complex (CT-complex) becomes easier to be formed.

 (5)

$$(1) \longrightarrow \underset{\textstyle R}{CH_2=\overset{+}{C}H}\cdots\underset{\textstyle R}{\overset{-\,\cdot\cdot}{C}H_2\text{-}\dot{C}H} \longrightarrow (2) \qquad (5)$$

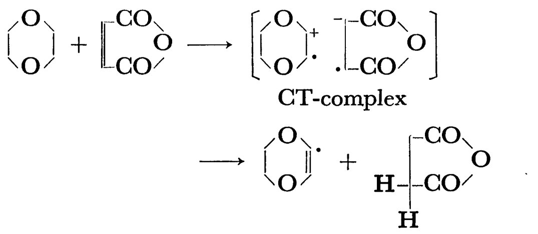
CT-complex

This initiating mechanism corresponds well to the Flory's mechanism which was proposed as Eq. (6) in 1937.[3)]

 (6)

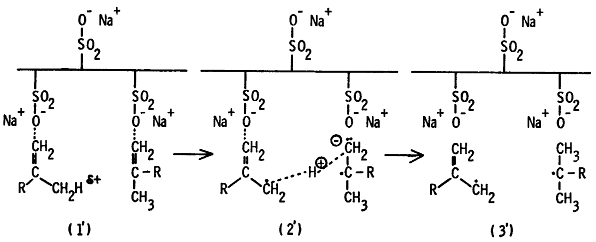
$$2\underset{\textstyle R}{CH_2=CH} \xrightarrow[\text{of H· atom}]{\text{Transfer}} \underset{\textstyle R}{CH_3\text{-}\dot{C}H} + \underset{\textstyle R}{CH_2=C\cdot} \qquad (6)$$

This mechanism was denied from the standpoint of the reaction energy. However, recently the Flory's mechanism involving hydrogen transfer was taken up as an initiation mechanism of the radical polymerization which proceeds through a charge-transfer (CT) complex. For example, one of the present authors (M. Imoto)[8)] assumed the following initiation mechanism as shown in Eq. (7):



(7)

Otsu and Sato succeeded to prove this H· transfer mechanism using the spin-trapping method.[9] Accordingly, the mechanism proposed as shown in Scheme 1 may be recognizable to be reasonable.



Scheme 2. Initiation of the polymerization of MMA. ($R-COOCH_3$)

In the case of MMA having no hydrogen atom at the vinyl carbon atom attached directly to the substituent, the transfering hydrogen atom is considered to be one in the α-CH_3 group. The mechanism is concluded to be as in Scheme 2. One of the generated radicals is an allyl radical which may make easier the hydrogen transfer.

The authors wish to express their hearty thanks to Dr. T. Takada of Toho Beslon Co. for his affording of methallyl sulfonate.

References

1) Part 340: T. Kimura, T. Nakaya, M. Imoto, *Makromol. Chem.*, **176**, 1945 (1975).
2) M. Imoto, T. Ouchi, Y. Nakamura, and H. Ogushi, *J. Polym. Sci., Polym. Lett. Ed.*, **13**, 131 (1975).
3) P. J. Flory, *J. Am. Chem. Soc.*, **59**, 241 (1937).
4) R. A. Gregg and C. Walling, *J. Am. Chem. Soc.*, **69**, 2141 (1947).
5) R. Quelet, *Bull. Soc. Chem. Fr.*, **7**, 196 (1940).
6) G. E. Ham, "Copolymerization," Interscience Publisher, New York, (1964).
7) K. S. Bagdasariyan, "Theory of Radical Polymerization," (Moscow, 1966), p. 116.
8) M. Imoto, *Kobunshi*, **15**, 789 (1966).
9) T. Otsu and T. Sato, unpublished.