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Vinyl Polymerization by Metal Complexes. XXIII.* UV and Kinetic Studies on the Photopolymerization with Iron(III)-Amine-Carbon Tetrachloride Systems

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ABSTRACT

In order to elucidate the initiation reaction of the photopolymerization with iron(III)-amine-carbon tetrachloride systems, the photochemical reaction process among iron(III), amine, and carbon tetrachloride in methanol solution was followed at 0°C by UV spectroscopy as for iron(III) ion. The rate constants of both the reduction of iron(III) under irradiation with light and the oxidation of iron(II) in the dark were measured, and were related to the rates of photopolymerization of methyl methacrylate. Kinetic study on the photopolymerization of methyl methacrylate with iron(III)-triethylenetetramine-carbon tetrachloride system was made in parallel in methanol solution at 0°C. The initiation mechanism of the photopolymerization was postulated.

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*For Part XXII of this series, see Y. Inaki, S. Nakagawa, K. Kimura, and K. Takemoto, Angew. Makromol. Chem., In Press.

INTRODUCTION

In the previous papers of this series the photopolymerization of vinyl monomers initiated by metal complex systems was reported. Particularly, iron(III)-saccharide systems were found to be effective for the photopolymerization of acrylonitrile in aqueous solution at 0°C [1-3]. In these initiator systems it was suggested that the interaction between iron(III) ion and O-ligand of the saccharides was significant for initiating photopolymerization.

In the course of the successive investigation we became interested in studying the free radical formation through a photochemical reaction between metal ion and N-ligand. The photopolymerization of vinyl monomers has then been examined by the system of iron(III), amine, and carbon tetrachloride. Addition of amine to the initiating system generally accelerated the polymerization [4]. The present paper deals with the photochemical reaction of iron(III) and amine in the presence of carbon tetrachloride in methanol solution at 0°C, together with a kinetic study of the photopolymerization of methyl methacrylate with the initiator systems at 0°C. In this connection it is worth noting two reports [5, 6] on the reaction of amines with halomethanes, especially the reaction of primary amines with carbon tetrachloride under unusually mild conditions.

EXPERIMENTAL

Materials

As the multidentate ligands, commercial ethylenediamine (en), diethylenetriamine (dien), triethylenetetramine (trien), and tetraethylenepentamine (tetraen) were used. As the monodentate ligand, n-butylamine was chosen for comparison. They were purified by distillation before use. Methyl methacrylate, as well as methanol and carbon tetrachloride, were purified by the usual method.

Ultraviolet Spectra

Iron(III) ion concentration, which was consumed during the reaction, was determined spectrophotometrically at 325 nm at 0°C. The rate of iron(III) ion consumption was followed with a 124 model Hitachi double beam spectrophotometer. The methanol solution of iron(III), amine, and carbon tetrachloride was charged into a 10-cm quartz cell in the dark, degassed, and sealed in vacuo. After irradiation for the recorded time, UV spectra of the sample cell were measured immediately at 0°C.

Polymerization

Photopolymerization was carried out in a sealed tube of hard glass of 1.8 cm diameter and was irradiated by a 100-W high-pressure mercury vapor lamp (Toshiba SH-100UV-2; 300 to 600 nm) in a hard glass envelope, as was reported previously [4]. The tubes were rotated around the lamp at a constant distance of 10 cm. Vinyl monomer and the initiator system were charged into a tube in the dark. The evacuated tubes were then irradiated in an ice-cold water bath at 0°C. The polymerization was stopped by cooling with liquid nitrogen. Polymer was obtained as a colorless precipitate by pouring the contents into a large excess of methanol, and it was purified by reprecipitation.

RESULTS AND DISCUSSION

In the previous papers concerned with the photopolymerization of vinyl monomers by iron(III)-amine-carbon tetrachloride systems, it was found that lack of any one component of the initiator systems resulted in a considerable decrease of the rate of polymerization. Of the various metal ions, iron(III), showed the highest activity for initiating the photopolymerization of methyl methacrylate, regardless of the type of gegenion. Manganese(II) showed the next highest activity. These metal complexes exhibited, however, very little initiation activity in the absence of light at 0°C [4].

It has also been shown that the higher conversion was attained in the case where methanol and ethanol were used as the solvents. Addition of water to methanol solution decreased the conversion. From the results of photopolymerization of methyl methacrylate in the presence of various amines, the iron(III)-trien complex exhibited higher activity than other multidentate amines [4].

Since the photochemical reaction occurring the the systems including iron(III) complexes appears to generate free radical species which can initiate vinyl polymerization, we were interested in making quantitative measurements on the rate of photochemical reduction and oxidation of iron(III) complexes.

Photochemical Reaction of Iron(III)-Amine-CCl_4

The UV spectrum of the methanol solution of iron(III), trien, and carbon tetrachloride shows a charge transfer band of iron(III)-trien complex near 325 nm (0 in Fig. 1). The absorption band at 325 nm tended to decrease in absorption by irradiation with light at 0°C (1 and 2 in Fig. 1). When irradiation was stopped in the state of 2, the absorption band again began to increase with the lapse of time (to 3 and 4 in Fig. 1). This absorption change indicates that the iron(III) complex was reduced to iron(II) by irradiation with light, and the iron(II) complex thus formed was oxidized again to the iron(III) complex in the dark, as shown by

$$\text{Fe(III)-complex} \underset{\text{in dark, } k_2}{\overset{h\nu,\ k_1}{\rightleftharpoons}} \text{Fe(II)-complex} \qquad (1)$$

The iron(III) complex was found to be reduced to the iron(II) complex by irradiation even in the system without amine and/or carbon

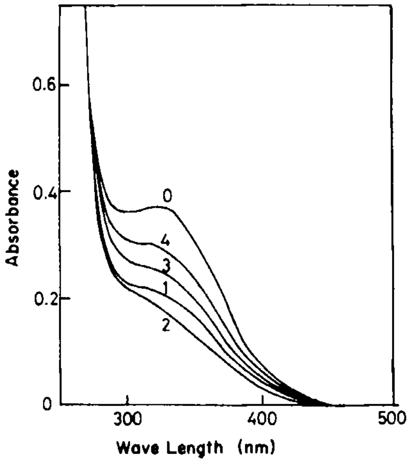


FIG. 1. Spectral change of the iron(III)-trien-CCl_4 system in methanol solution (0°C):

$$0 \xrightarrow{h\nu} 1 \xrightarrow{h\nu} 2 \xrightarrow{\text{dark}} 3 \xrightarrow{\text{dark}} 4$$

$[Fe(NO_3)_3] = 7.25 \times 10^{-5}$ mole/liter, $[\text{trien}] = 2.86 \times 10^{-2}$ mole/liter, and $[CCl_4]$ and 1.49 mole/liter. See text for the key to the curves.

tetrachloride. However, the iron(II) complex, which was derived from the reduction of iron(III), could be oxidized only when the system consisted of the three components, that is, iron(III), trien, and carbon tetrachloride. Though such reduction by irradiation was also observed in the one- and two-component systems such as iron(II)-trien, iron(III)-carbon tetrachloride, and iron(III), oxidation of these systems could not be observed in the dark. This fact suggests that the oxidation of iron(II) in the dark should be caused by the reaction of the iron(II)-trien complex with carbon tetrachloride, as shown by

$$\mathrm{Fe(II)(trien)_n} \xrightarrow{h\nu} \mathrm{Fe(II)(trien)_n}$$

$$\mathrm{Fe(II)(trien)_n} + \mathrm{CCl_4} \xrightarrow[k_2]{H^+} \mathrm{Fe(III)(trien)_{n-1}} + \mathrm{trien.HCl} + \cdot\mathrm{CCl_3} \tag{2}$$

From the absorption at 325 nm, the change in the concentration of the iron(III)-trien complex was determined and plotted against time as shown in Fig. 2. As can be seen from the figure, the concentration of the iron(III)-trien complex decreased rapidly by irradiation with light and reached an equilibrium concentration after 20 min. When light was switched off (indicated by an arrow), the concentration of the iron(III)-trien complex again increased slowly in the dark.

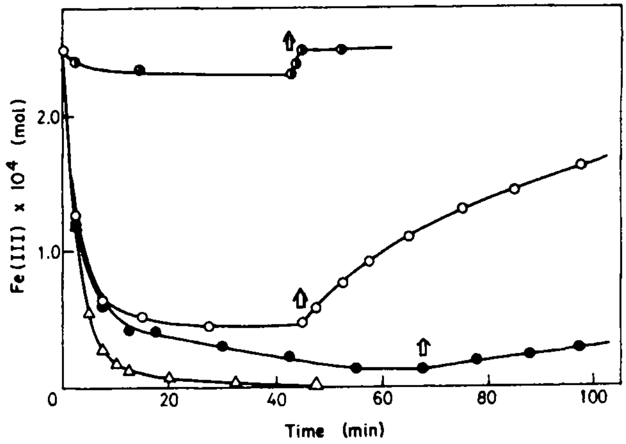


FIG. 2. Change in the concentration of iron(III) by irradiation with light in methanol solution 0°C. [Fe(NO$_3$)$_3$] = 2.5 × 10^{-4} mole/liter, [amine] = 1.0 × 10^{-1} mole/liter, and [CCl$_4$] = 1.5 mole/liter (○) n-Butylamine, (○) trien, (●) en, and (△) dien, tetraen.

In the cases of the systems of iron(III)-dien-CCl_4 and iron(III)-tetraen-CCl_4, the iron(III)-complexes included were completely reduced to iron(II) complexes by irradiating the light, whereas the iron(III)-complexes did not increase again in the dark as shown in Fig. 2. The behavior was quite different in the case of n-butylamine, because the concentration of its iron(III) complex decreased slowly by irradiation and came to the initial concentration when the light was switched off. The differences in behavior appears to be caused by differences in the structures of the complexes.

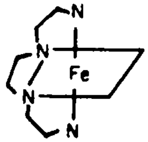
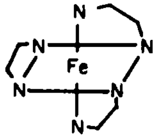
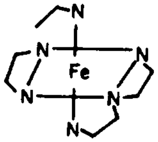
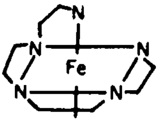
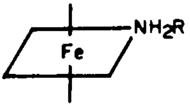
Plots of log[Fe(III)] against time for the photoreduction were found to be linear for the iron(III)-amine systems in the absence of carbon tetrachloride and yielded the first-order rate constants k_1 shown in Table 1. As Table 1 shows, the rate constants k_1 for the complexes with multidentate ligands such as en, dien, trien, and tetraen were greater than that with monodentate ligand, n-butylamine. This result may be related to the oxidation-reduction potentials of the iron complexes in question.

For the oxidation in the dark in the presence of excess amount of carbon tetrachloride, plots of $\log([Fe(III)]_0 - [Fe(II)])$ against time also yielded the apparent first-order rate constant k_2 as tabulated in Table 1, where $[Fe(III)]_0$ denotes the initial concentration of iron(III). The iron(III)-trien-CCl_4 system exhibits a large rate constant of oxidation reaction. In the cases in which en, dien, and trien were used as ligands, k_2 values were considerably or negligibly small as compared with the case of n-butylamine as ligand.

The specific activity of iron(III)-trien complexes toward the decomposition of hydrogen peroxide has been reported, the results of which showed similar behavior [7]. For this reaction, the iron(III)-trien system was really active, whereas the iron(III)-tetraen system was inactive. For this reason it has been assumed that two neighboring vacant coordination sites on which hydrogen peroxide can coordinate were necessary in the iron(III)-trien system. Taking into account this consideration also, the mechanisms of both the reduction and the oxidation of the iron(III)-trien-CCl_4 system are illustrated as in Scheme 1.

The iron(III)-trien complex (I) is thus reduced to the iron(II)-trien complex (II) by irradiation with light, yielding trien radical cation. Complex II forms complex III with trien and carbon tetrachloride, which converts again to I through an intermediate compound (IV) by the electron transfer process in the dark, yielding trichloromethyl free radical. Complex II requires two neighbored vacant coordination sites on which trien and carbon tetrachloride can coordinate. This is consistent with the fact that the activity of en, dien, and tetraen is far less than that of trien or n-butylamine, because the former three types of amine form

TABLE 1. Photoreduction and Photooxidation of Iron(III)-Amine System: First-Order Rate Constants in Eq. (1)[a]

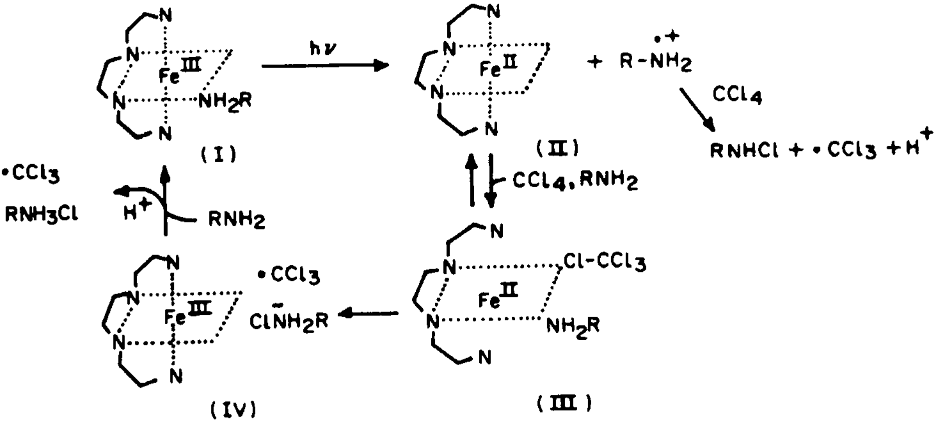
		k_1 (liter/min)	k_2 (liter/min)
Trien		9.0×10^{-1} $(4.8 \times 10^{-1})^b$	1.2×10^{-2} $(9.3 \times 10^{-3})^b$
En		3.5×10^{-1}	2.6×10^{-3}
Dien		3.1×10^{-1}	0
Tetraen		2.3×10^{-1}	0
n-Butylamine		5.5×10^{-2}	5.2×10^{-1}

[a] $[Fe(NO_3)_2 \cdot 9H_2O] = 1.43 \times 10^{-4}$ mole/liter; [amine] = 2.86×10^{-2} mole/liter; $[CCl_4] = 2.24$ mole/liter, in methanol solution.

[b] In methanol:water (9:1) mixture.

stable penta- or hexa-coordinated iron complexes, whereas the latter form only tetra-coordinated, labile complex.

The apparent first-order rate constant k_2 of the oxidation for the iron-trien-CCl_4 system in the dark was plotted against the concentrations of trien and carbon tetrachloride (Fig. 3). The apparent rate constant k_2 increased with trien concentration, and after saturation, decreased gradually. Trien concentration at the saturated k_2 value is about 100 molar ratios to iron(III). This suggests the presence of an



SCHEME 1.

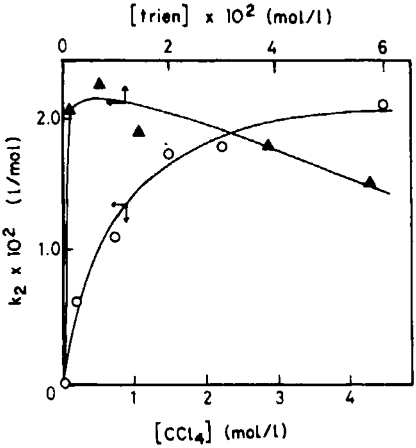
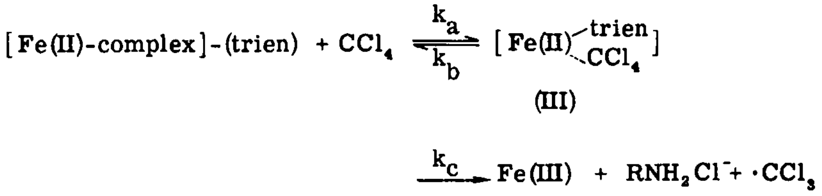


FIG. 3. Oxidation reaction of the iron(II) complex in the dark. Plots of k_2 against the trien and CCl_4 concentrations. 0°C. In methanol solution: $[Fe(NO_3)_3] = 7.25 \times 10^{-5}$ mole/liter.

intermediate compound such as III in Scheme 1 and also in Eq. (3). As the concentration of trien becomes excessive, carbon tetrachloride coordinated to iron(II) is replaced by trien, and therefore k_2 decreases:



$$[\text{Fe(II)-complex}]\text{-(trien)} + CCl_4 \underset{k_b}{\overset{k_a}{\rightleftharpoons}} \underset{\text{(III)}}{\left[\text{Fe(II)}\begin{smallmatrix}\text{trien}\\ CCl_4\end{smallmatrix}\right]} \xrightarrow{k_c} \text{Fe(III)} + RNH_2Cl^- + \cdot CCl_3 \qquad (3)$$

If the Michaelis-Menten type of rate equation can be applied to Eq. (3), the following equation can be derived:

$$\frac{d[\text{Fe(III)}]}{dt} = k_2\,[\text{Fe(II)}]_0 = k_c[\text{Fe(II)-trien----CCl}_4] = \frac{k_c K[\text{Fe(II)}]_0[CCl_4]}{1 + K[CCl_4]} \qquad (4)$$

$$\frac{1}{k_2} = \frac{1}{k_c K}\,\frac{1}{[CCl_4]} + \frac{1}{k_c} \qquad (5)$$

where $[\text{Fe(II)}]_0$ denotes the initial concentration of the iron(II)-trien complex and $K = k_a/k_b$.

Plots of Eq. (5) are shown in Fig. 4. The linear relationship observed supports Eq. (3) and gives the equilibrium constant as $K = 1.7 \times 10^{-2}$ and the rate constant as $k_c = 2.2 \times 10^{-2}$ sec. Thus the apparent rate constant k_2 for the oxidation reaction in the dark can be separated into K and k_c terms.

It has to be considered that the rate of oxidation in the dark might take another feature than that under irradiation with light. The rate of oxidation under irradiation can be determined from the equilibrium concentration in the course of reduction under irradiation shown in Fig. 2, as k_1 is known:

$$\text{Fe(III)} \underset{k_2}{\overset{h\nu,\ k_1}{\rightleftharpoons}} \text{Fe(II)} \qquad (6)$$

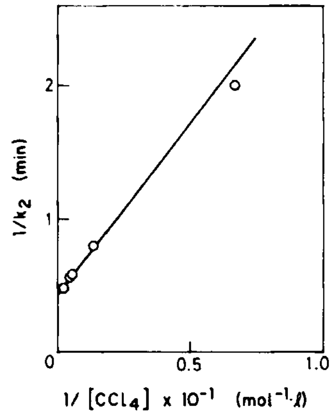


FIG. 4. Plot of Eq. (5) for the oxidation reaction of the iron(II)-trien-CCl_4 system in the dark. 0°C.

At the equilibrium state, the rate of reduction is equal to that of oxidation in the presence of an excessive amount of trien and CCl_4:

$$k_1[(Fe(III)] = k_2\,[Fe(II)] \tag{7}$$

$$k_2 = k_1\frac{[Fe(III)]}{[Fe(II)]} \tag{8}$$

The apparent rate constant k_2 thus obtained was larger than that obtained from the reaction in the dark tabulated in Table 1 by a factor of 10. It is suggested, therefore, that the oxidation reaction is accelerated by irradiation. It is further possible that even the iron (II)-dien and the -tetraen complexes are oxidized by carbon tetrachloride by irradiation with light.

Postpolymerization

The rates of reduction, as well as the oxidation of iron ion determined in the absence of monomer as tabulated in Table 1, should be related to the initiation activity for polymerizing methyl methacrylate reported previously.

The photopolymerization may be initiated by trichloromethyl free

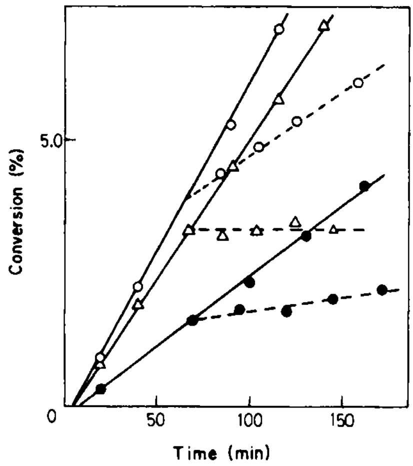


FIG. 5. Photo- and postpolymerization of methyl methacrylate by the iron(III)-amine-CCl_4 systems in methanol solution. 0°C. [$Fe(NO_3)_3$] = 1.43 × 10^{-3} mole/liter, [amine] = 2.86 × 10^{-2} mole/liter, [CCl_4] = 1.49 mole/liter and [MMA] = 2.65 mole/liter, (——) Under irradiation and (- -) in the dark. (○) Trien, (△) dien, and (●) n-butylamine. For dien only, [$Fe(NO_3)_3$] = 2.8 × 10^{-3} mole/liter and [amine] = 5.8 × 10^{-2} mole/liter.

radical, which seems to be derived from both reduction and oxidation steps. The photopolymerization and the postpolymerization of methyl methacrylate were then examined by using some iron(III)-amine-CCl_4 systems. The results, shown in Fig. 5, are found to be in agreement with expectations based on the results in Table 1. In the case in which trien was used, the polymerization proceeded after irradiation was stopped. If dien was used instead of trien, the polymerization ceased immediately by quenching the light. However, it cannot be decided whether the free radical is formed from the reduction or the oxidation step because direct oxidation is also possible, even for iron(II)-dien under irradiation.

Kinetic Study of the Photopolymerization

Based upon the photochemical reaction mechanisms of the iron(III)-amine-CCl_4 systems mentioned above, a kinetic study of photopolymerization initiated by these systems was made.

Photopolymerization of methyl methacrylate was carried out in different concentrations of each component at 0°C. Logarithms of the rate of polymerization (R_p) are plotted against those of the iron(III)-trien complex system ($[C]$) in Fig. 6. At lower concentrations of the complex, the rate of photopolymerization was nearly of 1/2 order in concentration. With increasing concentration of the complex, the reaction order tends to decrease and becomes of zeroth order in concentration of the complex. The reason appears not to be ascribable to the increase of the first radical termination, but rather to the decrease of the efficiency of free radical formation, because the degree of polymerization decreased only slightly with an increase in concentration of the complex.

At lower concentrations of the complex (1.43×10^{-4} mole/liter), the rate of polymerization was proportional to monomer concentration, and was represented by $R_p = k[C]^{1/2}[M]$. Dependence of the rate on the monomer concentration tended to be of 3/2 order at higher concentrations of the complex (Fig. 7). This may also be attributed to low efficiency of the free radical formation.

Addition of carbon tetrachloride accelerated the photopolymerization as shown in Fig. 8. With a larger excess of carbon tetrachloride the rate of polymerization was independent on the concentration of

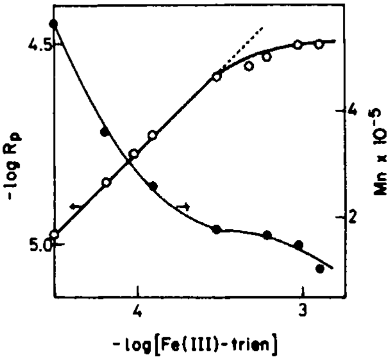


FIG. 6. Plots of the rate and the molecular weight of the polymers vs concentration of the complex for the photpolymerization of methyl methacrylate by the iron(III)-trien-CCl_4 system in methanol solution. 0°C, $[\text{trien}]/[Fe(NO_3)_3] = 20$. $[MMA] = 2.65$ mole/liter, $[CCl_4] = 1.49$ mole/liter, and $[\text{complex}] = [Fe(NO_3)_3]$.

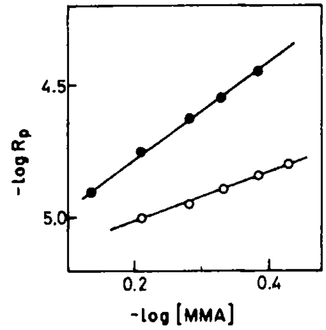


FIG. 7. Log R_p vs log [MMA] plots for the photopolymerization of methyl methacrylate by the iron(III)-trien-CCl_4 system in methanol solution. 0°C. $[Fe(NO_3)_3] = 1.43 \times 10^{-3}$ (●), 1.43×10^{-4} (○); [trien] $= 2.86 \times 10^{-2}$ (●), 2.86×10^{-3} (○); $[CCl_4] = 1.49$ mole/liter.

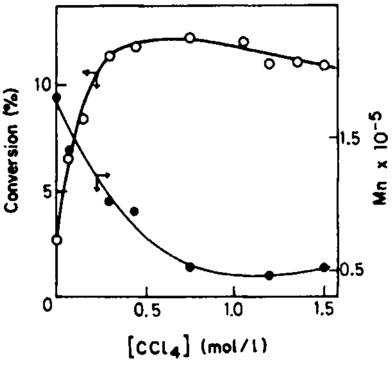


FIG. 8. Effect of carbon tetrachloride on the photopolymerization of methyl methacrylate by the iron(III)-trien-CCl_4 system in methanol solution. 0°C. $[Fe(NO_3)_3] = 1.43 \times 10^{-3}$ mole/liter, [trien] $= 2.86 \times 10^{-2}$ mole/liter, and [MMA] = 2.65 mole/liter.

carbon tetrachloride. From these findings, together with those mentioned above, the mechanism of the photopolymerization is assumed to be

$$\mathrm{Fe} + n(\mathrm{trien}) \rightleftharpoons \mathrm{Fe\text{-}(trien)}_n \qquad (9)$$

Initiation:

$$\mathrm{Fe\text{-}(trien)}_n + \mathrm{CCl_4} \underset{k_B}{\overset{k_A}{\rightleftharpoons}} [\mathrm{Fe\text{-}(trien)}_n \cdots\cdots \mathrm{CCl_4}] \xrightarrow[k_C]{h\nu}$$

$$\mathrm{Fe\text{-}(trien)}_{n-1} + \cdot\mathrm{CCl_3} + (\mathrm{trien})\,\mathrm{Cl^-} \qquad (10)$$

$$\cdot\mathrm{CCl_3} + \mathrm{M} \longrightarrow \mathrm{M}\cdot \qquad (11)$$

Propagation:

$$\mathrm{M}\cdot + \mathrm{M} \xrightarrow{k_p} \mathrm{M}\cdot \qquad (12)$$

Termination

$$\mathrm{M}\cdot + \mathrm{M}\cdot \xrightarrow{k_t} \mathrm{P} \qquad (13)$$

The polymerization may thus be initiated by the trichloromethyl free radical which is formed from the reduction-oxidation cycle, as shown in Scheme 1. As the light was irradiated throughout the polymerization, the Scheme 1 can be written as Eq. (10), where Fe is iron(II) and/or iron(III).

Treatment of the Michaelis-Menten type of rate equation for Eq. (10) gives

$$R_i = \frac{d[\cdot\mathrm{CCl_3}]}{dt} = \frac{k_C K[\mathrm{Fe}]_0[\mathrm{CCl_4}]}{1 + K[\mathrm{CCl_4}]} \qquad (14)$$

and

$$\frac{1}{R_i} = \frac{1}{k_C K[\mathrm{Fe}]_0}\;\frac{1}{[\mathrm{CCl_4}]} + \frac{1}{k_C[\mathrm{Fe}]_0} \qquad (15)$$

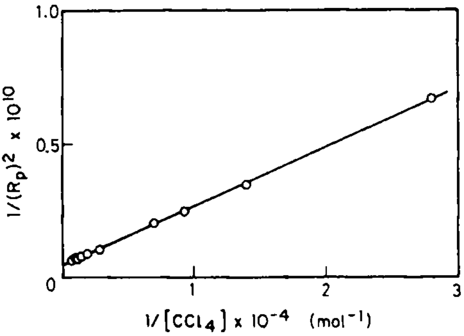


FIG. 9. Plots of Eq. (16) for the photopolymerization of methyl methacrylate by the iron(III)-trien-CCl_4 system in methanol solution. 0°C. $[Fe(NO_3)_3] = 1.43 \times 10^{-3}$ mole/liter, $[\text{trien}] = 2.86 \times 10^{-2}$ mole/liter, and $[\text{MMA}] = 2.65$ mole/liter.

where $[Fe]_0$ denotes the initial concentration of iron(III). As the rate of polymerization can be expressed as $R_p = (R_i/k_t)^{1/2} k_p[M]$, Eq. (15) becomes

$$\frac{1}{R_p^{\,2}} = \frac{k_t}{k_C K[Fe]_0 (k_p[M])^2}\,\frac{1}{[CCl_4]} + \frac{k_t}{k_C [Fe]_0 (k_p[M])^2} \qquad (16)$$

A plot of Eq. (16) is shown in Fig. 9. The linear relationship in this figure supports the initiation mechanism as postulated in Eq. (10).

REFERENCES

[1] T. Okimoto, Y. Inaki, and K. Takemoto, J. Macromol. Sci.—Chem., A7, 1313 (1973).
[2] T. Okimoto, Y. Inaki, and K. Takemoto, Ibid., A7, 1537 (1973).
[3] T. Okimoto, Y. Inaki, and K. Takemoto, Angew. Makromol. Chem., 36, 27 (1974).
[4] T. Okimoto, M. Takahashi, Y. Inaki, and K. Takemoto, Ibid., 38, 81 (1974).

[5] W. J. Lautenberger, E. N. Jones, and J. G. Miller, J. Amer. Chem. Soc., 90, 1110 (1968).
[6] C. J. Biaselle and J. G. Miller, Ibid., 96, 3813 (1974).
[7] J. H. Wang, Ibid., 85, 1958 (1963).

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