

Polymerization of Methyl Methacrylate by Charge-Transfer Mechanism with 2,2'-Bipyridine and Iron(III) Complex

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ABSTRACT: Polymerization of methyl methacrylate (MMA) by the charge-transfer complex formed by the interaction of 2,2'-bipyridine (bpy), MMA, and carbon tetrachloride (CCl_4) was studied in dimethylsulfoxide (DMSO) at 60°C. The rate of polymerization (R_p) is sensitive to the $[\text{CCl}_4]$ at low concentration of CCl_4 , but at a higher concentration it is practically independent of $[\text{CCl}_4]$. R_p is proportional to $[\text{MMA}]^{1.45 \pm 0.04}$ and $[\text{bpy}]^{0.52 \pm 0.04}$ when $[\text{CCl}_4] > [\text{bpy}]$, and the average rate constant, k , at 60°C for the polymerization of MMA was $7.14 \pm 0.40 \times 10^{-6} \text{ L mol}^{-1} \text{ s}^{-1}$. Kinetic studies showed that the polymerization proceeds through free radical intermediates. This article also reports the polymerization of MMA initiated by bpy and CCl_4 and accelerated by Lewis acid, hexakis(dimethylsulfoxide)iron(III) perchlorate $[\text{Fe}(\text{DMSO})_6](\text{ClO}_4)_3$ at 60°C. The glass transition temperature and molecular weights of the samples were investigated by using differential scanning calorimetry and gel permeation chromatography techniques, respectively. Probable reaction mechanisms are proposed to explain the observed results. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 2097–2103, 1997

Key words: polymerization; methyl methacrylate; charge-transfer mechanism

INTRODUCTION

Much interest has been shown in the polymerization of vinyl monomers initiated by a charge-transfer (CT) mechanism.^{1–5} The CT initiation mechanism involves the formation of CT complexes, and afterward these complexes decompose to produce free radicals for initiation. In a recent study⁶ we reported the kinetic studies of the polymerization of methyl methacrylate (MMA) by a CT complex formed by the interaction of imidazole (Imy) and carbon tetrachloride (CCl_4). Studies^{5–7} 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.⁸

The mechanism of the catalytic activity of transition-metal ions in the CT polymerizations is ba-

sically similar to that of the transition-metal ion catalyzed atom transfer radical addition (ATRA) reactions, known as Kharasch addition reactions.⁹ In some of the ATRA reactions, the transition-metal catalyst acts as a carrier of the halogen atom in a reverse redox process.^{10,11} Recently several methods for controlled/living radical polymerization reactions have been reported.^{12–14} In a transition-metal-catalyzed atom-transfer radical polymerization (ATRP) reaction, the molecular weight of polymers increases linearly with monomer conversion,¹⁴ whereas the molecular weight does not increase with conversion in a transition-metal catalyzed redox polymerization reaction. Transition-metal-catalyzed ATRP reactions are simple, inexpensive, and more general methods for controlled/living polymerization processes than the other living radical polymerization systems.¹⁴

We previously studied the mechanism of transition-metal-ion-catalyzed CT polymerizations of vinyl monomers and showed that in all the cases the metal ions acted as the Lewis acids.^{2,5,6} In

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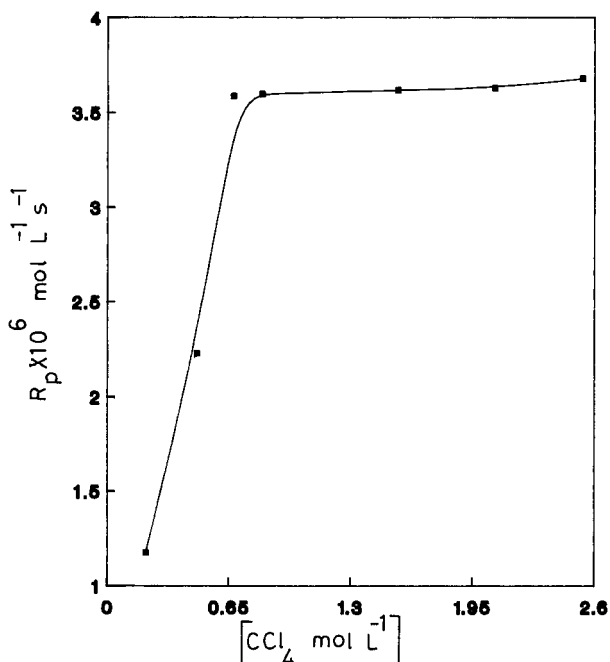


Figure 1 Plot of R_p vs. $[\text{CCl}_4]$ at 60°C . Concentrations: $[\text{MMA}] = 1.87 \text{ mol L}^{-1}$; $[\text{bpy}] = 4.40 \cdot 10^{-2} \text{ mol L}^{-1}$.

the presence of Lewis acids, the electron donating capacity of a donor molecule became larger and the rate of formation of free radicals became rapid. The chemistry of transition-metal complexes of chelating nitrogen ligands like 2,2'-bipyridine (bpy) and 1,10-phenanthroline have been extensively studied and their chemical stability, redox chemistry, and electron transfer properties are well established.¹⁵ But their effect on the polymerization of vinyl monomers is still unabated and continues to attract attention in this area. This article reports the polymerization of MMA initiated by CT complexes formed between MMA, bpy, and CCl_4 at 60°C in the presence and absence of the complex hexakis(dimethylsulfoxide)iron(III) perchlorate, $[\text{Fe}(\text{DMSO})_6](\text{ClO}_4)_3$ (B) in DMSO medium. The complex formed between complex B and bpy was well characterized.

EXPERIMENTAL

The purification of MMA, CCl_4 , DMSO, and tetrahydrofuran (THF) were essentially the same as described in a previous study.⁵ The bpy (Merck) was used without further purification. Complex B was prepared as previously.⁵

The rate of polymerization (R_p) was deter-

mined gravimetrically and dilatometrically as previously.⁵

Gel permeation chromatography (GPC) was performed using a Waters model 510 solvent delivery system at a flow rate of 1.0 mL min^{-1} through a set of four ultrastyrigel 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 eluent. A differential refractometer model R401 from Waters was used as the detector. Sample concentration was 0.2% (w/v), and the volume injected was $50 \mu\text{L}$. The GPC curves were analyzed with the calibration curve obtained by nine narrow molecular weight distribution 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 the polymers were carried out at a heating rate of $10^\circ\text{C min}^{-1}$. All experiments were carried out in a nitrogen atmosphere, and the measurement was started as soon as the heat flow in the DSC cell stabilized.

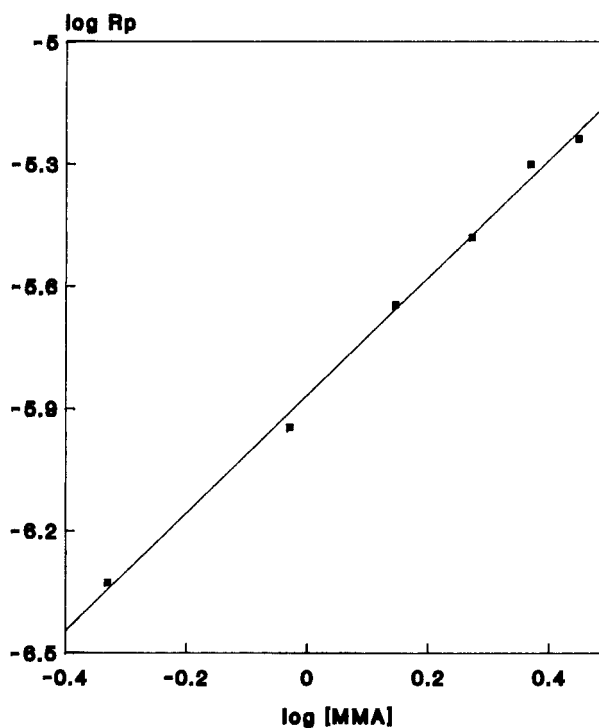


Figure 2 Relationship between $\log R_p$ and $\log[\text{MMA}]$ at 60°C . Concentrations: $[\text{bpy}] = 4.40 \times 10^{-2} \text{ mol L}^{-1}$; $[\text{CCl}_4] = 0.83 \text{ mol L}^{-1}$.

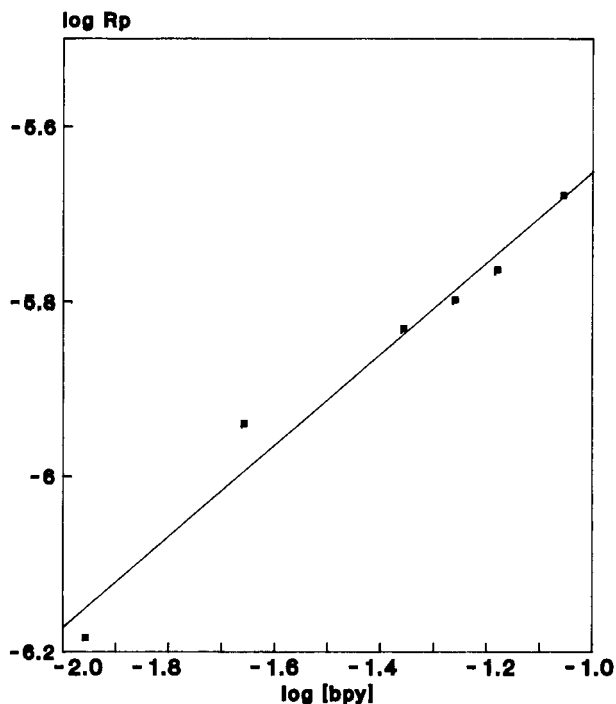


Figure 3 Plot of $\log R_p$ vs. $\log[\text{bpy}]$ at 60°C . Concentrations: $[\text{MMA}] = 1.87 \text{ mol L}^{-1}$; $[\text{CCl}_4] = 0.83 \text{ mol L}^{-1}$.

RESULTS AND DISCUSSION

Rate Measurement with bpy and CCl_4

MMA was polymerized by bpy in the presence of CCl_4 at 60°C in DMSO. No polymerization was

observed even after 6 h in the absence of either bpy or CCl_4 .

It was found that R_p increased rapidly with an increase of $[\text{CCl}_4]$ up to 0.60 mol L^{-1} , but beyond that R_p became independent of $[\text{CCl}_4]$ (Fig. 1). In the present study, therefore, CCl_4 was used in excess to eliminate the effect of $[\text{CCl}_4]$ on R_p .

The dependence of the concentrations of MMA and bpy on R_p was examined to derive the polymerization rate expression. The plot of $\log R_p$ against $\log[\text{MMA}]$ and $\log[\text{bpy}]$ gave straight lines with slopes of 1.45 ± 0.04 (Fig. 2) and 0.52 ± 0.04 (Fig. 3), respectively, when $[\text{CCl}_4] > [\text{bpy}]$. The square root dependence of R_p on the $[\text{bpy}]$ indicated that bimolecular termination was preferred in the CT polymerization system. The average rate constant, k , was found to be $7.14 \pm 0.40 \times 10^{-6} \text{ L mol}^{-1} \text{ s}^{-1}$, when $[\text{CCl}_4] > [\text{bpy}]$. This agreed well with the rate constants at 60°C for the polymerization of MMA with other nitrogenous donor compounds.^{2,5}

The effect of variation of $[\text{bpy}]$, $[\text{MMA}]$, and $[\text{CCl}_4]$ on the molecular weight of poly(MMA) (PMMA) obtained with the bpy- CCl_4 CT initiator system is shown in Table I. The molecular weight increased with the increase of $[\text{MMA}]$ but decreased with the increase of $[\text{bpy}]$. 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 broadened in a complex way that depended on whether termination occurred at a constant rate or at a rate that

Table I Dependence of Molecular Weight (\bar{M}_n) and Glass Transition Temperature (T_g) on MMA, bpy, and CCl_4 Concentrations

[MMA] (mol L ⁻¹)	[bpy] × 10 ² (mol L ⁻¹)	[CCl ₄] (mol L ⁻¹)	\bar{M}_n	T_g (°C)
0.47	4.40	0.83	119,000	120.8
0.94	4.40	0.83	188,000	121.5
1.40	4.40	0.83	220,000	122.2
1.87	4.40	0.83	264,000	123.4
2.34	4.40	0.83	281,000	123.8
2.81	4.40	0.83	312,000	124.4
1.87	1.10	0.83	365,000	123.3
1.87	2.20	0.83	350,000	125.0
1.87	6.60	0.83	255,000	125.5
1.87	8.80	0.83	241,000	125.2
1.87	4.40	0.21	260,000	126.2
1.87	4.40	0.48	262,000	126.1
1.87	4.40	1.55	237,000	124.5
1.87	4.40	2.07	230,000	124.3

The solvent was DMSO, temperature was 60°C , and time was 5 h.

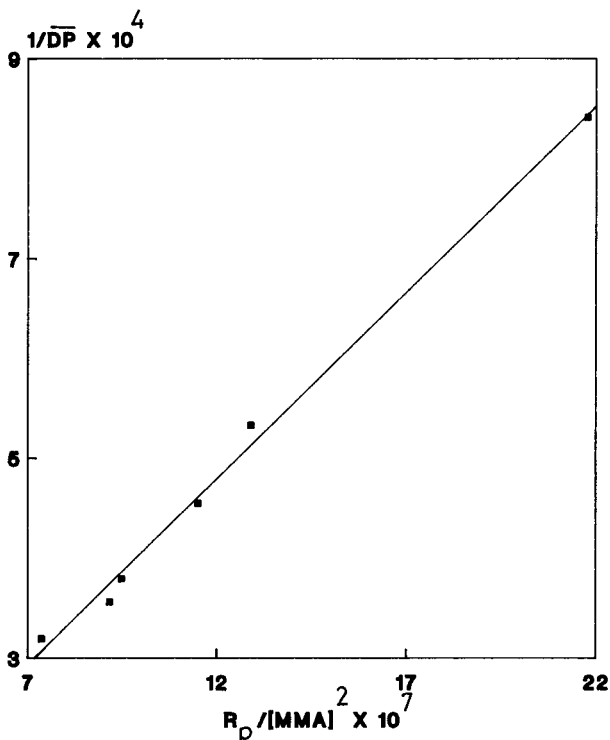


Figure 4 Plot of $1/\overline{DP}$ as a function of $R_p/[MMA]^2$. Concentrations: $[bpy] = 4.40 \times 10^{-2} \text{ mol L}^{-1}$; $[CCl_4] = 0.83 \text{ mol L}^{-1}$.

varied with conversion.¹⁶ It was also found that the molecular weight of PMMA was independent of $[CCl_4]$ up to 0.60 mol L^{-1} ; above this concentration, molecular weights decreased with $[CCl_4]$. It is also quite interesting to note that the molecular weights of PMMA obtained with bpy as the nitrogen donor compound were much higher than those obtained with other nitrogenous donor compounds.

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:

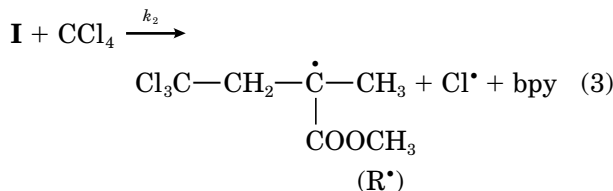
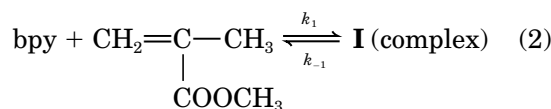
$$1/\overline{DP} = (k_t/k_p^2) \times (R_p/[MMA]^2) + 1/\overline{DP}_o \quad (1)$$

where \overline{DP} is the number average degree of polymerization and \overline{DP}_o is the value of \overline{DP} in the absence of transfer. Neglecting the chain transfer to monomer, the plot of $1/\overline{DP}$ versus $R_p/[MMA]^2$ at constant $[bpy]$ and $[CCl_4]$ was linear in a first approximation (Fig. 4) and from the slope of the curve the value of $k_p/k_t^{1/2}$ was found to be 0.08. This value is quite in conformity with the literature value,¹⁶ which suggests that the polymerization must be initiated by the free radicals produced from the decomposition of CT complexes.

The glass transition temperatures (T_g) of

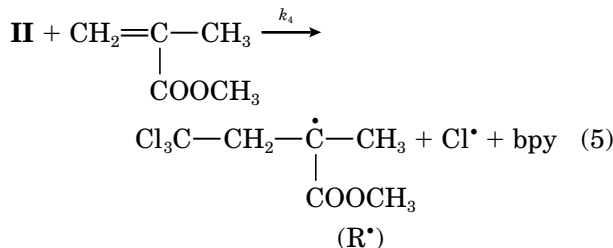
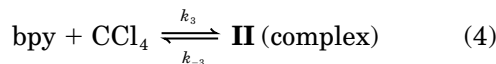
PMMA increases in a relatively linear manner with the increase of molecular weight. Although many reports^{17,18} confirmed the original Fox-Flory relation¹⁹ on linear chain length dependence of T_g , deviations from linearity have also been reported by several investigators.^{20,21}

The mechanism for initiation of vinyl monomers by the CT complexes formed by the interaction of bpy and CCl_4 as well as bpy and vinyl monomers is not certain. According to one school¹ the CT complex (1 : 1 associated complex), **I**, formed between a nitrogen donor compound and monomer, interacts with CCl_4 to produce primary free radical and ionic species. In the present study involving bpy as the nitrogen donor compound, the following mechanism may be proposed for the polymerization of MMA: initiation,



where **I** is the 1 : 1 associated CT complex formed between bpy and MMA, **R**^{*} is the primary free radical formed, and all the k values are the respective rate constants.

According to another school,²² the initiation is due to the CT complex formed between a nitrogen donor compound and CCl_4 , which interacts with MMA and produces primary free radical. Similarly, for the present system the mechanism may be postulated as



where **II** is the CT complex formed between bpy and CCl_4 . Presumably, both mechanisms are possible.^{2,5}

Spectroscopic identification of the CT complex formed between the aliphatic amine (donor) and CCl_4 (acceptor) was reported by Lautenberger et al.²³ Therefore, it may be adequate to assume a similar type of complex for a bpy- CCl_4 mixture.

The spectrum of a typical reaction mixture containing bpy and MMA in DMSO at 30°C showed an absorption maximum at 300 nm. The individual absorption maxima of MMA at 275 nm and that of bpy at 285 nm disappeared and the new band may be attributed to the CT interaction between bpy and MMA.

By investigations on the polymerization of MMA with certain nitrogen donor compounds,^{2,5} it was established that when $[\text{CCl}_4]/[\text{bpy}] \leq 1$, then mechanism (4) predominates. By applying the steady-state assumption, the overall rate of polymerization, R_p , is given by

$$R_p = k_p k_3^{1/2} (2k_t)^{-1/2} [\text{MMA}]^{1.0} [\text{bpy}]^{0.5} [\text{CCl}_4]^{0.5} \\ = k [\text{MMA}]^{1.0} [\text{bpy}]^{0.5} [\text{CCl}_4]^{0.5} \quad (6)$$

(assuming $k_4[\text{MMA}] \gg k_{-3}$), where k_p and k_t are the propagation and termination rate constants.

Again, when $[\text{CCl}_4]/[\text{bpy}] > 1$, then mechanism (2) predominates and R_p becomes independent of $[\text{CCl}_4]$. Under this condition the rate expression becomes

$$R_p = k_p k_1^{1/2} (2k_t)^{-1/2} [\text{MMA}]^{1.5} [\text{bpy}]^{0.5} \\ = k [\text{MMA}]^{1.5} [\text{bpy}]^{0.5} \quad (7)$$

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

Equation (7) shows that the rate of polymerization is proportional to the square root of $[\text{bpy}]$ and to the 1.5th power of $[\text{MMA}]$. From the experimental results it may be assumed that the proposed mechanism is applicable to the bpy- CCl_4 CT initiation system.

The above initiation mechanism suggests that the polymeric radical should contain an end- CCl_3 group. The polymers obtained by the bpy- CCl_4 donor-acceptor system were found by the dye-partition test²⁴ to contain a halogen (Cl) end group, which supports the proposed mechanism for polymerization. The incorporation of CCl_3 end groups from the chain transfer with CCl_4 is neglected, because the transfer constant of PMMA radical²⁵ with CCl_4 is 2.4×10^{-4} . Studies on the polymerization of MMA with a metal carbonyl- CCl_4 CT system revealed that the initiating radical was $\dot{\text{C}}\text{Cl}_3$ and it incorporated the CCl_3 end group in the polymer chain.²⁶

Effect on Rate of Polymerization of Adding bpy to B Complex

As reported previously,⁶ the polymerization of MMA by the Imy- CCl_4 donor-acceptor system

was found to be considerably accelerated at 60°C in the presence of complex B. The acidic NH proton of Imy forms a salt (or coordinating complex) with Fe(III). The coordination between the pyridine-type nitrogen and transition-metal ions are reported in the literature.⁶ In the light of such a mechanism, the CT complex with MMA, complex B, and bpy may thus be predicted and the accelerative effect of complex B in the polymerization of MMA can also be similarly explained. The electron transfer from the macroradical to the central metal ion depends on the redox potential of various complex ions. Therefore, it was quite interesting to study the effect of different nitrogen donor compounds on the Lewis acid catalyzed CT polymerization of vinyl monomers.

The rate of polymerization of MMA by the bpy- CCl_4 CT system was too slow to be followed dilatometrically. Therefore, it was assumed that the CT complexes were weak, but the polymerization was vastly accelerated by Lewis acids like complex B (Fe^{3+}). Under the experimental conditions used, no polymerization was observed even after 4 h with complex B alone in the absence of bpy and CCl_4 , but rapid polymerization occurred when all three components (i.e., bpy, CCl_4 , and complex B) were present in the reaction system.

In the presence of complex B, R_p increased rapidly with $[\text{CCl}_4]$ up to 0.60 mol L⁻¹, but at a higher concentration it was independent of $[\text{CCl}_4]$. A similar phenomenon in the polymerization system was also observed in the absence of complex B. Therefore, the conditions were so chosen that CCl_4 was always present in excess.

The effect of bpy on the Lewis acid catalyzed polymerization of MMA at 60°C was followed dilatometrically by adding different amounts of bpy to a constant composition of MMA, CCl_4 , and complex B in DMSO. The formation of a CT complex with bpy, complex B, CCl_4 , and MMA may explain the accelerative effect of Fe^{3+} ions present in the system. A few of the rate curves obtained from dilatometric experiments are shown in Figure 5. The plots are linear and pass through the origin, indicating that there is no induction period involved. The bpy had a pronounced effect on the Lewis acid catalyzed CT polymerization of MMA. At constant $[\text{B}]$, the rate of polymerization was found to be retarded with increasing $[\text{bpy}]$ up to 1 : 3 molar ratio of $[\text{B}] : [\text{bpy}]$. It was confirmed spectroscopically that complex B with bpy in the molar ratio of $[\text{B}] : [\text{bpy}] = 1 : 3$ produced only $\text{Fe}(\text{bpy})_3^{3+}$ and no other complex even in the presence of excess bpy. The reduction of R_p with increased $[\text{bpy}]$ up to 1 : 3 molar ratio of $[\text{B}] : [\text{bpy}]$

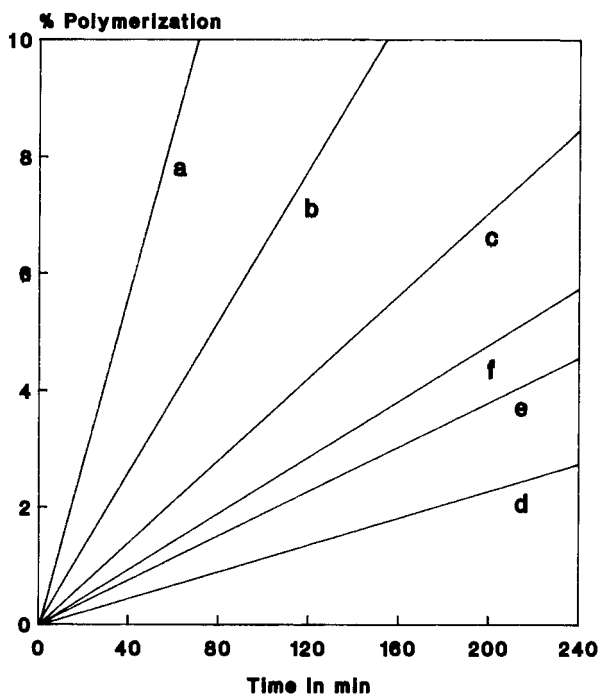
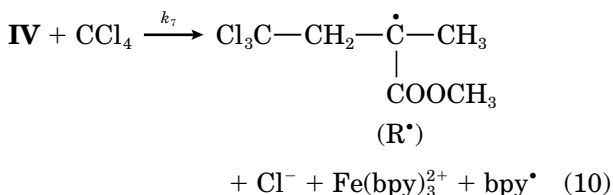
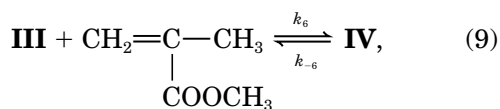
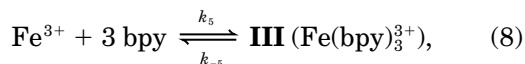


Figure 5 Polymerization of MMA in DMSO initiated by a charge-transfer complex formed by the interaction of bpy and CCl_4 with complex B at 60°C . Concentrations: $[\text{MMA}] = 1.87 \text{ mol L}^{-1}$; $[\text{CCl}_4] = 0.83 \text{ mol L}^{-1}$; $[\text{B}] = 1.34 \times 10^{-2} \text{ mol L}^{-1}$. Molar ratio of $[\text{B}] : [\text{bpy}] =$ (a) 1 : 0.25, (b) 1 : 0.5, (c) 1 : 1.5, (d) 1 : 3, (e) 1 : 6, (f) 1 : 8.

may have been due to the deactivation of complex B by saturating its coordination sphere, thus reducing the rate of polymerization. A chelating nitrogen ligand like bpy forms low spin complexes that are fairly inert to substitution by other ligands.¹⁵ If the $[\text{B}] : [\text{bpy}]$ exceeded 1 : 3, further acceleration of polymerization rates were observed. This may be due to the CT initiation of excess bpy present in the system. The following scheme may explain the mechanism of the reaction: initiation,



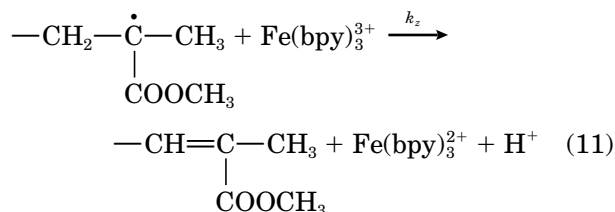
Termination includes mutual termination by

Table II Dependence of Number Average Molecular Weight (\bar{M}_n) and Glass Transition Temperature (T_g) on $[\text{B}] : [\text{bpy}]$ Molar Ratios

$[\text{B}] : [\text{bpy}]$	\bar{M}_n	T_g ($^\circ\text{C}$)
8.00	43,500	108.7
6.00	45,100	112.8
3.00	45,400	121.2
1.50	45,700	125.4
0.50	46,200	128.5
0.25	48,200	128.9

Concentrations were $[\text{MMA}] = 1.87 \text{ mol L}^{-1}$; $[\text{B}] = 1.44 \times 10^{-2} \text{ mol L}^{-1}$; $[\text{CCl}_4] = 0.83 \text{ mol L}^{-1}$. The solvent was DMSO and temperature was 60°C .

disproportionation and also an additional step [eq. (11)]:



In this structure (III) represents the complex $\text{Fe}(\text{bpy})_3^{3+}$, formed between B and bpy at a molar ratio of $[\text{B}] : [\text{bpy}] = 1 : 3$. It is suggested that for the polymerization of MMA in the presence of III and CCl_4 , complex III reacts with MMA to form a coordinating complex IV. The formation of the coordinating complex IV consisting of complex III and MMA was confirmed experimentally. $\text{Fe}(\text{bpy})_3^{3+}$ shows an absorption maximum at 525 nm while MMA has no absorption maximum in the visible region. The absorption maximum shifts to 510 nm on the addition of MMA to complex $\text{Fe}(\text{bpy})_3^{3+}$, which indicates the complex formation between $\text{Fe}(\text{bpy})_3^{3+}$ and MMA. The coordinated complex IV then reacts with CCl_4 to yield a primary free radical (R^*) and ionic species. The termination rate constant of the interaction of polymer radical with Fe^{3+} complex is k_z .

The effect of variation of $[\text{B}] : [\text{bpy}]$ molar ratio on the molecular weight of PMMA is shown in Table II. The molecular weight increased with decreasing $[\text{B}] : [\text{bpy}]$. The molecular weight of polymers obtained in the presence of complex B were lower than those obtained without complex B. This may have been due to the increase of growing chain population for the presence of complex B, which in turn enhanced the polymerization rate and simultaneously lowered the molecular weight of polymer formed.

The T_g values of PMMA prepared with different molar ratios of [B] : [bpy] are also presented in Table II. It was found that T_g increased linearly with the increase of molecular weight. While the general trend in the increase of T_g with an increase in molecular weights¹⁷⁻¹⁹ was observed, it is difficult to draw definite conclusions from these results. In the absence of an accepted theoretical model^{20,21} for chain length dependence of T_g , more experimental and theoretical work is needed to derive a consensus relation on chain length dependence of T_g .

The mechanism of interaction of PMMA radical with $\text{Fe}(\text{bpy})_3^{3+}$ is uncertain, but there is a possibility that electron transfer between Fe^{3+} and Fe^{2+} is facilitated by a bridge activated complex mechanism.²⁸ The rate with bpy will be high because bpy has low lying vacant π orbitals. The rapid electron transfer from PMMA radical to Fe^{3+} is likely, because the oxidation potential of the redox pair $\text{Fe}(\text{bpy})_3^{3+}/\text{Fe}(\text{bpy})_3^{2+}$ is 0.96 V.¹⁵ Because Lewis acids are good electron acceptors, complex B therefore enhances the electron donating capacity of bpy and the rate of formation of free radical becomes rapid. The acceleration of the reaction in the presence of complex B in the system may be due to the back donation of electrons from the filled molecular orbital of metal to bpy.²⁹ The net electron transfer from metal to bpy 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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