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Photoinitiation of methyl methacrylate with a novel iron(III) oxalato complex

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Summary

The photopolymerization of methyl methacrylate (MMA) by the photoinitiator iron(III) tris(oxalato) ferrate(III) tetrahydrate, $Fe[Fe(C_2O_4)_3].4H_2O$ (A) has been studied under UV radiation of 254 nm at 35°C in DMSO. The initial rate of polymerization, R_p is proportional to $[MMA]^{1.11\pm0.13}$. R_p also varies linearly with the square root of [A] up to 5.00×10^{-4} mol l^{-1} and above this concentration, R_p decreases with the increase of [A]. It is likely that at a higher concentration of the complex A, the termination of the polymer chain occurs through interaction between the molecules of the complex. A suitable mechanism has been proposed to explain the kinetics of the reaction.

Introduction

The photoinitiation of vinyl monomers by oxalato complexes of transition metal ions has been a subject of increasing interest(1-3). The ferrioxalate complex undergoes (4) a photo redox reaction quite similar to the reactions of ion pairs (5) and on light absorption, the ferrioxalate complex decomposes to yield Fe(II) and CO_2. In the primary photochemical process (6), the photolysis of the ferrioxalate complex involved an electron transfer from the oxalato ligand to the central Fe(III) ion, resulting in the formation of Fe(II) ion and a free radical. The formation of free radical was further supported by proton magnetic resonance studies (7).

In the photopolymerization of MMA (1) by potassium tris-(oxalato) ferrate(III) in aqueous acidic solution with light of wavelength 365 nm, dissolved oxygen caused induction periods and instant polymerization occurs when the reaction mixture was deaerated and then irradiated. Based on the evidence from the production of significant concentrations of $\dot{C}_2O_4$ radical anions a kinetic expression was also derived. Baumann et al. (2,3) studied the photopolymerization of acrylamide by oxalato complexes of iron and cobalt, and reported that the rate was inefficient because the produced nucleophilic CO_2 radicals were oxidized or were deactivated by interaction with polymer radicals. The cobaltate complexes

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possesses higher polymerization quantum yield than ferrate complexes for the polymerization of acrylamide.

A thorough understanding of the factor determining the efficiency of the initiation step has been achieved due to the background provided by several previous studies on the photopolymerization by oxalato complexes (1-3). However, no such studies have been reported with the bimetallic oxalato complex of the type $M[M(C_2O_4)_3].nH_2O$ where M is the same transition metal ion and the detail chemistry of photoinitiation of transition metal ions is not perspicuous. The synthesis and characterization of iron(III) tris(oxalato) ferrate(III) tetrahydrate, $Fe[Fe(C_2O_4)_3].4H_2O$ (A) is well known (8). On photoreduction of complex A only Fe(II) ions are formed but irradiation of potassium tris oxalato ferrate(III) results in the reduction of Fe(III) to Fe(II) alongwith formation of K-salt. The purpose of the study is to gain a better insight into the photochemical behaviour of iron(III) tris(oxalato) ferrate(III). The photopolymerization is carried under UV radiation of 254 nm at 35°C in dimethyl sulfoxide (DMSO).

Experimental

MMA and DMSO were purified as in the literature (9). The complex $Fe[Fe(C_2O_4)_3].4H_2O$ (A) was prepared as before (8).

The photopolymerization reactions were conducted with the help of an immersion well photochemical reactor (Applied Photophysics). The reactant were irradiated by UV light produced by low pressure lamp of 16W which emit more than 90% of its radiation at 254 nm. The lamp was located in a cooled, double walled immersion well. Despite their low power (16W), the UV lamp produce over 3×10^{18} photons/s (measured by ferrioxalate actinometry in a quartz well), which have a long life and a negligible warm-up time.

The photochemical reactor was immersed in a constant temperature thermostatic bath at 35°C and polymerizations were conducted by irradiating the filler tubes at a fixed distance from the photochemical reactor. After desired time periods the contents of the tubes were precipitated in a non-solvent containing traces of hydroquinone. Percent conversion and subsequently rates of polymerization were calculated from the weight of polymer formed.

Differential scanning calorimetry (DSC) for the analysis of glass transition temperature (T_g) of polymers was carried out at a heating rate of 10°C/min on a Perkin Elmer PC series DSC 7 with 2-5 mg of polymer samples weighed in aluminium pans. All experiments were carried in nitrogen atmosphere and the measurement was started as soon as the heat flow in the DSC cell was stabilized.

Intrinsic viscosities were determined at 25°C using a Schott Gerate model AVS 400 automated viscometer in benzene.

Molecular weights ($\bar{M}_n$) were computed from intrinsic viscosity data by using the relation (10):

$$[\eta] = 8.69 \times 10^{-5} \bar{M}_n^{0.76}$$

Results and Discussion

The initial polymerization rate, R_p, shows a linear dependence on [MMA] (Table I) with a slope of 1.11±0.13. This is in accordance with the general equation for the steady state free radical photoinitiated polymerization.

TABLE I

Data for the relationship between R_p, molecular weight ($\bar{M}_n$) and glass transition temperature (T_g) on [MMA] at 35°C in DMSO initiated by complex A, $Fe[Fe(C_2O_4)_3].4H_2O$
$[A] = 5.00 \times 10^{-4}$ mol l^{-1}; irradiated wavelength = 254 nm.

[MMA] Mol l^{-1}	Irradiation time min.	$R_p \times 10^6$ mol $l^{-1}s^{-1}$	$\bar{M}_n$	T_g °C
1.40	180	2.49	18700	125.6
1.87	180	3.13	22300	126.5
2.34	180	4.58	34500	132.1
2.80	180	5.18	42100	132.8

The relationship between R_p and photoinitiator concentration, [A], at fixed monomer concentration in DMSO is shown in Fig. 1. The slope in the first part of the curve is approximately 0.5 (0.45±0.03) which indicates the square root dependence of R_p on [A]. This is in accordance with the general equation for steady state photopolymerization. When complex concentration of above 5.00×10^{-4} mol l^{-1} is used, R_p exhibits a decreasing trend. Hence, it is likely that at a high concentration of A an appreciable participation of primary radical termination takes place. Under these conditions, R_p decreases as the participation of termination processes by primary radical increases. From the slope of the final portion of the curve it can be seen that R_p is inversely proportional to the square root (-0.42±0.01) of [A]. This is in agreement with the analytical expression developed by Schultz and Joshi (11) for the kinetics of photoinitiated polymerization under non-stirred condition. A similar trend at high complex concentration was reported by various workers (1,12,13). Under our experimental conditions attempts have been made to polymerize MMA using a complex concentration below 5.00×10^{-5} mol l^{-1}, but the trace quantity of polymer formed is practically irrecoverable.

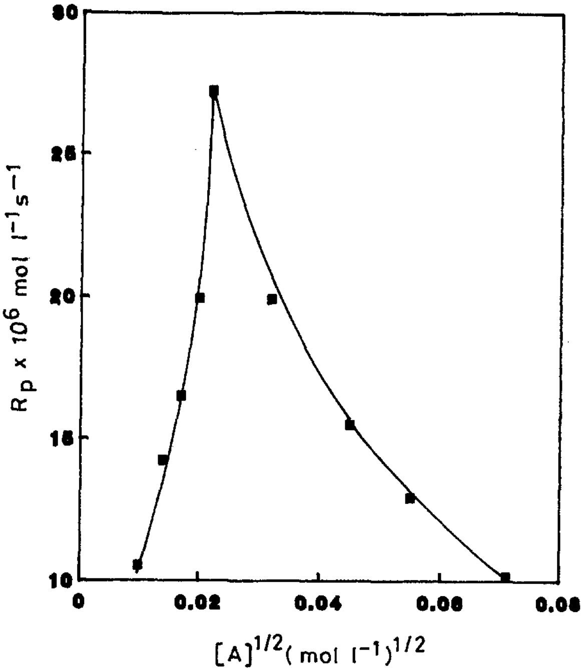

Fig. 1. Plot of rate of photopolymerization, R_p, of MMA as a function of square root of photoinitiator (A) concentration. [MMA] = 1.87 mol l^{-1}; irradiated wavelength = 254 nm.

The average rate constant at 35°C calculated from a first order plot for the photopolymerization of MMA initiated by the complex A is found to be $3.63 \pm 0.18 \times 10^{-6}$ s^{-1}.

General kinetic expression for photopolymerization:

The ferrioxalato complexes have been reported to undergo a photoredox reaction yielding $\dot{C}_2O_4^-$ and $\dot{C}O_2^-$ free radicals for photopolymerization by an electron transfer process. The mechanism for the photopolymerization of MMA initiated by iron(III) tris(oxalato) ferrate(III) as photoinitiator may be represented as (1,2):

$$[Fe^{3+}(C_2O_4)_3]^{3-} \xrightarrow{h\nu} [Fe^{2+}(C_2O_4)]^{2-} + \dot{C}_2O_4^-/\dot{C}O_2^- + CO_2 \qquad (1)$$

$$[Fe^{3+}(C_2O_4)_3]^{3-} + \dot{C}O_2^- \xrightarrow{k_{ox}} [Fe^{2+}(C_2O_4)_2]^{2-} + C_2O_4^{2-} + CO_2 \qquad (2)$$

$$\underset{(R^\cdot)}{\dot{C}_2O_4^-} \longrightarrow \underset{(R^\cdot)}{\dot{C}O_2^-} + CO_2 \qquad (3)$$

where R˙ is the initiating free radical.

The experimental results are in accordance with the general expression for steady state free radical photopolymerization. Photopolymerization rate expression is normally expressed as (14):

$$R_p = k_p[M](\phi I_a/k_t)^{1/2} \qquad (4)$$

$$= k_p[M](\phi I_o[1 - e^{-\epsilon[PI]l/k_t]^{1/2}} \qquad (5)$$

where k_p and k_t are the rate constants for propagation and termination, respectively, I_a and I_o are the intensities of the incident and absorbed light (in einstein l^{-1} s^{-1}, PI is the species which undergoes photoexcitation, ϵ is the molar extinction coefficient of PI at the irradiated wavelength (254 nm), l is the distance of the reaction system from the light source and ϕ is the quantum yield for the initiation.

For small absorbance (ϵ [PI]l << 1), eq. 5 became:

$$R_p = (k_p/k_t^{1/2})[M].(2.3\phi I_o\,\epsilon\,[PI]l)^{1/2} \qquad (6)$$

In fact, by keeping [PI] $\leq 10^{-5}$ mol l^{-1}, I_a practically did not vary appreciably throughout the thickness of the reaction vessel and under these conditions the initial R_p varies linearly with square root of [PI].

For higher [PI] ($>10^{-4}$ mol l^{-1}), $I_a = I_o(1 - 10^{-\epsilon[PI]l}) \approx I_o$ and the initial R_p must be independent of [PI]. For polymerization carried out in an unstirred system, a decrease of the initial R_p as the PI concentration increases was observed at high absorbance values (15). This agrees with the expression developed by Schultz and Joshi (11) for kinetics of photoinitiated polymerization under non-stirring conditions:

$$R_p = (k_p/k_t^{1/2}).(\{(\phi I_o)^{1/2}[M]\}/\{\epsilon[PI]l\})^{1/2}.(1 - 10^{-\epsilon[PI]l/2}) \qquad (7)$$

Equation (7) shows that R_p is inversely proportional to the square root of [PI] at higher concentration. The value of $k_p/k_t^{1/2}$ was calculated using the Mayo equation (15). The value obtained was 0.08, which is quite in conformity with the literature value for MMA (14). $\bar{M}_n$ values for poly(MMA) obtained using complex A as photoinitiator at different [MMA] are given in Table I.

Table I also presents the DSC results on the T_g of poly(MMA) samples whose molecular weights were determined viscometrically. The results showed that within experimental error the T_g's of poly(MMA) are seen to increase in a linear way with increasing monomer concentration and levels off at about 132.8°C. This indicates that T_g of a given polymer is a function of its chain length (16,17).

As shown from our studies, the complex A appears to be very efficient photoinitiator for producing fast photopolymerization. Besides, being a much more effective photoinitiator than conventional oxalato complexes, iron(III) tris(oxalato) ferrate(III) also improves the properties of polymer formed, in particular its hardness and scratch resistance. As a non-toxic and low cost compound, this photoinitiator should prove to be most valuable in photopolymer applications. Our study on the photopolymerization of MMA by ferri oxalato complex provides further evidence for the production of significant amount of $\dot{C}_2O_4^-$ radical anions and today photopolymerization is probably the most widely studied system of photochemical image formation. The results obtained with this photoinitiator system and its potential application have encouraged us to continue our study to gain better insight into their photochemical behavior and the photoinitiated polymerization.

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