BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 51 (12), 3574—3578 (1978)

Vinyl Polymerization. 375.[1] Radical Polymerization of Vinyl Monomer in Water Initiated with Tin Mercaptides and Iron(III) Ion

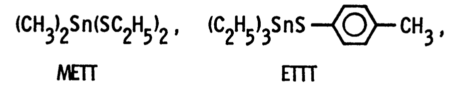
Yoshiaki NAKAMURA, Tatsuro OUCHI, and Minoru IMOTO*
Department of Applied Chemistry, Faculty of Engineering, Kansai University, Suita-shi, Osaka 564

(Received April 12, 1978)

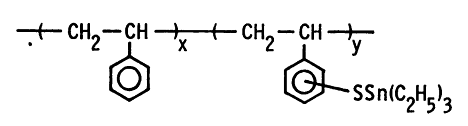
The polymerization of the vinyl monomer was carried out in water, using either dimethylbis(ethylthio)tin or triethyl(*p*-tolylthio)tin as an initiator. The polymerization required the coexistence of the iron(III) ion. The initiating species was concluded to be a thiyl radical. Macromolecular tin mercaptide was much more effective than monomeric tin mercaptide.

The present authors[2–4] have reported that dibutyltin dilaurate containing metal-oxygen bonds and tetrabutyltin or dimethylmercury bearing metal-carbon bonds are able to polymerize vinyl monomers in the presence of various metal chlorides. The present paper reports the polymerization in water, using either dimethylbis(ethylthio)tin (METT) or triethyl(*p*-tolylthio)tin (ETTT) as the organotin compound containing the metal-sulfur bond. Furthermore, in order to study the polymeric effects of organotin compounds, the polymerization of the monomer with macromolecular tin mercaptide has been conducted.

Tin mercaptides are used as stabilizers for poly(vinyl chloride) resins, and as catalysts for the ring-opening polymerization of epoxides and the reaction of isocyanate with alcohol. Ayrey *et al.*[5] conducted the radical polymerization of vinyl monomers initiated with α,α′-azobisisobutyronitrile in the presence of dibutylbis(ethylthio)tin. However, the radical polymerization of vinyl monomers initiated with tin mercaptide in the absence of the usual initiator has not been reported.



METT ETTT



PMT-S

Experimental

Materials. METT, ETTT, and partially tin mercaptidated polystyrene (PMT-S) were prepared from dimethyltin dichloride (MTC) and ethanethiol, from triethyltin chloride (ETC) and *p*-toluenethiol, and from ETC and partial mercapto polystyrene, respectively, according to Abel *et al.*[6] Partially mercaptidated polystyrene was prepared by Ogawara's method[7] from polystyrene whose degree of polymerization was about 30. PMT-S was assumed to be wholly composed of units having para-substituted $SSnEt_3$, according to the IR spectrum and elemental analysis; δ_{C-H}: 1290, 1165, 1115, 1025, 815 cm^{-1}; Found: C, 49.51; H, 6.96%. Calcd for $(C_{14}H_{22}SSn)_n$: C, 49.30; H, 6.50%. ETC and 1,3,5-triphenylverdazyl (TPV) were synthesized by Grignard's[8] and Kuhn's methods,[9] respectively. *N,N′*-diphenylpicrylhydrazil (DPPH), metal chlorides and iron(III) compounds were of special grade, and used without further purification. Methyl methacrylate (MMA), styrene (St) and acrylonitrile (AN) were purified by the usual methods. The water was ion-exchanged and distilled.

Polymerization Procedure. The required amounts of monomer, tin mercaptide, metal compound and water were placed in a tube. The tube was cooled in a Dry Ice/methanol bath, thawed three times with nitrogen, and sealed under vacuum. The tube was shaken in a thermostat at 85 °C. After a specific interval, the contents were poured into a large amount of methanol to precipitate the polymer. The polymer was dried under vacuum until constant weight and the conversion determined from the polymer weight. In the case of PMT-S, the conversion was calculated by the following equation.

$$\text{Conversion (\%)} = \frac{\left(\begin{array}{c}\text{Weight of}\\ \text{precipitate (g)}\end{array}\right) - \left(\begin{array}{c}\text{Added weight}\\ \text{of PMT-S (g)}\end{array}\right)}{\text{Initial weight of monomer (g)}} \times 100$$

The number-average molecular weight ($\bar{M}_n$) of poly-MMA was calculated by the GPC method (Toyo Soda Co., Ltd., Model HLC-801A).

Results and Discussion

Polymerization of Vinyl Monomer Initiated with METT. Effect of Various Metal Chlorides: Table 1 shows the results of the polymerization of MMA in the presence of various metal chlorides. It was found that the polymerization of MMA was accelerated particularly with $FeCl_3$. As METT was immediately decomposed by the aqueous solution of $SnCl_4$, $HgCl_2$, $CuCl_2$, or CuCl, these chlorides were not applied to the polymerization system.

TABLE 1. EFFECT OF VARIOUS METAL CHLORIDES ON THE POLYMERIZATION OF MMA
(MMA 5 cm^3, METT 0.5 cm^3, H_2O 3 cm^3, metal chloride 5.32×10^{-4} mol; 85 °C, 6h.)

Metal chloride	Conversion (%)
None	1.5
$FeCl_3$	74.6
$FeCl_2$	3.3
$CdCl_2$	2.8
$MnCl_2$	1.8
$NiCl_2$	1.9
$CoCl_2$	1.6
$CeCl_3$	1.3

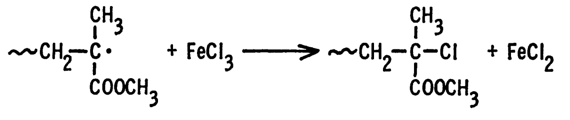
Selectivity of Vinyl Monomer: In order to observe the selectivity of METT for vinyl monomer, three kinds of vinyl monomer were used and the observed data are

Table 2. Polymerization of vinyl monomer initiated with METT in the presence of iron(III) chloride (Monomer 5 cm^3, $FeCl_3$ 5.32×10^{-4} mol, H_2O 3 cm^3; 85 °C, 6h.)

METT (cm^3)	Conversion (%)		
	MMA	AN	St
0	1.8	2.3	4.8
0.5	74.6	7.8	12.7

shown in Table 2. The polymerizations of the three monomers were promoted by the chlorides.

Effect of Amount of Iron(III) Chloride on the Polymerization: The effect of added iron(III) chloride on the polymerization was studied, by keeping the amounts of water, monomer and METT constant and varying the amount of $FeCl_3$. The conversion of MMA and the molecular weight ($\bar{M}_n$) of poly-MMA were remarkably affected by the added amount of $FeCl_3$, as shown in Fig. 1. After exceeding a certain limit, $FeCl_3$ inhibited the polymerization of MMA through the following mechanism;[10]



$$\sim\sim CH_2-\overset{CH_3}{\underset{COOCH_3}{C}}\cdot + FeCl_3 \longrightarrow \sim\sim CH_2-\overset{CH_3}{\underset{COOCH_3}{C}}-Cl + FeCl_2$$

The inhibition was supported by the rapid decrease of $\bar{M}_n$ with the increase of added $FeCl_3$, as shown in Fig. 1.

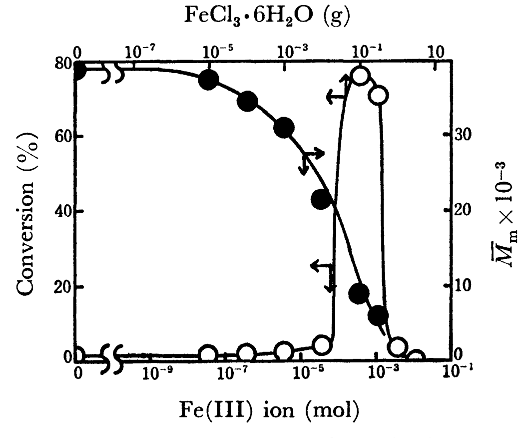


Fig. 1. Effect of the amount of iron(III) ion on the polymerization. MMA 5 cm^3, METT 0.5 cm^3, H_2O 3 cm^3: 85 °C, 6 h.

Effect of the Kind of Anionic Part of the Iron(III) Compound: MMA 5 cm^3 was polymerized with METT 0.5 cm^3 and Fe(III) ion (5.32×10^{-4} mol) in water 3 cm^3. The relationship between pK_a[11] of the protic acid (H_mX) of the anionic part (X^{m-}) and the conversion of MMA are shown in Table 3 and Fig. 2. It was found that the polymerization of MMA was promoted with iron(III) compounds, having the anion whose protic acid has a pK_a value less than 2 and the conversion was directly proportional to the pK_a. Iron(III) compounds having a pK_a value less than 2 were soluble, but those more than 2 were insoluble in water and ineffective in promoting the polymerization.

Table 3. Polymerization of MMA with iron(III) compound (MMA 5 cm^3, METT 0.5 cm^3, Fe(III) ion 5.32×10^{-4} mol, H_2O 3 cm^3; 85 °C, 6h.)

Iron(III) compound	Anion part (X^{m-})	pK_a of H_mX[11]	Conversion (%)
None	—	—	1.5
$FeBr_3$	Br^-	−7.74	86.0
$FeCl_3$	Cl^-	−4.74	74.6
$Fe(NO_3)_3$	NO_3^-	−1.34	45.1
$Fe_2(SO_4)_3$	SO_4^{2-}	2.00[a]	11.6
$FePO_4$	PO_4^{3-}	—	1.5
FeF_3	F^-	3.16	1.0
$Fe(OH)_3$	OH^-	15.74	0.4
Fe_2O_3	O^{2-}	—	0

a) First equivalent point.

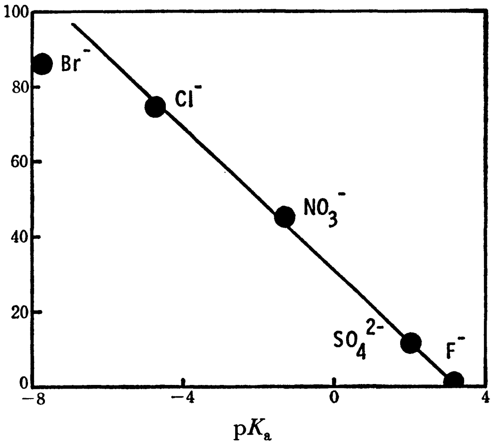


Fig. 2. Relationship between pK_a of H_mX and conversion of MMA.

Subsequent experiments were carried out, using iron(III) chloride.

Effect of Amount of Water on the Polymerization: Since it became clear that the dissociation of iron(III) ion was playing an important role in the polymerization, it was reasonable that the polymerization was required to be carried out in water. As shown in Fig. 3, the conversion of MMA increased with increasing amounts of water, and water was found to be indispensable for the polymerization.

Proof of Radical Mechanism: As shown in Table 1, the conversion of MMA amounted to 74.6%. Alternatively,

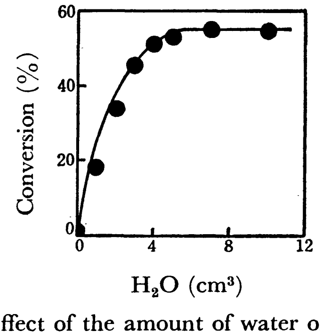


Fig. 3. Effect of the amount of water on the polymerization. MMA 5 cm^3, METT 0.5 cm^3, $FeCl_3$ 5.32×10^{-4} mol; 85 °C, 4 h.

0.1 g of DPPH or TPV, as radical scavenger, was added to the polymerization mixture. The polymerization was retarded with DPPH and inhibited with TPV, thus, it was concluded that the polymerization proceeded through a radical mechanism. Furthermore, the radical mechanism was verified by the method of copolymerization of MMA (M_1) with St (M_2) as shown in Fig. 4. By the Fineman-Ross method, r_1 and r_2 were estimated as 0.45 and 0.63, respectively (lit,[12] 0.46 and 0.57).

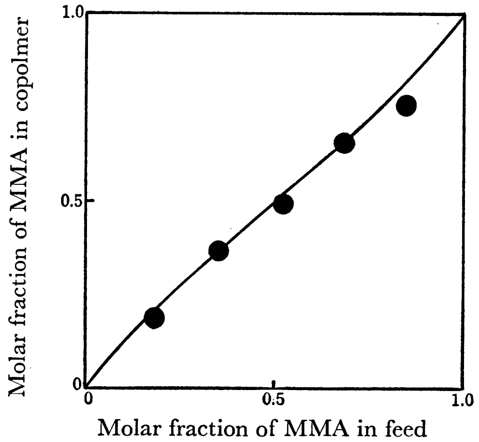


Fig. 4. Monomer-copolymer composition curve. (MMA+St) 6 cm³, METT 0.5 cm³, H_2O 3 cm³, $FeCl_3$ 5.32×10^{-4} mol, 85 °C, 6 h.

Polymerization of Vinyl Monomer Initiated with ETTT. In order to compare the activity of the aliphatic mercaptide with that of the aromatic one, the polymerization was carried out with triethyl(*p*-tolylthio)tin (ETTT).

MMA 5 cm³ was reacted with ETTT 0.1 cm³ and a varied amount of iron(III) chloride in water 3 cm³ at 85 °C for 6 h (Fig. 5). ETTT gave similar results to those obtained with METT. The molar quantity of $FeCl_3$ which gave maximum conversion was equal to the amount of ETTT applied and consequently, it was concluded that the reaction of ETTT and $FeCl_3$ took place by a 1 : 1 molar ratio.

Maintaining the amounts of monomer, ETTT, $FeCl_3$, and water constant, the polymerizations of three kinds of vinyl monomer were carried out at 85 °C for 6 h.

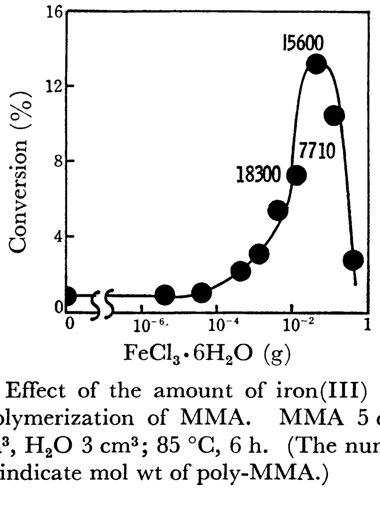


Fig. 5. Effect of the amount of iron(III) chloride on the polymerization of MMA. MMA 5 cm³, ETTT 0.1 cm³, H_2O 3 cm³; 85 °C, 6 h. (The numbers in the figure indicate mol wt of poly-MMA.)

TABLE 4. POLYMERIZATION OF VINYL MONOMER INITIATED WITH ETTT
(Monomer 5 cm³, $FeCl_3\cdot6H_2O$ 0.06 g, H_2O 3 cm³; 85 °C, 6h.)

ETTT (cm³)	Conversion (%)		
	MMA	AN	St
0	0.6	0.7	0.6
0.1	13.2	43.5	7.2

By the present initiating system, all monomers could be polymerized as shown in Table 4.

As shown in Table 4, the conversion of MMA amounted to 13.2%. However, when 0.1 g of DPPH or TPV was added as a radical scavenger to this system, the polymerization did not proceed. Furthermore, the copolymerization of MMA (M_1) with St (M_2) was carried out. The composition curve obtained is shown in Fig. 6. By the Fineman-Ross method, r_1 and r_2 were estimated as 0.50 and 0.52, respectively (lit,[12] 0.46 and 0.57). From these results, it was concluded that the polymerization proceeded through a radical mechanism.

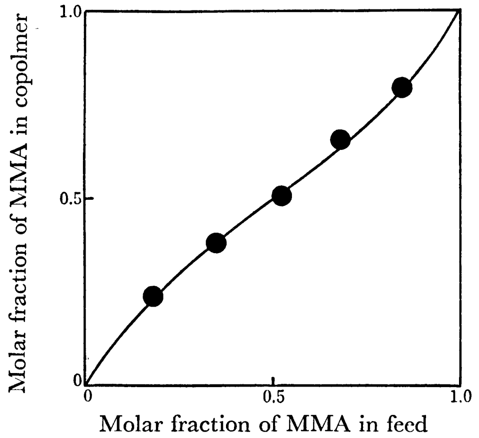


Fig. 6. Monomer-copolymer composition curve. (MMA+St) 6 cm³, ETTT 0.1 cm³, H_2O 3 cm³, $FeCl_3\cdot6H_2O$ 0.06 g; 85 °C, 6 h.

Determination of the Initiating Radical Species. *The Reaction of METT with $FeCl_3$*: In a tube, METT (1.06×10^{-2} mol), iron(III) chloride (2.13×10^{-2} mol) and water 8 cm³ were placed. The tube was evacuated and warmed at 85 °C for 8 h under shaking. The reaction mixture was fractionated into three portions by the procedure shown in Fig. 7.

Organic Layer I: The organic layer I gave a distillate having a boiling point of 41.5 °C/10 mmHg and a yield

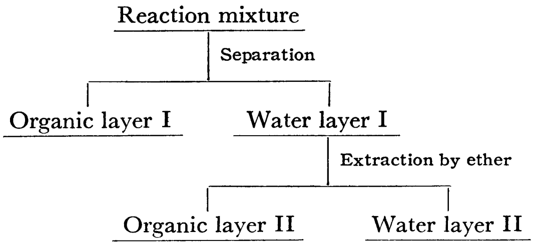


Fig. 7. Separation of the reaction mixture of METT with iron(III) chloride.

of 0.838 g. The IR spectrum and the gas chromatogram (GLC) of the distillate agreed completely with the reference diethyl disulfide (EDS) (bp 40 °C/10 mmHg[13]). Accordingly, the distillate was identified as EDS.

Organic Layer II: The ether extract was evaporated and a white solid residue was obtained. A white needle crystalline compound was obtained by the recrystallization from toluene (1.7 g). Mp and molar weight were 107—107.5 °C and 220.1 (by VPO-method in benzene at 37 °C), respectively. In the literature,[14] mp of dimethyltin dichloride (MTC) is 106 °C. The mixed mp of the crystals with the reference MTC was 107—108 °C. The organic layer II was identified as MTC; Found: C, 10.89; H, 2.74%. Calcd for $C_2H_6SnCl_2$: C, 10.93; H, 2.75%; mol wt 219.7.

Water Layer II: The water layer II was evaporated and the residue recrystallized from methanol to give blue-green powder-like crystals (3.85 g). The aqueous solution of the crystals gave a white precipitate of AgCl by adding a drop of $AgNO_3$ solution and a deep blue precipitate by potassium ferricyanide solution. Consequently, the crystalline compound from water layer II were concluded to be iron(II) chloride.

The Reaction of ETTT with $FeCl_3$: ETTT reacted with iron(III) chloride in a manner similar to METT. The reaction mixture was treated as shown in Fig. 8 and separated into the residue, the organic layer and the water layer.

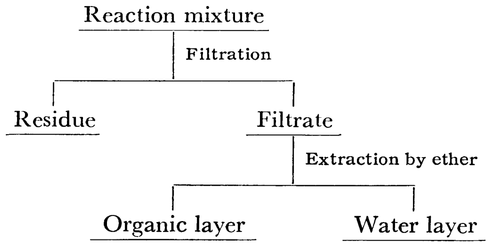


Fig. 8. Separation of the reaction mixture of ETTT with iron(III) chloride.

Residue: The residue was recrystallized from methanol and gave white needle-like crystals. Mp, mol wt and elemental analysis of the crystals were compared with those of di-*p*-tolyl disulfide (TDS), as shown in Table 5. Thus, the compound was identified as TDS.

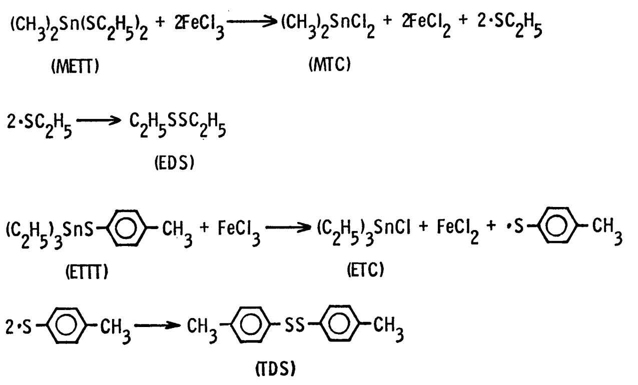
Table 5. Crystals from the residue

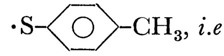
	Found	Theor. values of TDS[15]
Mp (°C)	46.5—47	47—48
Mol wt	245.7	246.4
Elemental analysis (%)	C, 68.72	C, 68.25
	H, 5.69	H, 5.73

Organic Layer: The ether-extract was evaporated, distilled under reduced presure, and the middle fraction (bp 90—91 °C/10 mmHg) separated. From the IR spectrum, the GLC and elemental analysis of the distillate, the fraction was identified as triethyltin chloride (ETC). Found: C, 29.81; H, 6.27%. Calcd for $C_6H_{15}SnCl$: C, 29.86; H, 6.27%; bp of ETC was 91 °C/10 mmHg.[16]

Water Layer: The water layer was similarly treated as in the case of METT and $FeCl_2$ identified.

From these results, the reactions were concluded to proceed as follow:



It was concluded that the initiating radical species for the polymerization were thiyl radicals, *i.e.*, $\cdot SC_2H_5$ or  *i.e.*, the initiation reaction took place by a redox reaction; an electron transfered from tin to iron(III) ion. Fe(II), Cd(II), Co(II), Mn(II), Ni(II), and Ce(II) ions accept electrons with difficulty, so they were inactive to polymerization, as shown in Table 1.

Polymerization of Vinyl Monomer Initiated with PMT-S. In order to observe the polymer effect of the initiator, PMT-S was used. MMA 5 cm³ was polymerized in water 3 cm³ in the presence of PMT-S 0.1 g and various amounts of iron(II) chloride. The results are shown in Fig. 9. The polymerization proceeded in a similar fashion as in the cases of METT and ETTT.

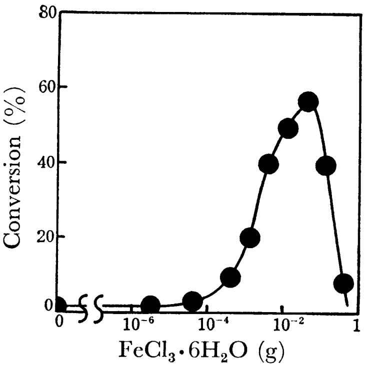


Fig. 9. Effect of the amount of iron(III) chloride on the polymerization of MMA. MMA 5 cm³, PMT-S 0.1 g, H_2O 3 cm³; 85 °C, 1 h.

Table 6. Polymerization of vinyl monomer initiated with PMT-S

(Monomer 5 cm³, $FeCl_3 \cdot 6H_2O$ 0.06 g, H_2O 3 cm³; 85 °C, 1h.)

PMT-S (g)	Conversion (%)		
	MMA	AN	St
0	0.3	0.3	0.5
0.1	56.3	30.7	13.7

Table 6 shows the results of the polymerizations of three kinds of vinyl monomers initiated with PMT-S in the presence of water and $FeCl_3$. The results were the same as in the above cases. From Tables 2, 4, and 6 and Figs. 1, 5, and 9, it may be seen that the rate of polymerization by PMT-S was larger than that by METT and ETTT. Thus the polymer effect of the initiator was clearly observed.

TABLE 7. EFFECT OF RADICAL SCAVENGER ON THE POLYMERIZATION OF MMA
(MMA 5 cm^3, PMT-S 0.1 g, $FeCl_3 \cdot 6H_2O$ 0.06 g, H_2O 3 cm^3, radical scavenger 0.1 g; 85 °C, 1h.)

Radical scavenger	Conversion (%)
None	56.3
DPPH	4.7
TPV	0

In order to confirm the radical mechanism, DPPH or TPV 0.1 g was added to the reaction system and the results are shown in Table 7. The polymerization was retarded with DPPH and inhibited with TPV. Thus, it was concluded that the polymerization proceeded through a radical mechanism.

It may be concluded that the polymerization with PMT-S was initiated through the same initiation mechanism as in the cases with METT and ETTT.

References

1) Part 374. M. Imoto, H. Suzuki, T. Yamada, and T. Ouchi, in preparation.

2) M. Imoto, Y. Nakamura, and T. Ouchi, *Nippon Kagaku Kaishi*, **1973**, 2244.

3) Y. Nakamura, T. Ouchi, and M. Imoto, *Kobunshi Ronbunshu*, **31**, 676 (1974).

4) M. Imoto, Y. Nakamura, and T. Ouchi, *Bull. Chem. Soc. Jpn.*, **48**, 1280 (1975).

5) G. Ayrey, B. C. Head, and C. Poller, *J. Polym. Sci., Polym. Chem. Ed.*, **13**, 69 (1975).

6) E. W. Abel and D. B. Brady, *J. Chem. Soc.*, **1965**, 1192.

7) S. Ogawara, Y. Onishi, and E. Imoto, *Kogyo Kagaku Zasshi*, **64**, 226 (1961).

8) G. J. M. Van Der Kerk, and J. G. A. Luijten, *Org. Synth.*, Coll. Vol. IV, 881 (1963).

9) R. Kuhn and H. Trishmann, *Monstsh. Chem.*, **95**, 457 (1964).

10) M. Imoto, K. Takemoto, and Y. Iikubo, *Bull. Chem. Soc. Jpn.*, **34**, 186 (1961).

11) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley, New York (1965), p. 93.

12) T. Ito and T. Otsu, *J. Macromol. Sci., Chem.*, **3**, 197 (1969).

13) D. T. McAllan, T. V. Cullum, R. A. Dean, and F. A. Fidler, *J. Am. Chem. Soc.*, **73**, 3627 (1951).

14) R. Okawara, D. E. Webster, and E. G. Rechow, *J. Am. Chem. Soc.*, **82**, 3287 (1960).

15) "Handbook of Chemistry and Physics," 52 ed, Chemical Rubber Co. (1971—1972), p. C-274.

16) S. Matsuda and H. Matsuda, *Bull. Chem. Soc. Jpn.*, **35**, 208 (1962).