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### Vinyl Polymerization by Metal Complexes. VIII. On the Kinetics of Photopolymerization of Vinyl Monomers by Fe(III) Salt-Saccharide Systems

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**Vinyl Polymerization by Metal Complexes.  
VIII. On the Kinetics of Photopolymerization  
of Vinyl Monomers by Fe(III)  
Salt-Saccharide Systems**

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**ABSTRACT**

The photopolymerization of acrylonitrile and acrylamide initiated by Fe(III) salt-saccharide systems was studied kinetically in aqueous solution. The interaction between Fe(III) ion and different saccharides was investigated by spectrophotometry, and the results are discussed in terms of the problems of complex formation and polymerizability of the initiating systems.

**INTRODUCTION**

In the previous papers of this series, the polymerization of vinyl monomers initiated by copper complex has been reported [1-6]. In the immediately preceding paper, the photopolymerization of vinyl monomers

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\*For Part VII of the series, see T. Okimoto, Y. Inaki, and K. Takemoto, J. Macromol. Sci.—Chem., A7(6), 1313 (1973).

initiated by metal ion and saccharide systems was carried out in different solvents, and Fe(III) ion-saccharide systems were found to be capable of initiating polymerization efficiently in rather mild conditions [7].

Although the photopolymerization of vinyl monomers by Fe(III) salt has received considerable interest recently [8-10], attention does not seem to have been paid to the photopolymerization initiated by Fe(III) salt-saccharide systems, except for our preceding paper. The photochemical reaction scheme between Fe(III) ion and saccharide is expected to be similar to the redox reaction of a Ce(IV)-saccharide initiating system which has been studied [11].

This paper is concerned with the photopolymerization of acrylonitrile and acrylamide initiated by Fe(III)-saccharide systems in aqueous solution, and seeks to clarify the accelerating effect caused by the addition of saccharide to the Fe(III) salt system and to suggest a detailed polymerization scheme.

## EXPERIMENTAL

### Materials

Acrylonitrile was purified by repeated distillation under reduced pressure. Acrylamide was dissolved in acetone and recrystallized using a freezing mixture of Dry Ice-methanol, mp 84.5°C. Both metal salts and saccharides used were of commercial origin. *cis*-1,2-Cyclohexanediol was synthesized according to the method given by Clark and Owen [12].

### Polymerization

Photopolymerization was carried out in a sealed tube of hard glass of 1.8 cm diameter. The light source was a high-pressure mercury vapor lamp (Toshiba SH-100UV-2) in a hard-glass envelope so that the light below about 300 m $\mu$  was screened off. The tubes were rotated around the lamp at a constant distance of 10 cm. Vinyl monomer, metal salt, and saccharide solution were charged successively into a tube in the dark. The evacuated tubes were then irradiated in an ice-cold water bath at 0°C. Polymer was obtained as a colorless precipitate by pouring the contents into a large excess of methanol, and it was purified by reprecipitation.

### Molecular Weight of the Polymers

Molecular weight of the polymers was determined by viscometry, using the following equations:

for acrylonitrile:  $[\eta] = 2.43 \times 10^{-4} \underline{M}^{0.75}$  (in DMF at 25°C) [13]

for acrylamide:  $[\eta] = 6.80 \times 10^{-4} \underline{M}^{0.66}$  (in H<sub>2</sub>O at 30°C) [14]

### Determination of Fe(III) Ion and Glucose Concentration

Fe(II) ion concentration, which was produced during the reaction, was determined colorimetrically at 510 m $\mu$  with o-phenanthroline as a reagent, and thus the concentration of the residual Fe(III) ion was estimated [15]. The glucose concentration was also measured colorimetrically at 625 m $\mu$  using the anthrone method [16].

## RESULTS AND DISCUSSION

### Rate of Polymerization

The photopolymerization of acrylonitrile and acrylamide initiated by Fe(III) nitrate-glucose system was carried out in aqueous solution at 0°C. Time-conversion curves are shown in Fig. 1. As the figure shows, conversion increased linearly with reaction time and a very short induction period was observed.

The relationship between conversion and glucose concentration is shown in Figs. 2 and 3. It can be seen from these figures that the rate

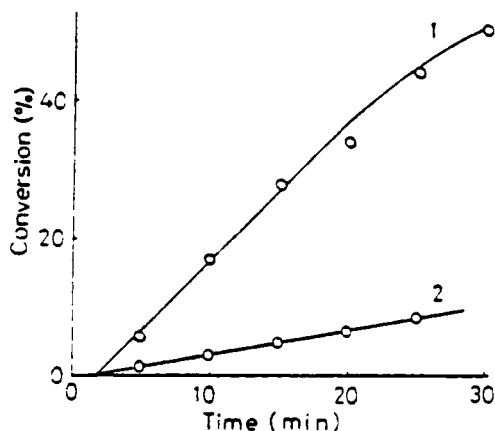


FIG. 1. Time-conversion curves of photopolymerization of acrylonitrile (0°C in H<sub>2</sub>O). [Acrylonitrile] = 1.01 moles/liter. [Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O] = 5.0 × 10<sup>-3</sup> mole/liter. (1) [Glucose] = 0.111 mole/liter. (2) [Glucose] = 0.000 mole/liter.

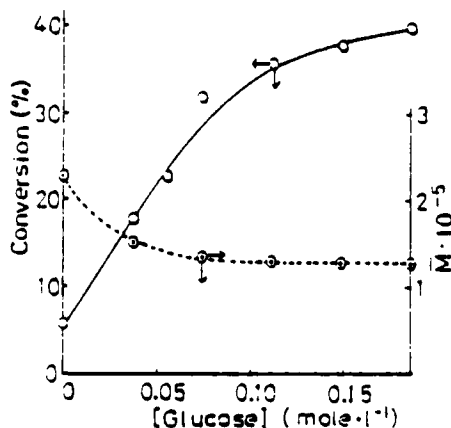


FIG. 2. Conversion and molecular weight vs glucose concentration (at 0°C in H<sub>2</sub>O, 20 min). [Acrylonitrile] = 1.01 moles/liter. [Fe(NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O] = 5.0 × 10<sup>-3</sup> mole/liter. (○): Conversion. (⊖): Molecular weight.

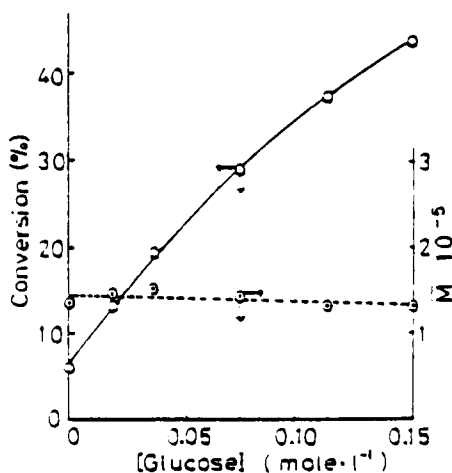


FIG. 3. Conversion and molecular weight vs glucose concentration (at 0°C in H<sub>2</sub>O, 10 min). [Acrylamide] = 0.94 mole/liter. [Fe(NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O] = 5.0 × 10<sup>-3</sup> mole/liter. (○): Conversion. (⊖): Molecular weight.

of polymerization increases linearly at first with increasing glucose concentration and, particularly in the case of acrylonitrile, the slope gradually becomes flat. On the other hand, the molecular weight of the polymers produced is approximately constant or even slightly decreases with increasing glucose concentration, suggesting that the accelerating effect caused in the presence of glucose may be associated with the initiating step.

The photopolymerization of these monomers was also carried out under condition in which the initial polymerization systems are homogeneous. The results are shown in Figs. 4 and 5. Plots of the rate of polymerization vs monomer concentration in logarithms give straight lines. In the case of acrylonitrile, the rate of polymerization is proportional to  $[M]^{1.4}$  in the absence of glucose and  $[M]^{1.6}$  in the presence of glucose. On the other hand, the polymerization of acrylamide gives a rate which is proportional to  $[M]^{0.9}$  in the absence of glucose and  $[M]^{1.1}$  in the presence of glucose.

Judging merely from these results, it seems likely that acrylonitrile may participate in the initiation mechanism. Dainton and Seamen have carried out the free-radical polymerization of acrylonitrile in aqueous solution, and the critical monomer concentration has been suggested [17]. We have carried out photopolymerization of acrylonitrile alternatively with potassium persulfate in aqueous solution, and the rate of polymerization obtained was plotted against  $[M]$  and  $[M]^2$ , together with the results of polymerization initiated by Fe(III) ion and the saccharide system (Figs. 6 and 7, respectively). From these

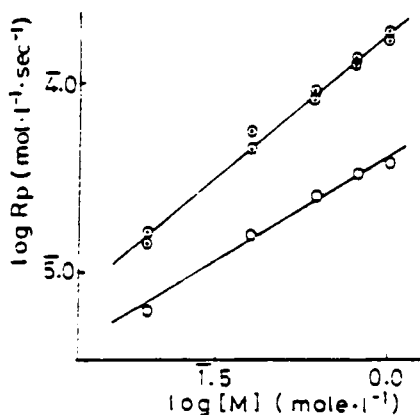


FIG. 4.  $\log R_p$  vs  $[M]$  in the photopolymerization of acrylonitrile (at  $0^\circ\text{C}$  in  $\text{H}_2\text{O}$ ).  $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}] = 5.0 \times 10^{-3}$  mole/liter. ( $\odot$ ):  $[\text{Glucose}] = 0.111$  mole/liter. ( $\circ$ ):  $[\text{Glucose}] = 0.000$  mole/liter.

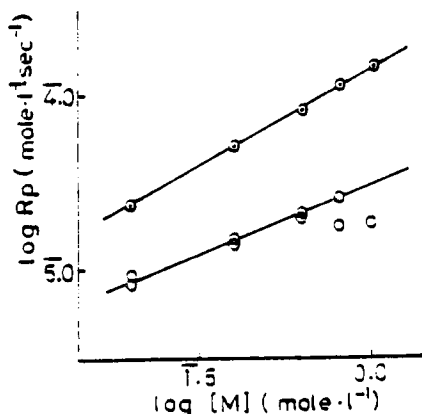


FIG. 5.  $\log R_p$  vs  $\log [M]$  in the photopolymerization of acrylamide (at  $0^\circ\text{C}$  in  $\text{H}_2\text{O}$ ).  $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}] = 5.0 \times 10^{-3}$  mole/liter. ( $^\circ$ ):  $[\text{Glucose}] = 0.111$  mole/liter. ( $^\circ$ ):  $[\text{Glucose}] = 0.000$  mole/liter.

figures it is found in both cases that the rate is proportional to  $[M]^2$  at lower monomer concentrations and proportional to  $[M]$  at higher monomer concentrations. These results might show that the polymerization initiated by  $\text{Fe}(\text{III})$  ion and the saccharide system follows normal kinetics in heterogeneous systems and, in accordance with the results given by Dainton and Seamen, that participation of the monomer in the initiation mechanism seems to be unimportant.

As shown in Fig. 8, propionitrile has no accelerating effect on the photopolymerization of acrylonitrile. From this fact it seems reasonable that acrylonitrile may be considered to play no substantial part in producing free radicals in the initiation step.

The polymerization of acrylonitrile was then carried out in an aqueous solution in which the initial  $\text{Fe}(\text{III})$  ion concentration was varied. The results are shown in Fig. 9. The upper curve is the result obtained in the presence of 0.111 mole/liter of glucose, and the lower curve is that obtained in the absence of glucose. Beyond the inflection point it appears that the rate of polymerization is independent of the  $\text{Fe}(\text{III})$  ion concentration. The relationship between the molecular weight of the polymers obtained and the  $\text{Fe}(\text{III})$  ion concentration shown in Fig. 10 also shows trends corresponding to the results of Fig. 9. It can be assumed, therefore, that the mutual termination between polymer growing radicals seems to be dominant at lower concentrations of the  $\text{Fe}(\text{III})$  ion, while the termination of the polymer radicals by the  $\text{Fe}(\text{III})$  ion seems to be significant at higher concentrations of the  $\text{Fe}(\text{III})$  ion.

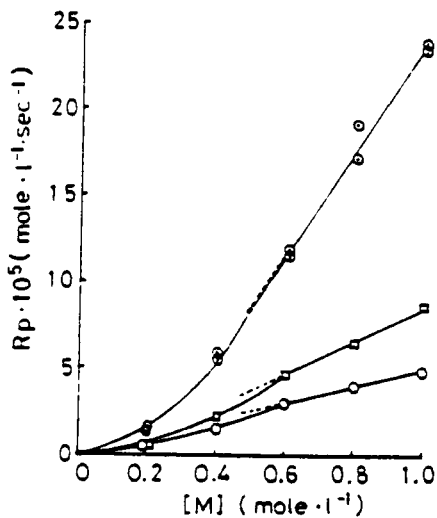


FIG. 6.  $R_p$  vs  $[M]$ . (○), (□): The data in Fig. 4. (○): At 0°C in  $H_2O$ .  $[K_2S_2O_8] = 5.0 \times 10^{-3}$  mole/liter (acrylonitrile).

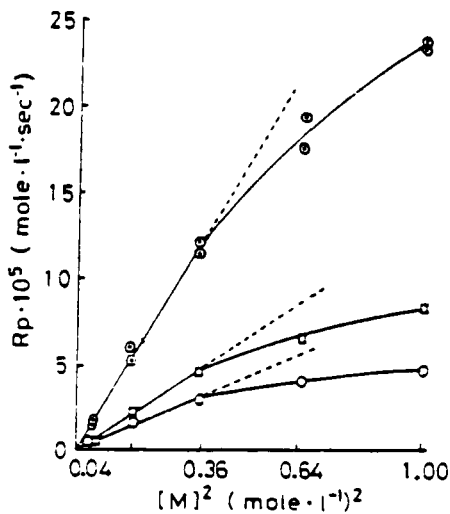


FIG. 7.  $R_p$  vs  $[M]^2$ .



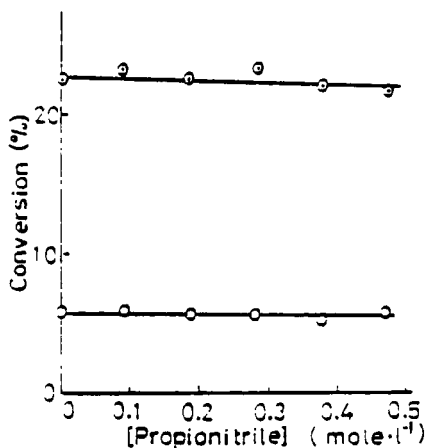


FIG. 8. Effect of the concentration of propionitrile on the photopolymerization of acrylonitrile (at 0°C in H<sub>2</sub>O, 20 min). [Acrylonitrile] = 0.56 mole/liter. [Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O] = 5.0 × 10<sup>-3</sup> mole/liter. (○): [Glucose] = 0.111 mole/liter. (⊖): [Glucose] = 0.000 mole/liter.

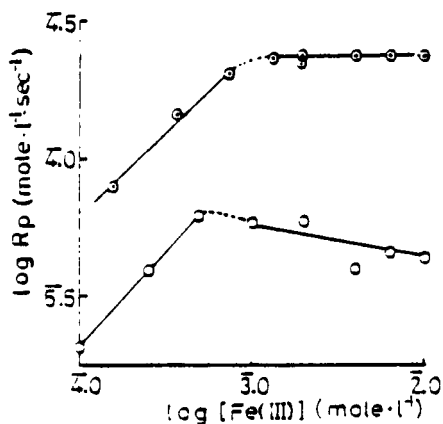


FIG. 9. Log R<sub>p</sub> vs log [Fe(III)] (at 0°C in H<sub>2</sub>O). [Acrylonitrile] = 1.01 moles/liter. [Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O] = 5.0 × 10<sup>-3</sup> mole/liter. (○): [Glucose] = 0.111 mole/liter. (⊖): [Glucose] = 0.000 mole/liter.

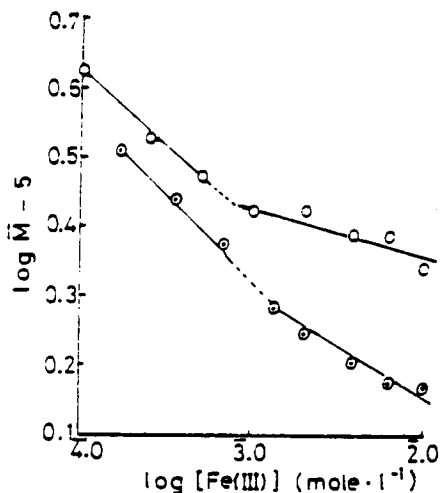
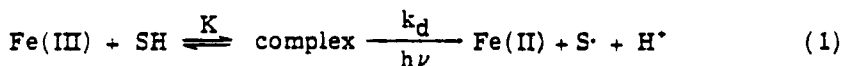


FIG. 10. Log  $\bar{M}$  vs log [Fe(III)].

#### Rate of Fe(III) Ion Consumption

From the results mentioned above, the initiation mechanism can be presented as follows: Fe(III) ion reacts first with saccharide (SH) to form a reversible complex consisting of a saccharide molecule and an Fe(III) ion, and then the complex decomposes slowly to afford a primary radical (S·):



where  $K$  is the equilibrium constant of the complex formation and  $k_d$  the rate constant for the decomposition of the complex. In the presence of excess amount of saccharide as compared with that of the Fe(III) ion, the rate of Fe(III) ion consumption is pseudo-first-order with respect to the total Fe(III) ion concentration:

$$-d[\text{Fe(III)}]/dt = k[\text{Fe(III)}] \quad (2)$$

that is,

$$\log[\text{Fe(III)}] = -kt + C \quad (3)$$

where  $k$  is the pseudo-rate constant of Fe(III) ion consumption and  $C$  is a constant. As shown in Fig. 11, plots of the logarithm of the Fe(III) ion concentration vs reaction time were always linear with respect to each glucose concentration. The  $k$  values obtained from Fig. 11 vs glucose concentration are shown in Fig. 12. From this figure the  $k$  values were found to increase linearly with increasing glucose concentration, and this curve shows trends quite similar to those in Figs. 2 and 3.

### Decomposition of Glucose

If saccharide is photooxidized by Fe(III) ion to produce a free radical and Fe(II) ion, a decrease of saccharide should be observed. In this respect, glucose remaining after photoirradiation was determined by the anthrone method. The result is shown in Fig. 13. Fe(III) nitrate was found to be precipitated by adding anthrone so that Fe(III) chloride, which is quite soluble in the system, was used throughout the experiment. It was ascertained that glucose decomposed during photoirradiation in the presence of Fe(III) chloride.

### UV and Visible Spectra of Fe(III) Ion and Saccharide Systems

UV and visible spectra of the Fe(III) ion and saccharide systems were measured in aqueous solution at room temperature. As shown in

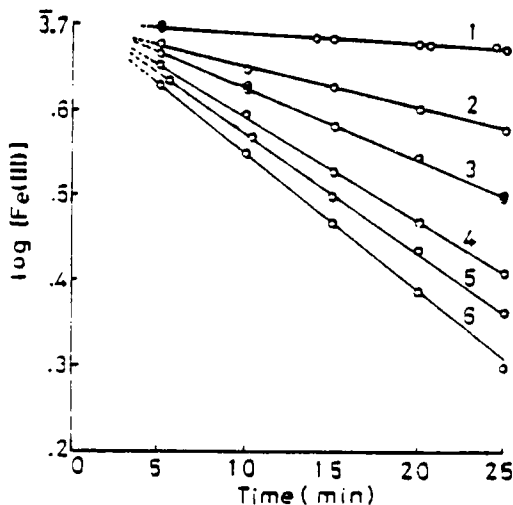


FIG. 11. The consumption rate of Fe(III) ion (at 0°C in H<sub>2</sub>O). [Glucose] = 0.000 (1), 0.037 (2), 0.074 (3), 0.111 (4), 0.148 (5), and 0.185 (6) mole/liter.

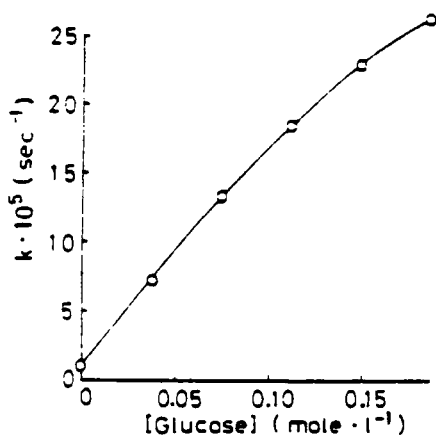


FIG. 12. The pseudo-first-order rate constant vs glucose concentration.

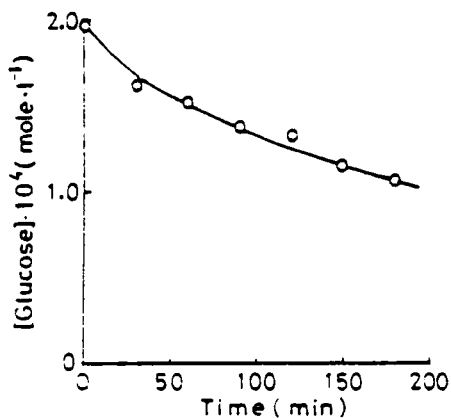


FIG. 13. Decomposition of glucose (at 0°C in H<sub>2</sub>O).

Fig. 14, Fe(III) nitrate exhibits a weak absorption above 350 m $\mu$  (Curve a). When glucose was added to the Fe(III) nitrate solution, the absorption is enhanced (Curve b), though saccharide itself has no absorption in this region. To compare the enhancement of the absorption in the case of other Fe(III) ion and saccharides or

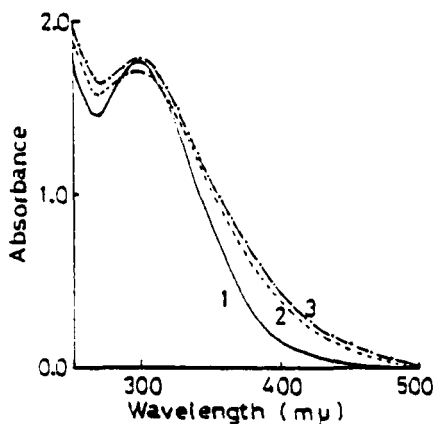


FIG. 14. UV and visible spectra of Fe(III) ion and glucose system (in  $\text{H}_2\text{O}$  at room temperature). (1)  $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}] = 9.4 \times 10^{-4}$  mole/liter. (2)  $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}] = 9.4 \times 10^{-4}$  mole/liter, and  $[\text{glucose}] = 0.16$  mole/liter. (3)  $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}] = 9.4 \times 10^{-4}$  mole/liter,  $[\text{glucose}] = 0.16$  mole/liter, and  $[\text{acrylonitrile}] = 0.89$  mole/liter.

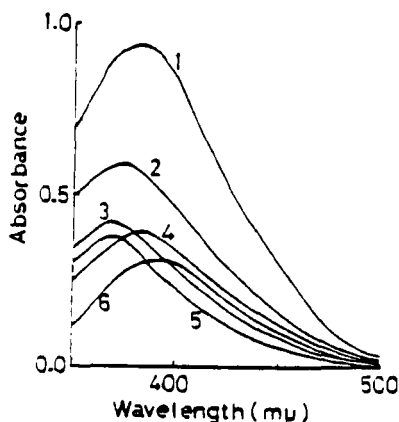


FIG. 15. Absorbance of Fe(III) ion and saccharide systems (in  $\text{H}_2\text{O}$  at room temperature).  $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}] = 4.0 \times 10^{-3}$  mole/liter.  $[\text{Saccharide}] = 0.25$  mole/liter. (1) Fructose, (2) glucose, (3) sucrose, (4) lactose, (5)  $\alpha$ -methyl-D-glucoside, and (6) maltose.

alcohol systems with each other, visible spectra using a Fe(III) nitrate solution as a reference were measured, the results of which are shown in Figs. 15 and 16.

The absorption spectra of these systems show broad peaks at about 370 m $\mu$ . The order of the absorbance decreased in the following order; fructose > glucose > sucrose > lactose >  $\alpha$ -methyl-D-glucoside > maltose  $\gg$  glycerin > ethylene glycol > methanol > ethanol. In the previous paper, we have shown that fructose, glucose, lactose, and maltose show a remarkable acceleration effect on vinyl polymerization, while sucrose and  $\alpha$ -methyl-D-glucoside show only a small effect. In the case of alcohols, the order of absorbance seems to be in fair agreement with the polymerization behavior.

### Equilibrium Constants of the Complex Formation

Equilibrium constants K (in Eq. 1) were determined spectrophotometrically according to [18]:

$$1/(A-A_0) = 1/\Delta\epsilon[\text{Fe(III)}] + 1/\Delta\epsilon K[\text{Fe(III)}][\text{SH}] \quad (4)$$

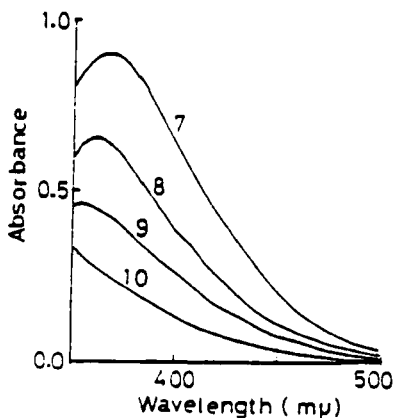


FIG. 16. Absorbance difference of Fe(III) ion and alcohol systems (in H<sub>2</sub>O at room temperature).  $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}] = 4.0 \times 10^{-3}$  mole/liter.  $[-\text{OH}] = 3.0$  moles/liter. (7) Glycerin, (8) ethylene glycol, (9) methanol, and (10) ethanol.

where  $A$  is the absorbance of the saccharide and Fe(III) ion mixture,  $A_0$  is the absorbance of the Fe(III) ion solution, and  $\Delta\epsilon$  is the difference in the extinction coefficient of the complex and Fe(III) ion. Plots of  $(A - A_0)^{-1}$  against  $[\text{SH}]^{-1}$  were found to be linear (Fig. 17). The  $K$  values obtained from the slopes are summarized in Table 1. In the case of  $\alpha$ -methyl-D-glucoside, the rather small value seems to be responsible for its lower polymerizability. The  $K$  value for glycerin is larger than that for ethylene glycol, which seems to show that any chelating effect of hydroxyl groups is significant.

### Effect of Alcohols and Aldehydes on the Polymerization

The photopolymerization of acrylonitrile was then carried out with the initiating systems in which saccharide was replaced by other hydroxy compounds. The results are shown in Table 2. Considerable acceleration was observed, and the order of acceleration was found to be as before with the exception of methanol: trihydroxy > dihydroxy > monohydroxy alcohol. Cyclohexanol and cis-1,2-cyclohexanediol as well as *n*-butyraldehyde showed little effect. These results seem to indicate that the mechanism for initiating polymerization is similar to the case in which the Fe(III) ion and saccharide initiating system was used.

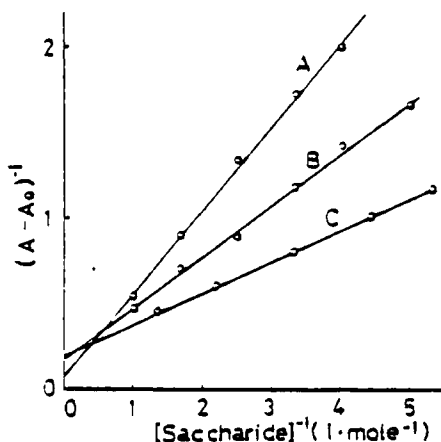


FIG. 17. Reciprocal plots of spectrophotometric data (at 380  $m\mu$ ).  $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}] = 5.0 \times 10^{-3}$  mole/liter. (A)  $\alpha$ -Methyl-D-glucoside, (B) glucose, and (C) fructose.

TABLE 1. Complex Formation Constant<sup>a</sup>

Substrate	K (mole <sup>-1</sup> )
Glucose	0.60
$\alpha$ -Methyl-D-glucoside	0.17
Fructose	0.96
Lactose	0.57
Maltose	1.45
Sucrose	0.61
Ethylene glycol	0.14
Glycerin	0.35

<sup>a</sup> Measured in the air at room temperature (at 380 m $\mu$ ).  $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}] = 5.0 \times 10^{-3}$  mole/liter.

TABLE 2. Photopolymerization of Acrylonitrile with Various Fe(III) nitrate-alcohol Systems<sup>a</sup>

Additives	Mole/liter	Yield (%)	$\bar{M} \times 10^{-5}$
CH <sub>3</sub> OH	0.556	11.8	2.31
C <sub>2</sub> H <sub>5</sub> OH	0.556	8.7	2.36
(CH <sub>3</sub> ) <sub>2</sub> CHOH	0.556	7.1	1.52
(CH <sub>3</sub> ) <sub>3</sub> COH	0.556	7.0	2.70
HOCH <sub>2</sub> CH <sub>2</sub> OH	0.278	10.7	2.52
CH <sub>2</sub> (OH)CH(OH)CH <sub>2</sub> OH	0.185	16.3	1.96
Cyclohexanol	0.312	5.5	0.64
cis-1,2-Cyclohexandiol	0.312	5.5	2.64
HCHO	0.111	7.1	2.64
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CHO	0.111	9.5	1.58
None <sup>b</sup>	-	6.0	2.51
Glucose <sup>b</sup>	0.111	36.7	1.71

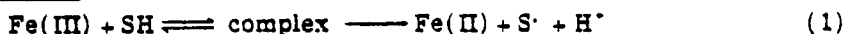
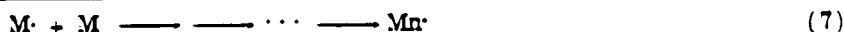
<sup>a</sup>  $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}] = 5.0 \times 10^{-3}$  mole/liter,  $[\text{AN}] = 1.01$  mole/liter, 0°C, 20 min, in H<sub>2</sub>O.

<sup>b</sup> Data from the previous paper [7].



Polymerization Scheme

Although there exist some problems based upon heterogeneity of the polymerization system and the efficiency of photoabsorption, the complex formation between Fe(III) ion and saccharide was clearly indicated spectrophotometrically, and consumption of both Fe(III) ion and glucose during photoirradiation was confirmed. Further, it may be reasonably assumed that at lower Fe(III) ion concentrations, mutual termination of the growing polymer radicals is predominant, while at higher Fe(III) ion concentrations, termination of the polymer radicals by Fe(III) ion, and/or reaction of primary radical with Fe(III) ion, becomes significant. Thus the elementary photopolymerization scheme can be described as follows:

InitiationPropagationTermination

where M, M<sup>·</sup>, and Mn<sup>·</sup> (Mm<sup>·</sup>) denote monomer, monomer radical, and polymer radical, respectively.

Further study should elucidate the effect of neutral salts or the pH of the polymerization systems on photopolymerization in order to reveal the initiating species in more detail.

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