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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Tsubakiyama, Kyoji , Fujisaki, Setsuo , Tabata, Eizo and Nakahara, Saburo(1991) 'Photosensitized Polymerization of Organic Vinyl Monomers by Ferrocene', Journal of Macromolecular Science, Part A, 28: 5, 557 – 573

To link to this Article: DOI: 10.1080/00222339108052107

URL: <http://dx.doi.org/10.1080/00222339108052107>

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PHOTOSENSITIZED POLYMERIZATION OF ORGANIC VINYL MONOMERS BY FERROCENE

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ABSTRACT

Ferrocene (Fc)-sensitized photopolymerizations of vinyl monomers such as methyl methacrylate (MMA), acrylonitrile (AN), styrene (St), and isobutyl vinyl ether (IBVE) have been investigated by means of kinetic and spectroscopic analyses. The sensitizing effect of Fc has been found to be specific for AN; Fc acts as a sensitizer for AN but not for the other monomers. In the presence of carbon tetrachloride (CCl_4), Fc is an effective sensitizer for MMA, AN, and IBVE, but it acts as an inhibitor for St. The polymerizations of AN by Fc and of MMA by Fc/ CCl_4 proceed by a radical mechanism, whereas the polymerization of IBVE by Fc/ CCl_4 proceeds in a cationic fashion. Kinetic studies gave the following relationships: $R_p = k_1[\text{Fc}]^{0.38}[\text{AN}]^{1.7}$ for the polymerization of AN by Fc in dimethylformamide; $R_p = k_2[\text{Fc}]^{0.48}[\text{CCl}_4]^{0.42}[\text{MMA}]^{1.5}$ for the polymerization of MMA by Fc/ CCl_4 in benzene. Spectroscopic analysis indicated that the charge-transfer complexes are formed between Fc and a monomer or CCl_4 . The initiating species of the polymerizations are produced by the photochemical dissociation of the complexes.

INTRODUCTION

Metal π -complexes such as metallocenes have been used as soluble metallic catalysts for polymerization [1, 2]. Many reports on the polymerization of vinyl monomers with ferrocene (Fc) have appeared in the literature. It has been shown that Fc is able to induce polymerization in the presence of carbon tetrachloride (CCl_4) at a relatively high temperature, though Fc alone cannot induce it [3-7]. On the other hand, a few publications have reported on the photoinitiation of vinyl polymerization by Fc [8, 9]. A preliminary report on photoinitiation was made previously by the present authors [10]. It was found that Fc acts as a sensitizer for acrylonitrile (AN) but not for styrene (St) and methyl methacrylate (MMA). In addition, the Fc- CCl_4 system also serves as a sensitizer for MMA, but it is an inhibitor for St. It has been suggested that Fc acts as a sensitizer only when it has some electronic interaction with a monomer or additive (CCl_4) in the polymerization system. In the present paper the authors report the results of kinetic and spectroscopic studies and discuss the photoinitiation mechanism.

EXPERIMENTAL

Materials

Ferrocene [$(\text{C}_5\text{H}_5)_2\text{Fe}$, Wako Pure Chemical Industry Ltd.] was purified by repeated sublimations under reduced pressure. Organic vinyl monomers were distilled twice in the presence of calcium hydride under reduced pressure and distilled *in vacuo* just before use. Spectroscopic grade CCl_4 was used without further purification. Benzene was refluxed over sodium and then distilled twice. Other solvents were purified in a similar manner.

Photopolymerization

The polymerization was carried out by the sealed tube method. The sample solution in a glass tube (18 mm diameter) was degassed by several freeze-pump-thaw cycles under high vacuum and then sealed off. Irradiation was done in a water bath kept at a constant temperature with a 100-W high-pressure mercury lamp (Ushio UM102). The wavelength of irradiating light was controlled by using Toshiba glass filters (UV-D25,

UV-39, V-Y42). After a definite time of irradiation, the sample solution was poured into a poor solvent for the polymer. The precipitated polymers were dried at 50°C for 24 h. The conversion of monomer was determined gravimetrically. The rate of polymerization was measured by use of a dilatometer consisting of a cylindrical cell (1.0 cm thickness, 3.7 cm diameter) and a capillary tube (0.8 mm diameter).

Measurements

Compositions of MMA-St and AN-St copolymers were determined by infrared (IR) spectrum, the ratios of the specific absorbances for two comonomer units of the polymers were determined with a KBr disk. A JASCO A-3 IR spectrophotometer for the IR spectra and a Shimadzu QR-50 spectrophotometer for ultraviolet (UV)/visible spectra were used. Flash photolysis was carried out at room temperature by using a microsecond flash apparatus (input energy, 150 J; half value of duration time, 16 μ s) [11]. Viscosities were measured in benzene at 30°C with an Ubbelohde viscometer.

RESULTS AND DISCUSSION

Photopolymerization of Acrylonitrile Initiated by Fc

The effect of added Fc on the photopolymerization of organic vinyl monomers was first examined in bulk at 21°C with unfiltered irradiation ($\lambda > 280$ nm). The results obtained are shown in Figs. 1-4. As can be seen from a comparison of Curve 2 (Fc added) with Curve 4 (blank) in these figures, the polymerization of AN (Fig. 1) is accelerated by the presence of small amounts of Fc, whereas the reactions of MMA (Fig. 2) and St (Fig. 3) are depressed because of the inner filter effect. IBVE cannot be polymerized at all by Fc alone (Fig. 4). It is therefore concluded that Fc itself acts as a sensitizer only for the photopolymerization of AN.

The photopolymerization of AN by Fc was completely inhibited by the addition of α, α -diphenyl- β -picrylhydrazyl (DPPH) or oxygen. The photoinduced copolymerization of AN (M_2) with St (M_1) by Fc gave almost the same composition curve as that reported for the radical copolymerization ($r_1 = 0.40$ and $r_2 = 0.04$ [8, 12]), as shown by Curve A in Fig. 5. Therefore, it is evident that the photopolymerization of AN by Fc proceeds by a radical mechanism.

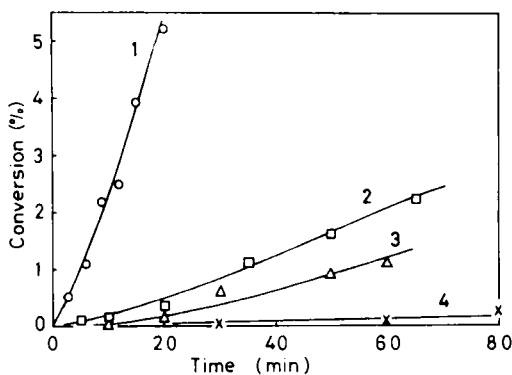


FIG. 1. Photopolymerization of AN in the presence of Fc and CCl_4 : AN = 10 mL; (1) Fc (6 mg) + CCl_4 (0.2 mL), (2) Fc (6 mg), (3) CCl_4 (0.2 mL), (4) blank.

The absorption spectra of Fc measured in cyclohexane are shown in Fig. 6. Fc exhibits two weak absorption bands in the wavelength region from 300 to 550 nm; one is centered at 325 nm ($\epsilon = 60$) and the other at 440 nm ($\epsilon = 90$). In the presence of AN, a new absorption band was found to appear in the 300–370 nm region. This new band was also observed in various solvents such as benzene, ethanol, acetonitrile, and dimethylformamide (DMF). Fc is known to be a strong electron donor,

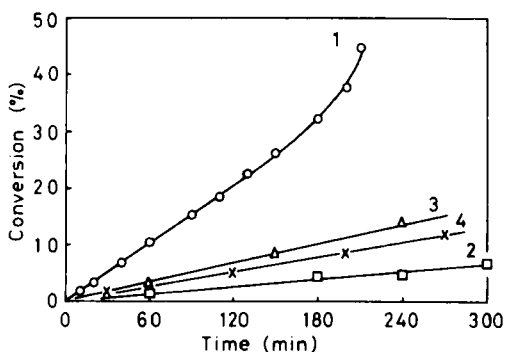


FIG. 2. Photopolymerization of MMA in the presence of Fc and CCl_4 : MMA = 10 mL; (1) Fc (5 mg) + CCl_4 (0.5 mL), (2) Fc 5 (mg), (3) CCl_4 (0.5 mL), (4) blank.

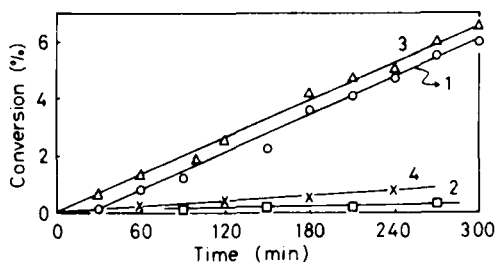


FIG. 3. Photopolymerization of St in the presence of Fc and CCl₄: St = 10 mL; (1) Fc (5 mg) + CCl₄ (0.5 mL), (2) Fc (5 mg), (3) CCl₄ (0.5 mL), (4) blank.

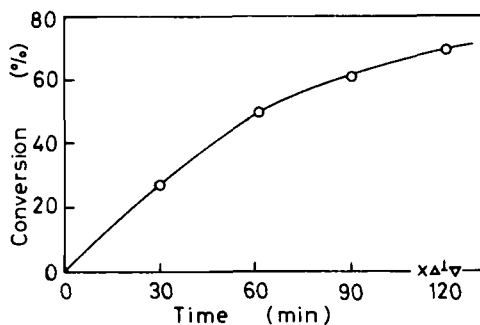


FIG. 4. Photopolymerization of IBVE in the presence of Fc and CCl₄: IBVE = 10 mL; (○) Fc (5 mg) + CCl₄ (0.5 mL), (△) Fc (5 mg), (▽) CCl₄, (×) blank.

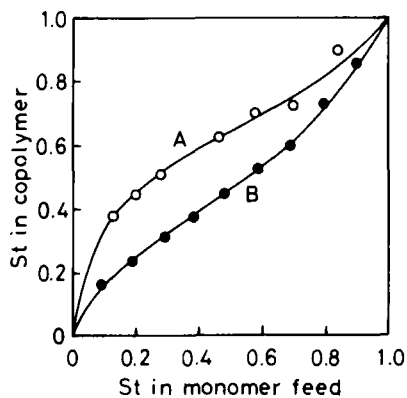


FIG. 5. Composition curves for photoinitiated copolymerizations in bulk: (A) AN (M₂)/St (M₁), [Fc] = $5.4 \times 10^{-3} M$; (B) MMA (M₂)/St (M₁), [Fc] = $2.6 \times 10^{-3} M$, [CCl₄] = 0.5 M.

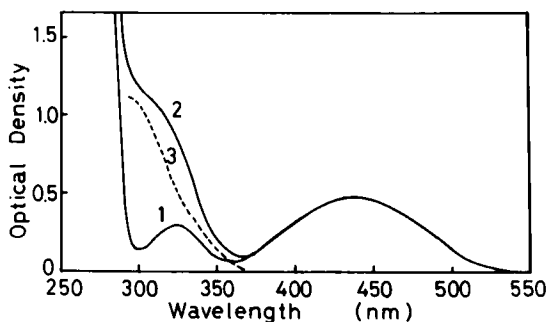


FIG. 6. Absorption spectra of Fc in the presence of AN in cyclohexane: (1) Fc ($5 \times 10^{-3} M$), (2) Fc ($5 \times 10^{-3} M$) + AN ($4.6 M$), (3) differential spectrum obtained by subtracting spectrum (1) from spectrum (2).

forming a charge-transfer (CT) complex with tetracyanoethylene and other compounds [13]. Therefore it can be considered that Fc does interact with AN as an electron donor [8], and that the new absorption band is attributable to a CT interaction. The photopolymerization of AN by Fc did not occur with filtered irradiation ($\lambda > 370$ nm); this shows that the effective wavelength of light for the photopolymerization exists in the 300 to 370 nm range. It is therefore thought that the photopolymerization of AN by Fc is induced by the excitation of the CT complex formed between Fc and AN.

The kinetic studies of the photopolymerization of AN by Fc in DMF were carried out at 20°C with filtered light ($400 > \lambda > 300$ nm). The dependence of the photopolymerization rate (R_p) on the concentrations of Fc and AN monomer is shown in Fig. 7. From these results, the following relationship was obtained:

$$R_p = k_1[\text{Fc}]^{0.38}[\text{AN}]^{1.7}$$

This result suggests that the bimolecular termination reaction proceeds in homogeneous solution and that the monomer participates in the initiation reaction of the photopolymerization.

The effect of temperature on the photopolymerization of AN by Fc was examined in bulk at $3\text{--}40^\circ\text{C}$. The Arrhenius plot of R_p is shown by Line A in Fig. 8. The overall activation energy of the photopolymerization was estimated to be 6.8 kcal/mol. This value is close to that reported for the radical polymerization of AN in DMF (5–6.4 kcal/mol) [14, 15].

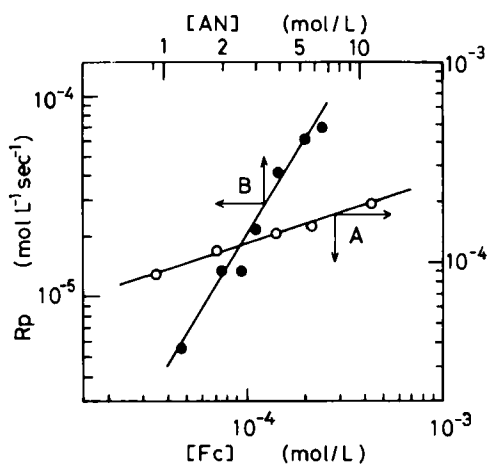


FIG. 7. Dependence of the photopolymerization rate of AN on the concentration of Fc (A) and AN (B) in DMF: (A) $[\text{AN}] = 7.6 \text{ M}$; (B) $[\text{Fc}] = 3.2 \times 10^{-3} \text{ M}$.

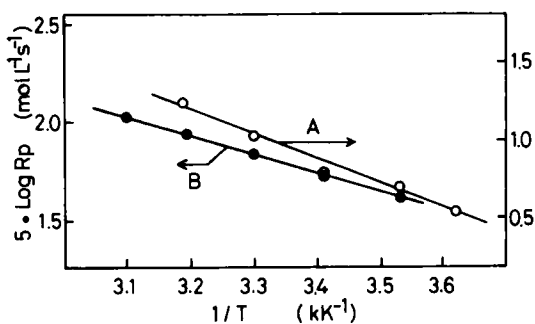


FIG. 8. Effect of temperature on the rate of photopolymerization in bulk for AN by Fc (A) and for MMA by Fc-CCl_4 (B). (A): $[\text{Fc}] = 3.2 \times 10^{-3} \text{ M}$; (B): $[\text{Fc}] = 2.6 \times 10^{-3} \text{ M}$, $[\text{CCl}_4] = 0.5 \text{ M}$.

Photopolymerization of Various Vinyl Monomers Initiated by the Fc and CCl_4 System

Methyl Methacrylate

As can be seen from Figs. 1 and 2, the photopolymerization rates of AN and MMA increase significantly with addition of both Fc and CCl_4 , though the rates increase slightly with addition of CCl_4 alone [16]. Similarly, methyl acrylate and methacrylonitrile (MAN) were polymerized effectively by the Fc- CCl_4 system. These results show clearly that Fc becomes an effective sensitizer in the presence of CCl_4 for the photopolymerization of these monomers.

The photopolymerization of MMA with the Fc- CCl_4 system was depressed by the addition of DPPH, hydroquinone, or oxygen. As shown by Curve B in Fig. 5, the composition curve of the photoinduced copolymerization of MMA (M_2) with St (M_1) fits in with that reported for the radical copolymerization ($r_1 = 0.52$ and $r_2 = 0.46$) [17]. These facts indicate that the photopolymerization of MMA by Fc- CCl_4 proceeds by a radical mechanism.

In the presence of CCl_4 , Fc exhibits a new absorption band in the wavelength region of 300 to 380 nm ($\lambda_{\text{max}} \approx 310$ nm), as shown in Fig. 9. It is known that this type of absorption band of Fc appears in halo-methane solvents such as CCl_4 , chloroform, and bromoform [18, 19]. Bozak [20] suggested that this new band is due to a CT complex formed between Fc and CCl_4 , the iron atom serving as an electron donor and the

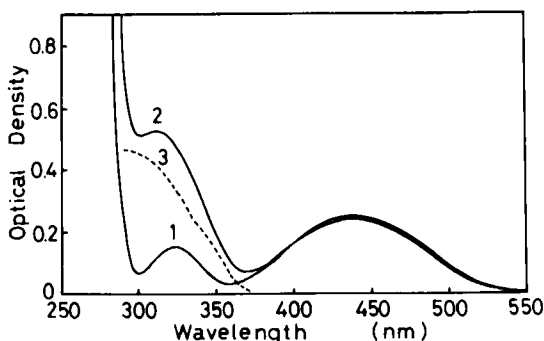


FIG. 9. Absorption spectra of Fc in the presence of CCl_4 in cyclohexane: (1) Fc ($2.5 \times 10^{-3} M$), (2) Fc ($2.5 \times 10^{-3} M$) + CCl_4 ($2.1 M$), (3) differential spectrum obtained by subtracting spectrum (1) from spectrum (2).

chlorine atom as an electron acceptor. From the experiments with filtered irradiation, it was found that the effective wavelength of light for the photopolymerization of MMA by Fc-CCl₄ is in the range of 300 to 370 nm. Therefore we presume that the primary process of photochemical initiation of the polymerization is the absorption of light by this complex, and the initiating species is formed by the photochemical dissociation of this complex [10].

Kinetic investigations were performed in benzene at 20°C with filtered irradiation (400 > λ > 300 nm). The dependence of the photopolymerization rate (*R_p*) on the concentrations of Fc, CCl₄, and MMA monomer was examined. From the results shown in Fig. 10, the kinetic relationship was obtained as follows:

$$R_p = k_2[\text{Fc}]^{0.47}[\text{CCl}_4]^{0.42}[\text{MMA}]^{1.5}$$

This relationship indicates that the bimolecular termination occurs in the photopolymerization and that MMA monomer takes part in the initiation reaction of the polymerization by the Fc-CCl₄ system.

The temperature dependence of the photopolymerization of MMA in bulk by Fc-CCl₄ was studied in the range of 10 to 50°C. The Arrhenius relationship shown by Line B in Fig. 5 gave the value of 4.4 kcal/mol as

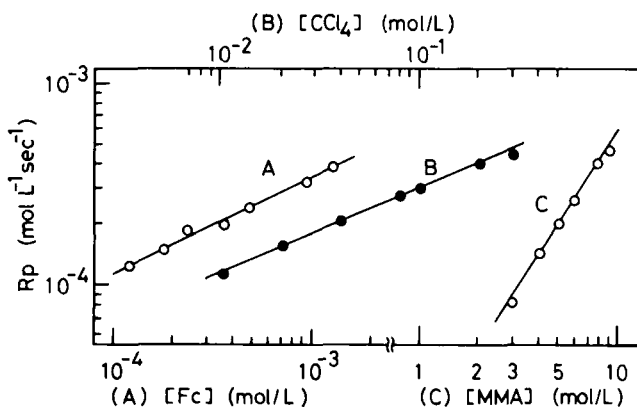


FIG. 10. Dependence of the photopolymerization rate of MMA on the concentration of (A) Fc, (B) CCl₄, and (C) MMA in benzene: (A) [MMA] = 8.0 M, [CCl₄] = 0.94 M; (B) [MMA] = 8.0 M, [Fc] = 4.9 × 10⁻³ M; (C) [Fc] = 2.0 × 10⁻³ M, [CCl₄] = 0.3 M.

the overall activation energy of the polymerization. This value is in good agreement with that reported for the photoinitiated radical polymerization of MMA by benzoyl peroxide [15, 21].

Styrene

The effects of addition of Fc and CCl_4 on the photopolymerization of St are shown in Fig. 3. It is noted that the Fc- CCl_4 system does not sensitize the photopolymerization of St and gives an induction period as compared with the case of CCl_4 alone [16].

Figure 11 shows the effects of concentration of Fc on the photopolymerization of St by the Fc- CCl_4 system. When the concentration of Fc increases, the induction period becomes longer, while the rate of polymerization remains almost unaltered. The polymer obtained has a pale orange color, which could not be removed by reprecipitations, and the polymer exhibited characteristic absorption of Fc at 440 nm; this suggests that Fc is incorporated into the polymer chain in the course of polymerization. Photopolymerization in the presence of either Fc or CCl_4 has no induction period (Fig. 3), and the products are colorless. These observations indicate that Fc becomes an inhibitor for the photopolymerization of St in the presence of CCl_4 .

As can be seen from Fig. 11, on the other hand, the molecular weight (viscosity) of the polymer decreases with increasing concentration of Fc. Imoto et al. also reported a similar decrease of molecular weight of the

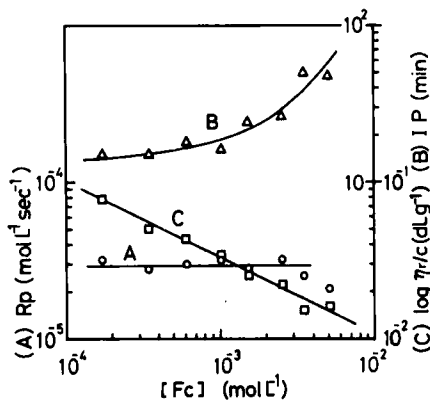


FIG. 11. Effects of concentration of Fc on the photopolymerization of St by Fc- CCl_4 : (A) the rate of polymerization, (B) induction period, (C) η_{rel}/C for the polymer obtained; $[\text{CCl}_4] = 0.5 M$.

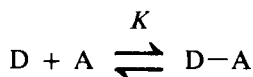
polymers obtained in thermal polymerization of MMA with Fc-CCl₄ in benzene at 85°C [7]. CCl₄ is a chain transfer reagent [15], whereas Fc is not reactive with propagating radicals [5]. Therefore, it is thought that the chain transfer ability of CCl₄ may be strengthened by the CT interaction with Fc. However, details of this chain transfer reaction are not clear at present.

Isobutyl Vinyl Ether

As shown in Fig. 4, it was found that IBVE is also efficiently polymerized by the Fc-CCl₄ system. The photopolymerization is not induced by Fc or CCl₄ alone. It is known that IBVE inherently has a high ability for cationic polymerization but it has no ability for radical homopolymerization [6]. The photopolymerization of IBVE by the Fc-CCl₄ system is therefore considered to proceed by a cationic mechanism. The absorption spectrum of the poly(IBVE) obtained indicates that Fc is not incorporated in the polymer.

Analysis of CT Complex of Fc with Monomer or CCl₄

As can be seen from Figs. 3 and 8, the absorption band due to the CT complex for the Fc-AN system is almost the same in shape and in position as that for the Fc-CCl₄ system. Similar absorption bands were also observed for systems with other acceptor monomers such as MAN and MMA. In these systems Fc acts as an electron donor (D) and monomer or CCl₄ acts as an electron acceptor (A). In order to get further information on the CT interaction, the spectra of these systems were analyzed on the basis of the following D-A complex formation:



The association constant K was evaluated by use of the following equation [22]:

$$[A]/(d/[D] - \epsilon_D) = 1/K(\epsilon_C - \epsilon_D) + [A]/(\epsilon_C - \epsilon_D) \quad (1)$$

where d is the absorbance of the system (per 1 cm light-path length); $[D]$ and $[A]$ are the initial concentrations of D and A, respectively; and ϵ_C and ϵ_D are the molar extinction coefficients of the complex (D-A) and D, respectively. The absorbance at 300 nm was measured in cyclohexane under the condition of $[A] \gg [D]$ at room temperature.

Plots of the left-hand term of Eq. (1) against $[A]$ are shown in Fig. 12. A linear relationship holds for all the systems, indicating that the 1:1 associated species is formed. From the gradient of the straight line and the extrapolated intercept, the values of K and ϵ_c were evaluated. The results obtained for the systems of Fc and monomer are summarized in Table 1. For the CT complex of Fc with AN monomer having a larger e -value, a larger value of K was obtained, and the binding energy ($-\Delta H$) was estimated to be 1.0 kcal/mol from the experimental results on temperature dependence of K [22]. For the Fc- CCl_4 system, on the other hand, the gradient of the line is equal to zero (Fig. 12), leading to values of $K \approx 0$ and $\epsilon_c = \infty$. This result indicates that the CT interaction between Fc and CCl_4 is very weak and that a contact CT complex is formed [22]. Such a contact CT interaction has been also suggested for the vinylferrocene and CCl_4 system [23].

Initiation Mechanism

In the present study the CT complex of Fc with monomer or CCl_4 was found to play an important role in the photoinitiation of polymerizations. It was also found that the sensitizing effect of Fc or Fc- CCl_4

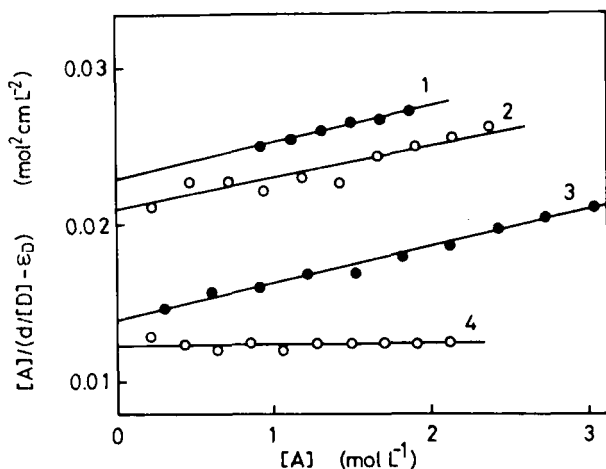


FIG. 12. Plots of Eq. (1) for CT-complexes of Fc with various acceptors in cyclohexane measured at 300 nm: (1) Fc-MMA, (2) Fc-MAN, (3) Fc-AN, (4) Fc- CCl_4 .

TABLE 1. Values of K and ϵ_C for CT Complexes of Ferrocene with Monomers^a

Monomer	e^b	K	ϵ_C (300 nm)
AN ^c	1.20	0.17	460
MAN	0.81	0.09	550
MMA	0.40	0.10	420

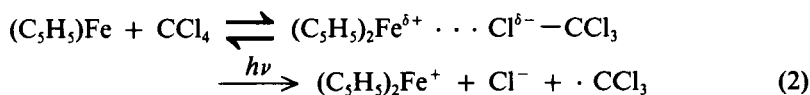
^aMeasured in cyclohexane at 24°C.

^b e -Value of Alfrey-Price [14].

^c $-\Delta H = 1.0$ kcal/mol and $\Delta S = -7.4$ cal·mol⁻¹·K⁻¹ were obtained from the temperature dependence of K by using the relationship: $\ln K = \Delta S/R - (\Delta H/R)(1/T)$ [22].

depends on the kind of monomer. In the case of the AN-Fc system, the UV spectrum of the reaction solution did not change with photoirradiation, and any transient species could not be detected with microsecond flash photolysis. The detailed initiation mechanism is therefore not clear at present. However, the experimental results described above suggest that the photopolymerization may proceed by a radical mechanism involving a photoreaction of the CT complex [13].

In the case of the MMA-Fc-CCl₄ system, UV spectra of the reaction solutions were observed to change with irradiation. As shown in Fig. 13, a new absorption band at 620 nm appears together with absorptions around 360 and 315 nm. The appearance of this new band indicates that Fc is photooxidized to ferricenium cation (C₅H₅)₂Fe⁺ (Fc⁺) [18, 19]. Flash photolysis experiments reveal that the cation is produced rapidly within the duration time of the flashlight and disappears very slowly with a long lifetime of 6.7 s, as can be seen from Fig. 14. Thus, the contact CT complex I between Fc and CCl₄ dissociates photochemically to form the cation Fc⁺ and trichloromethyl radical as follows:



However, it is thought that the trichloromethyl radical is unable to react directly with monomer. For the photopolymerization of MMA by Fc-

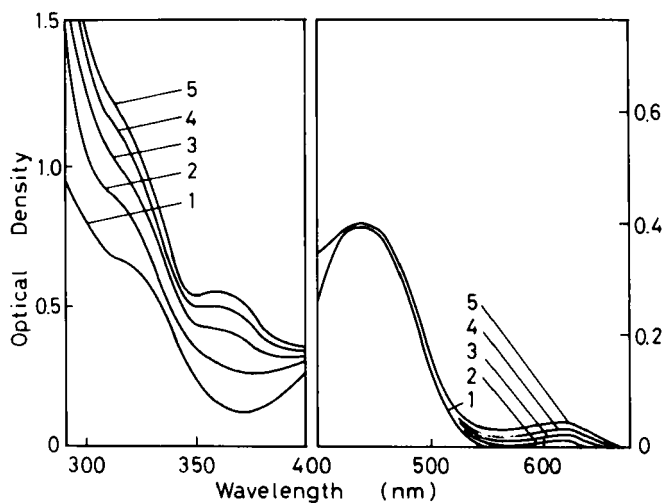


FIG. 13. Changes of absorption spectra for the photopolymerization system MMA-Fc- CCl_4 measured after irradiation for (1) 0 min, (2) 1 min, (3) 3 min, (4) 5 min, and (5) 7 min: $[\text{Fc}] = 4 \times 10^{-3} M$, $[\text{CCl}_4] = 1.0 M$, $[\text{MMA}] = 3.0 M$, in benzene.

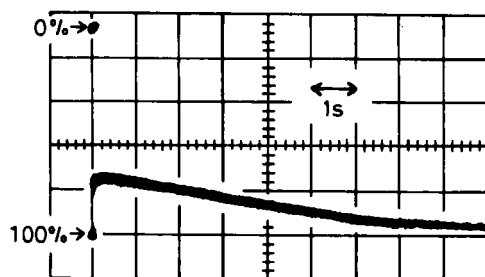
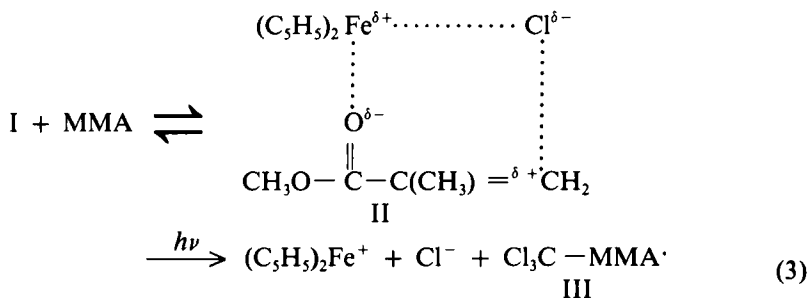
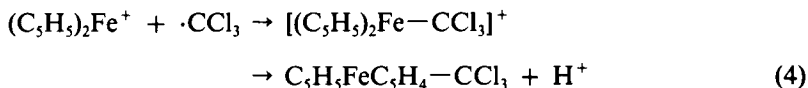


FIG. 14. Oscillogram of transient absorption of Fc^+ observed at 620 nm in benzene at room temperature: $[\text{Fc}] = 6 \times 10^{-3} M$, $[\text{MMA}] = 2.6 M$, $[\text{CCl}_4] = 1.2 M$.

CCl_4 , results of the kinetics indicate that MMA monomer takes part in the initiating step, and the spectroscopic analysis shows that Fc interacts with MMA to form a CT complex. From these experimental facts it is considered that the initiating species is produced as a consequence of the interaction of MMA monomer with the complex I. Thus the monomer radical III may be formed by the photodissociation of a tentative triplex II as follows:



On the other hand, the Fc- CCl_4 system does not sensitize the photopolymerization of St, because St is a donor monomer and cannot form a triplex like II. However, the UV absorption at 620 nm was also observed for the St-Fc- CCl_4 system; this implies the formation of Fc^+ . It is known that Fc^+ is reactive to radicals [24] but Fc does not [5]. Therefore the trichloromethyl radical seems to be consumed by the reaction with Fc^+ as follows [25]:



Fc^+ also react with polymer radicals [26] and terminates the polymerization; that is, the Fc- CCl_4 system is an inhibitor for St. The Fc- CCl_4 system also serves as a good sensitizer for the photoinduced cationic polymerization of IBVE; one of the initiation reactions is thought to be the addition of a proton (Eq. 4) to the monomer.

ACKNOWLEDGMENTS

We express our thanks to Prof. M. Yamamoto and Mr. M. Ohoka of Kyoto University for their valuable discussions and kind advice. We also thank The Textile Research Foundation for a Grant-in-Aid.

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Received August 28, 1990

Revision received January 13, 1991