

Polymerization of Methyl Methacrylate by Imidazole–Carbon Tetrachloride Charge-Transfer System

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SYNOPSIS

The kinetics of charge-transfer (CT) polymerization of methyl methacrylate (MMA) in the presence of imidazole (Imy) and CCl₄ was studied in dimethyl sulfoxide (DMSO) at 60°C. The rate of polymerization (R_p) is sensitive to the [CCl₄] up to a concentration of 0.60 mol L⁻¹, but at a higher concentration, it is practically independent of the [CCl₄]. When [CCl₄] > [Imy], R_p is proportional to [MMA]^{1.45±0.15} and [Imy]^{0.53±0.04} and the average rate constant for the polymerization of MMA is $3.25 \pm 0.41 \times 10^{-6}$ L mol⁻¹ s⁻¹. This article also reports the polymerization of MMA initiated by Imy and CCl₄ and accelerated by hexakis(dimethyl sulfoxide) iron(III) perchlorate, [Fe(DMSO)₆](ClO₄)₃ (A), at 60°C. The presence of Fe(Imy)₃³⁺ in the polymerization system produced well-defined induction periods. The rate constant at 60°C for the interaction of the poly(MMA) radical toward Fe(Imy)₃³⁺ is 7.19×10^4 L mol⁻¹ s⁻¹. A probable reaction mechanism for the polymerization system has been postulated to explain the observed results. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The charge-transfer (CT) initiation of vinyl monomers by nitrogen donor compounds in conjunction with organic halides is now well established.^{1–4} The detailed mechanism on the catalytic activity of transition-metal complexes^{5–9} in the polymerization of vinyl monomers has been recognized for many years and recent studies reveal that transition-metal complexes play a significant role in vinyl polymerization initiated by a CT mechanism. The efficiency of a complex to initiate the CT polymerization depends upon the liability of the complex.¹⁰ Lewis acids are good electron acceptors, and in the presence of Lewis acids like Fe³⁺ and Cu²⁺, the electron-donating capacity of the donor molecule becomes faster and the rate of formation of free radicals becomes rapid.³ Yamachita et al.¹¹ reported the formation of an adduct of methyl methacrylate (MMA) and imidazole (Imy) which acts as an anionic initiator for the an-

ionic polymerization of MMA. Duration of the propagation step was increased by the presence of the adduct. Stevenson and Coppinger¹² also reported that trimethylamine reacts with alkyl halide to produce a 1 : 1 CT complex. They assumed that metal ions like Fe²⁺ and Cu⁺ are oxidized by CCl₄ to produce CCl₃. Koyama and Nishimura¹³ reported that CCl₄ acts as the best initiator for the polymerization of vinyl monomers like MMA. They found that the rate of polymerization, R_p , increased rapidly with [CCl₄] until the limiting value for CCl₄ was reached. The objective of the present work was to synthesize polymers of desired molecular weight distribution by systematically selecting the polymerization conditions and, thus, polymers with a range of molecular weight became accessible which would be difficult to achieve by other means of initiation. This article reports the polymerization of MMA initiated by CT complexes formed between Imy and CCl₄ at 60°C in the presence and absence of the complex hexakis(dimethyl sulfoxide) iron(III) perchlorate, [Fe(DMSO)₆](ClO₄)₃, in DMSO medium. The complex formed between Fe³⁺ and Imy was well characterized.

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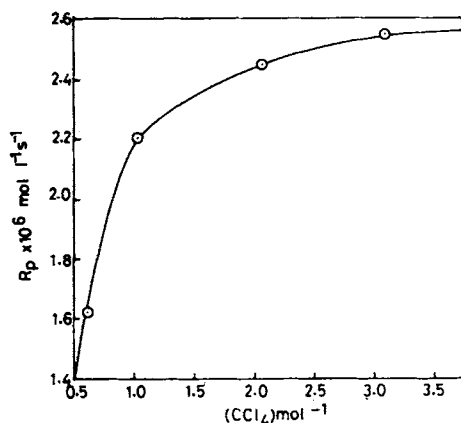


Figure 1 Relationship between R_p and $[\text{CCl}_4]$ at 60°C . $[\text{MMA}] = 1.87 \text{ mol L}^{-1}$; $[\text{Imy}] = 5.40 \times 10^{-2} \text{ mol L}^{-1}$. Reaction time = 5 h.

EXPERIMENTAL

The purification of methyl methacrylate (MMA), CCl_4 , DMSO, and tetrahydrofuran (THF) were essentially the same as described in the preceding articles.^{6,7} Imidazole (Merck) was used without further purification. The complex $[\text{Fe}(\text{DMSO})_6](\text{ClO}_4)_3$ (A) was prepared as before.⁷ The rate of polymerization (R_p) was determined gravimetrically and dilatometrically as before.⁷

Gel permeation chromatography (GPC) was performed using a Waters Model 510 solvent delivery system at a flow rate of 1.0 mL/min through a set of four Ultrastayragel columns (Waters) of exclusion sizes 10^6 , 10^5 , 10^4 , and 500 \AA . The analysis was performed at room temperature using purified high-performance liquid chromatography (HPLC)-grade THF as the eluent. A differential refractometer Model R401 from Waters was used as the detector. The sample concentration was 0.2% w/v, and the volume of the polymer injected was $50 \mu\text{L}$. The GPC curves were analyzed with the calibration curve obtained by nine narrow-MWD polystyrene samples (Waters).

Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer PC series DSC 7 with 2–5 mg of polymer samples weighed in aluminum pans. Heating scans for the analysis of the glass transition temperature (T_g) of polymers were carried out at a heating rate of $10^\circ\text{C}/\text{min}$. All experiments were carried in a nitrogen atmosphere and the measurement was started as soon as the heat flow in the DSC cell was stabilized. The characterization of the iron (III) complex in DMSO was done on a JASCO model 7800 (CRT) spectrophotometer.

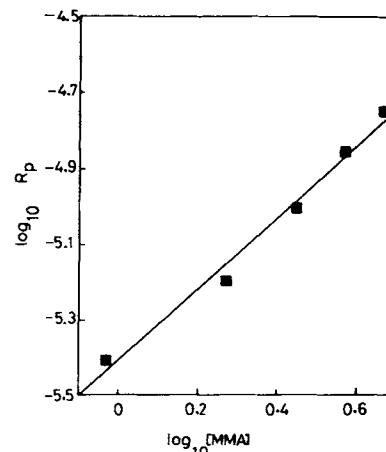


Figure 2 Relationship between $\log R_p$ and $\log[\text{MMA}]$ at 60°C . $[\text{Imy}] = 1.20 \times 10^{-2} \text{ mol L}^{-1}$; $[\text{CCl}_4] = 0.83 \text{ mol L}^{-1}$; reaction time = 5 h.

RESULTS AND DISCUSSION

Rate Measurement with Imidazole and CCl_4

MMA was polymerized by Imy which contains a donor nitrogen atom in the presence of CCl_4 at 60°C in DMSO. No polymerization was observed even after 6 h in the absence of either Imy or CCl_4 .

It was found that R_p increases rapidly with increase of $[\text{CCl}_4]$ up to 1.30 mol L^{-1} , but beyond that, R_p became independent of $[\text{CCl}_4]$ (Fig. 1). In the present study, therefore, CCl_4 was always used in excess to eliminate the effect of $[\text{CCl}_4]$ on R_p .

Experimentally, R_p was found to vary as $[\text{MMA}]^{1.45 \pm 0.15}$ (Fig. 2) and $[\text{Imy}]^{0.53 \pm 0.04}$ (Fig. 3) and the average rate constant, k , was found to be $3.25 \pm 0.41 \times 10^{-6} \text{ L mol}^{-1} \text{ s}^{-1}$ (when $[\text{Imy}]$

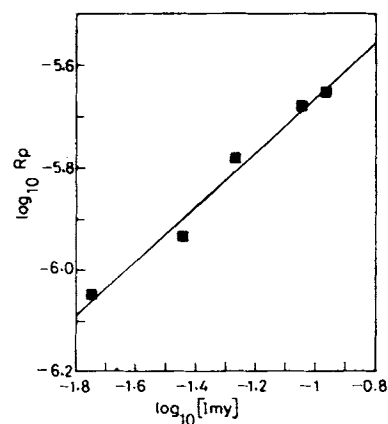


Figure 3 Relationship between $\log R_p$ and $\log[\text{Imy}]$ at 60°C . $[\text{MMA}] = 1.87 \text{ mol L}^{-1}$; $[\text{CCl}_4] = 0.83 \text{ mol L}^{-1}$; reaction time = 5 h.

> $[\text{CCl}_4]$). This agreed well with the rate constants at 60°C for the polymerization of MMA with other nitrogenous donor compounds.^{3,7}

The effect of variation of $[\text{Imy}]$, $[\text{MMA}]$, and $[\text{CCl}_4]$ on the molecular weight of poly(MMA) obtained with the Imy-CCl_4 CT initiator system is shown in Table I. It is found that the molecular weight increases with the increase of $[\text{MMA}]$ but decreases with the increase of $[\text{Imy}]$. This might be due to the deactivation of monomers as a result of an increase in $[\text{Imy}]$. Termination, which is slower relative to propagation, causes the deactivation of some growing chains at the same time as others continue to propagate. Therefore, the molecular weight distribution becomes broadened in a complex way which depends on whether termination occurs at a constant rate or at a rate which varies with conversion.¹⁴

The kinetic parameter $k_p/k_t^{1/2}$ at 60°C was evaluated by using the well-known Mayo expression in the following form:

$$1/\overline{DP} = (k_t/k_p^2) \times (R_p/[\text{MMA}]^2) + 1/\overline{DP}_0 \quad (1)$$

where \overline{DP} is the number-average degree of polymerization and \overline{DP}_0 is the value of \overline{DP} in the absence of transfer. Considering the amount of chain transfer to the monomer to be negligible, the plot of $1/\overline{DP}$ vs. $R_p/[\text{MMA}]^2$ at constant $[\text{Imy}]$ and $[\text{CCl}_4]$ should be linear. The plot is shown in Figure 4. From the figure, the value of $k_p/k_t^{1/2}$ for the polymerization of MMA was found to be 0.08. This value is quite in conformity with the literature value,¹⁵ which suggests that the initiation must be by the free radical produced from the decomposition

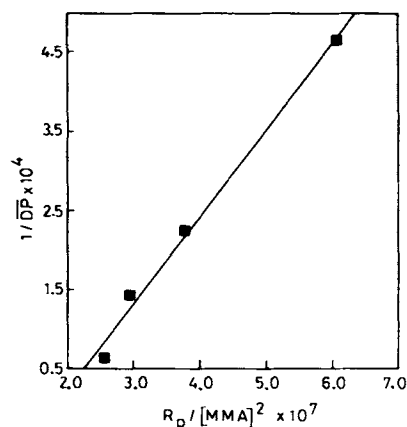


Figure 4 Plot of $1/\overline{DP}$ as a function of $R_p/[\text{MMA}]^2$. $[\text{Imy}] = 1.20 \times 10^{-2} \text{ mol L}^{-1}$; $[\text{CCl}_4] = 0.83 \text{ mol L}^{-1}$; $[\text{MMA}]$ variable.

of CT complexes. It was also found that the molecular weight of poly(MMA) obtained is independent of $[\text{CCl}_4]$ up to 0.83 mol L^{-1} , and above this concentration, it increases with $[\text{CCl}_4]$. It is also quite interesting to note that the molecular weights of poly(MMA) obtained with Imy are much higher than those obtained with other nitrogenous donor compounds.

The glass transition temperatures (T_g 's) of poly(MMA) as determined by DSC are also presented in Table I. The T_g 's seem to increase in a relatively linear manner with the increase of molecular weights. Figure 5 shows a typical DSC thermogram of poly(MMA) prepared by the Imy-CCl_4 CT system. Although many reports^{16,17} confirmed the original Fox-Flory relation¹⁸ on linear chain

Table I Dependence of Molecular Weights (\overline{M}_n and \overline{M}_w), Polydispersity Index, and Glass Transition Temperature (T_g) on MMA, Imy , and CCl_4 Concentrations^a

$[\text{MMA}]$ (mol L^{-1})	$[\text{Imy}] \times 10^2$ (mol L^{-1})	$[\text{CCl}_4]$ (mol L^{-1})	$R_p \times 10^7$ ($\text{mol L}^{-1} \text{ s}^{-1}$)	\overline{M}_n	\overline{M}_w	Polydispersity Index	T_g (°C)
0.94	1.20	0.83	2.88	214,800	1,176,400	5.47	115.2
1.87	1.20	0.83	7.14	444,100	1,567,100	3.52	118.8
2.81	1.20	0.83	15.67	695,400	2,575,900	3.70	123.7
3.74	1.20	0.83	19.85	1,542,600	3,659,500	2.37	127.1
1.87	1.80	0.83	8.95	516,800	1,122,300	2.17	—
1.87	5.40	0.83	16.68	267,300	2,316,400	8.66	119.1
1.87	9.00	0.83	20.90	204,800	1,129,700	5.51	—
1.87	10.80	0.83	22.20	165,500	550,600	3.32	—
1.87	5.40	0.62	16.36	287,200	1,285,727	4.47	119.5
1.87	5.40	1.04	23.00	419,700	2,636,000	6.28	118.2
1.87	5.40	2.07	24.63	477,200	1,428,000	3.40	—

^a Solvent = DMSO; temperature = 60°C; time = 5 h.

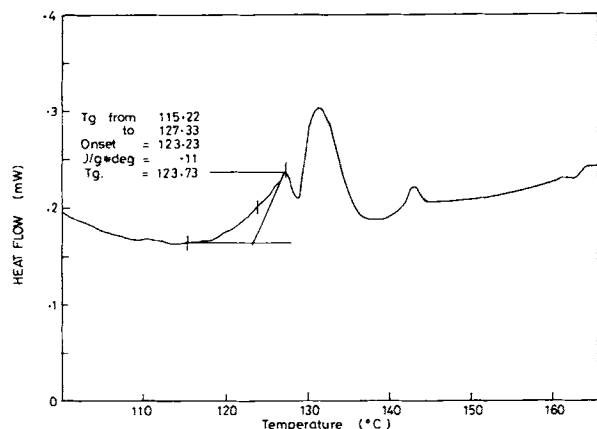


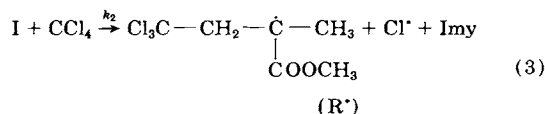
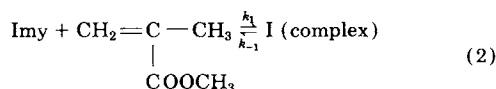
Figure 5 DSC thermogram of poly(MMA) at a scanning rate of 10°C/min, prepared by a charge-transfer complex at 60°C. [MMA] = 1.87 mol L⁻¹; [Imy] = 1.20 × 10⁻² mol L⁻¹; [CCl₄] = 0.83 mol L⁻¹.

length dependence of T_g , deviations from linearity have also been reported by several investigators.^{19,20}

The polymerization was also found to be inhibited by 1,1-diphenyl-2-picrylhydrazyl, indicating the free-radical mechanism of the reaction. Incorporation of the CCl₃ end group in the polymer chain and the existence of the Cl end group was confirmed by the dye-partition test.²¹

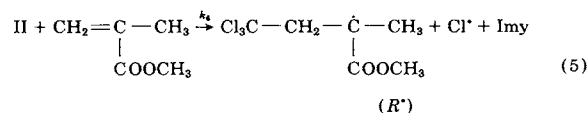
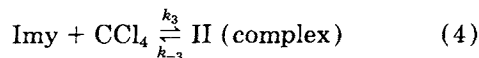
The mechanism for initiation of vinyl monomers by the CT complex formed by the interaction of Imy and CCl₄ as well as Imy and vinyl monomers is not certain. According to Matsuda et al.,² the CT complex (1 : 1 associated complex), *I*, formed between a nitrogen donor compound and monomer (*M*), interacts with CCl₄ to produce primary free-radical and ionic species. In the present study involving Imy as the nitrogen donor compound, the following mechanism may be proposed for the polymerization of MMA^{3,7}:

Initiation:



where *M* is MMA, *I* is the 1 : 1 associated CT complex formed between Imy and MMA, *R*'[•] is the primary free radical formed, and all the *k*'s are the respective rate constants.

According to Vofsi et al.⁸ and Lautenberger et al.,²² initiation is due to the CT complex formed between a nitrogen donor compound and CCl₄, which interacts with *M* and produces a primary free radical. Similarly, for the present system, the mechanism may be postulated as



where II is the CT complex formed between Imy and CCl₄. Presumably, both mechanisms are possible.^{3,6-7}

Spectroscopic identification of the CT complex formed between aliphatic amine (donor) and CCl₄ (acceptor) was reported by Lautenberger et al.²² Therefore, it may be adequate to assume a similar type of complex for Imy-CCl₄ mixture. The spectrum of a typical reaction mixture containing Imy and MMA in DMSO at 30°C showed a different absorption maximum at 300 nm in the UV region. The individual absorption maxima of MMA and Imy disappeared and the new band may be attributed to the CT interaction between Imy and MMA to produce free radicals responsible for the initiation of polymerization.

Investigations on the polymerization of MMA with certain nitrogen donor compounds established^{3,5-7} that when [CCl₄]/[Imy] ≤ 1 then mechanism (4) predominates, and by applying steady-state assumption, the rate expression may be represented as

$$R_p = k_p k_3^{1/2} (2k_t)^{-1/2} [M]^{1.0} [\text{Imy}]^{0.5} [\text{CCl}_4]^{0.5}$$

(assuming $k_4[M] \gg k_{-3}$)

$$= k[M]^{1.0} [\text{Imy}]^{0.5} [\text{CCl}_4]^{0.5} \quad (6)$$

Again, when [CCl₄]/[Imy] > 1, mechanism (2) predominates and *R_p* becomes independent of CCl₄. Under this condition, the rate equation may be expressed as

$$R_p = k_p k_1^{1/2} (2k_t)^{-1/2} [M]^{1.5} [\text{Imy}]^{0.5}$$

(when $k_2[\text{CCl}_4] \gg k_{-1}$)

$$= k[M]^{1.5} [\text{Imy}]^{0.5} \quad (7)$$

Equation (7) shows that *R_p* is proportional to the square root of [Imy] and to the 1.5th power of [M].

The above initiation mechanism suggests that the polymeric radical should contain the end $-\text{CCl}_3$ group. The polymers obtained by the $\text{Imy}-\text{CCl}_4$ donor-acceptor system are found to contain the halogen (Cl) end group by the dye-partition test²¹ which supports the proposed mechanism for polymerization. The incorporation of CCl_3 end groups from chain transfer with CCl_4 is neglected, since the transfer constant of the poly(MMA) radical¹⁵ with CCl_4 is 2.4×10^{-4} . Bamford et al.²³ studied the polymerization of MMA with the metal carbonyl- CCl_4 CT system. It was suggested that the initiating radicals were $\dot{\text{C}}\text{Cl}_3$ and it incorporated the CCl_3 end group in the polymer chain.

Characterization of the Complex Ion, $\text{Fe}(\text{Imy})_3^{3+}$

The formation of $\text{Fe}(\text{Imy})_3^{3+}$ in DMSO with a 1 : 3 molar ratio of $[\text{A}] : [\text{Imy}]$ was spectroscopically established. The UV and visible spectral curves of different solutions with a varied amount of A and Imy showed two distinct peaks at 335 and 738 nm, whereas the complex A alone showed only one peak at 335 nm in DMSO. Presumably, the peak at 335 nm exhibited by $\text{Fe}(\text{DMSO})_6^{3+}$ might be due to the CT transition²⁴ from coordinated solvent ligands to d -orbitals of Fe(III). The peak at 738 nm exhibited by $\text{Fe}(\text{Imy})_3^{3+}$ may be assigned to the $d-d$ transition and the maximum absorbency occurred at the $[\text{A}] : [\text{Imy}]$ molar ratio of 1 : 3. So, the peak must be due to the $\text{Fe}(\text{Imy})_3^{3+}$. Whether the complex formed was an inner- or outer-sphere or a simple salt remains obscure; however, for the sake of simplicity, it was assumed to be the inner complex $\text{Fe}(\text{Imy})_3^{3+}$. Assuming this to be true, the molar extinction coefficient of $\text{Fe}(\text{Imy})_3^{3+}$ at 738 nm was found to be $9.71 \times 10^2 \text{ L mol}^{-1} \text{ cm}^{-1}$. The equilibrium constant for the formation of $\text{Fe}(\text{Imy})_3^{3+}$ by the limiting logarithmic method at 738 nm was found to be $8.75 \times 10^2 \text{ L}^3 \text{ mol}^{-3}$.

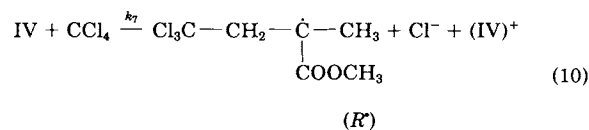
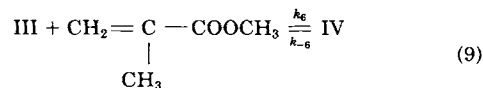
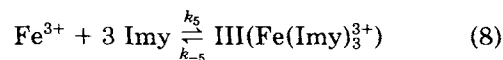
Effect of Addition on Iron(III) on the Charge-transfer-initiated Polymerization of MMA with Imidazole

It was found that the rate of polymerization of MMA by the $\text{Imy}-\text{CCl}_4$ donor-acceptor system is very slow to be followed dilatometrically. Therefore, it is assumed that the CT complexes are weak, but in the presence of Fe^{3+} , the polymerization was vastly accelerated. The rapid electron transfer from the poly(MMA) radical to Fe^{3+} is likely since the oxidation potential for the $\text{Fe}^{3+} + e \rightleftharpoons \text{Fe}^{2+}$ system is as high as 0.77 V.²⁵

The rates of polymerization of MMA were followed dilatometrically at 60°C by adding different amounts of Imy to a constant composition of MMA, CCl_4 , and complex A in DMSO. A few of the rate curves obtained from dilatometric experiments are shown in Figure 6. It was found that induction periods were reduced when the molar ratio of $[\text{A}] : [\text{Imy}]$ was less than 1 : 3. This indicates that $\text{Fe}(\text{Imy})_3^{3+}$ is partially formed before the molar ratio becomes 1 : 3; when this occurs, all the Fe^{3+} ions present in the system are converted into $\text{Fe}(\text{Imy})_3^{3+}$. It was also found that induction periods were less when $[\text{A}] : [\text{Imy}]$ exceeds 1 : 3. This may be due to the CT initiation of excess Imy present in the system. However, the rate curves after the induction period, i.e., after complete oxidation of poly(MMA) radical become parallel to the polymerization rate curve without the ideal retarder.

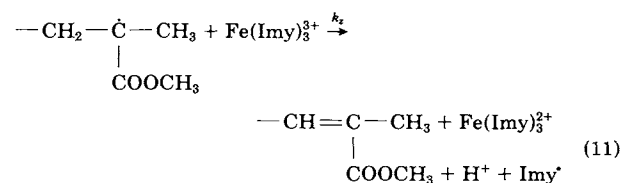
The following scheme may explain the mechanism of the reaction:

Initiation:



Termination:

Termination includes mutual by disproportionation and also an additional step [eq. (11)]:



In this scheme, (III) represents the complex $\text{Fe}(\text{Imy})_3^{3+}$ formed between A and Imy at a molar ratio of $[\text{A}] : [\text{Imy}] = 1 : 3$. It is suggested that for the polymerization of MMA (M) in the presence of $\text{Fe}(\text{Imy})_3^{3+}$ (III) and CCl_4 , complex III reacts with M to form an associated CT complex IV. The formation of an associated CT complex IV consisting of complex III and MMA was established spectroscopically. $\text{Fe}(\text{Imy})_3^{3+}$ shows an absorption maximum at 738 nm,

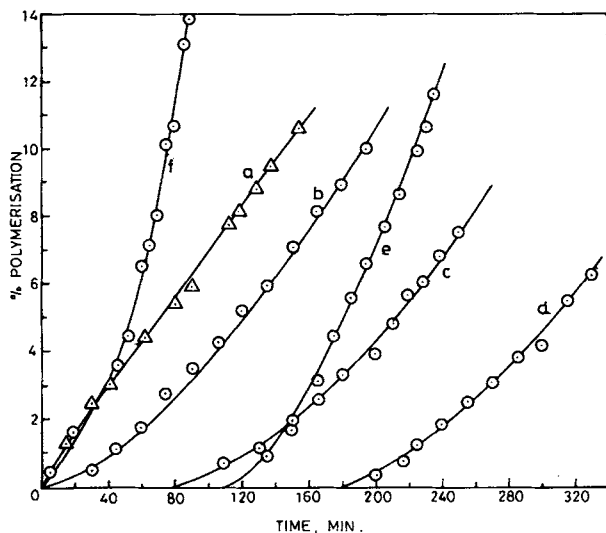


Figure 6 Polymerization of MMA in DMSO initiated by a charge-transfer complex formed by the interaction of Imy and MMA in the presence of CCl_4 with complex A at 60°C . $[\text{MMA}] = 1.87 \text{ mol L}^{-1}$; $[\text{CCl}_4] = 0.83 \text{ mol L}^{-1}$; $[\text{A}] = 1.20 \times 10^{-2} \text{ mol L}^{-1}$; $[\text{DMSO}] = 9.87 \text{ mol L}^{-1}$. Molar ratio of $[\text{A}] : [\text{Imy}]$ corresponding to curves (a) = 1 : 0.5, (b) = 1 : 1, (c) = 1 : 2, (d) = 1 : 3, (e) = 1 : 4, and (f) = 1 : 6.

while MMA has no absorption maximum in the visible region. The absorption maximum shifts to 720 nm on addition of MMA to the complex $\text{Fe}(\text{Imy})_3^{3+}$. The spectrum indicates the complex formation between $\text{Fe}(\text{Imy})_3^{3+}$ and MMA. The associated CT complex IV then reacts with CCl_4 to yield both a primary free-radical (R^*) and ionic species (Cl^- and IV^+). k_z is the termination rate constant for the interaction of the polymer radical with the ideal retarder $\text{Fe}(\text{Imy})_3^{3+}$.

Assuming the steady-state approximation during the initial stages of polymerization of vinyl monomers retarded by an ideal retarder, Z, Bamford et al.^{26,27} derived the following expression:

$$-(1/\phi_t) + \ln[(1 + \phi_t)/(1 - \phi_t)] = k_z[R^*]_s t + A^* \quad (12)$$

where ϕ_t is the ratio of the rate at any time t , R_p , in the presence of the retarder to the final maximum rate, R_{ps} , when the inhibitor has disappeared, i.e., $\phi_t = R_p/R_{ps}$; k_z is the rate constant for the interaction of polymer radical with the ideal retarder and A^* is the integration constant.

A detailed analysis of the rate curve measured with a 1 : 3 molar ratio of $[\text{A}] : [\text{Imy}]$ was made by the method of Bamford et al.^{26,27} and the plot of ϕ_t

vs. $k_z[R^*]_s t + A^*$ is shown in Figure 7. Reasonable agreement was found between the experimental and theoretical plot when $k_z[R^*]_s$ was $7.8 \times 10^{-4} \text{ s}^{-1}$ and $A^* = -10.2$, respectively, for Bamford's method, where k_z is the rate constant for the interaction of polymer radical with $\text{Fe}(\text{Imy})_3^{3+}$ [eq. (11)]. The theoretical curve was obtained by plotting ϕ_t vs. $-(1/\phi_t) + \ln[(1 + \phi_t)/(1 - \phi_t)]$, and the experimental one, by plotting ϕ_t vs. $k_z[R^*]_s t + A^*$.

The rate curve with a 1 : 3 molar ratio of $[\text{A}] : [\text{Imy}]$ was also analyzed by Bengough's methods I and II. Details of these methods are given elsewhere.^{27,28}

Experimental values of the concentration of monomers $[\text{M}]$ and the maximum rate of polymerization, R_{ps} , were 1.87 mol L^{-1} and $1.54 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$, respectively. Assuming k_p to be $734 \text{ L mol}^{-1} \text{ s}^{-1}$ at 60°C ,²⁹ the values of k_z calculated by Bamford's and Bengough's I and II methods were 6.97×10^4 , 7.40×10^4 , and $7.21 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$, respectively. Hence, the average value of k_z was $7.19 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$ at 60°C . This agrees well with the rate constants at 60°C for the interaction of the poly(MMA) radical with different Fe^{3+} ions.³

The effect of variation of $[\text{MMA}]$ and $[\text{CCl}_4]$ with a 1 : 3 molar ratio of $[\text{A}] : [\text{Imy}]$ on the molecular weights of poly(MMA) is shown in Table II. It was found that the molecular weight increases with increasing $[\text{MMA}]$ and also increases with $[\text{CCl}_4]$ up to 1.55 mol L^{-1} , and above this concentration of CCl_4 , it is independent of $[\text{CCl}_4]$. The higher polydispersity index may be due to the termination in a complex way, which depends on the whether termination occurs at a constant rate or at a rate which

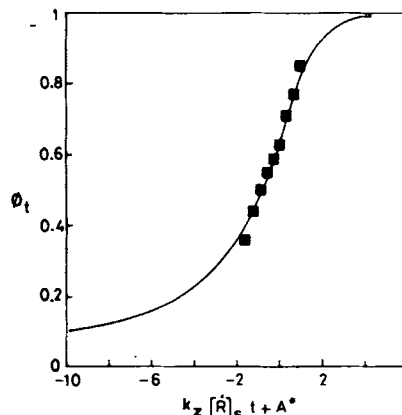


Figure 7 Reduced rate ϕ_t as a function of t expressed as $k_z[R^*]_s t + A^*$: (■) experimental points; (—) calculated curve; temperature = 60°C . Molar ratio of $[\text{A}] : [\text{Imy}] = 1 : 3$; $[\text{MMA}] = 1.87 \text{ mol L}^{-1}$; $[\text{CCl}_4] = 0.83 \text{ mol L}^{-1}$; $[\text{DMSO}] = 9.87 \text{ mol L}^{-1}$; $[\text{A}] = 1.20 \times 10^{-2} \text{ mol L}^{-1}$.

Table II Dependence of Molecular Weights (\bar{M}_n and \bar{M}_w), Polydispersity Index, and Glass Transition Temperature (T_g) on MMA and CCl_4 Concentrations with [A] : [Imy] Molar Ratios of 1 : 3^a

[MMA] (mol L ⁻¹)	[Imy] × 10 ² (mol L ⁻¹)	[CCl ₄] (mol L ⁻¹)	$R_p \times 10^6$ (mol L ⁻¹ s ⁻¹)	\bar{M}_n	\bar{M}_w	Polydispersity Index	T_g (°C)
0.94	3.60	0.83	3.93	20,144	68,140	3.38	125.2
2.81	3.60	0.83	9.96	34,537	186,239	5.39	129.7
1.87	3.60	0.83	4.01	28,654	175,346	6.11	—
1.87	3.60	1.55	4.70	33,004	196,068	5.94	127.5
1.87	3.60	2.33	4.88	34,521	181,235	5.25	—

^a [A] = 1.20×10^{-2} mol L⁻¹; solvent = DMSO; temperature = 60°C.

varies with conversion.¹⁴ The molecular weights of poly(MMA) in the presence of complex A were lower than those obtained without complex A. This is expected since the increase in [A] increases the growing chain population, which, in turn, enhances the polymerization rate and simultaneously lowers the molecular weight of the polymer formed.⁷ The T_g of poly(MMA) prepared with different molar ratios of [A] : [Imy] are also shown in Table II. It was found that the T_g increases in a linear way with increasing molecular weights, which indicates that the T_g of a given polymer is a function of its chain length.

In imidazole, the electrophilic reagent would attack the unshared electron pair on N-3, but it cannot attack on the pyrrole nitrogen, since it is a part of the aromatic sextet. An electrophilic attack on the imidazole at a ring nitrogen can involve the neutral species, the conjugated base, or conjugated acid. When either nitrogen of the neutral molecule could be attacked by the electrophilic reaction is normally confirmed to the multiple bonded nitrogen which has an unshared electron pairs orthogonal to the ring.³⁰ When imidazole has free —NH groups, intermolecular hydrogen bonding gives rise to linear associates of molecules in the crystals in nonprotic solvents. Reaction with the NH nitrogen would require the use of two electrons from the system to form a bond, disrupting the aromaticity. The NH proton in imidazole is really acidic. Thus, imidazole is able to form salt (or coordinated complexes) with a number of metals. The coordination between the pyridine type nitrogen and transition-metal ions are reported in the literature.³¹

The electron transfer for the macroradical to the central metal ion depends on the redox potential of various complex ions. If the redox potential is favorable, the electron transfer becomes very rapid. The rapid reaction in the presence of Fe^{3+} is due to the back donation of electrons from the filled molecular orbital of the metal to the ligand imidazole.³²

The net electron transfer from metal to ligand (imidazole) may proceed to such a point that an electron is transferred from the metal to the activated center, giving a free radical as proposed in eq. (11).

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