

Effect of Fe(III) on the Polymerization of Butyl Methacrylate Initiated by a Charge-Transfer Mechanism

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SYNOPSIS

The effect of the Lewis acid, iron(III) tris(oxalato)ferrate(III) tetrahydrate ($\text{Fe}[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 4\text{H}_2\text{O}$) (A) on the polymerization of butyl methacrylate (BuMA) initiated by a charge-transfer mechanism has been studied in dimethyl sulfoxide (DMSO) at 60°C. 2,4-dinitrophenylhydrazine (DNPH) was used as a nitrogen donor compound to initiate the polymerization in the presence of carbon tetrabromide (CBr_4). Induction periods are observed for the polymerization initiated by DNPH and CBr_4 . The rate constant at 60°C for the polymerization of BuMA in the presence of A is $1.70 \times 10^5 \text{ L/mol s}^{-1}$. The molecular weight of polymers decreases with the increase of [A]. A probable reaction mechanism is proposed to explain the observed results. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Studies¹⁻⁶ reveal that transition metal complexes play a significant role in vinyl polymerization initiated by charge-transfer mechanism. Bamford et al.^{7,8} showed that with metal carbonyl-halide charge-transfer complex system the rates of polymerization with carbon tetrabromide (CBr_4) were considerably higher than with carbon tetrachloride (CCl_4). Recently, it was reported⁹ that the polymerization of methyl methacrylate (MMA) can be initiated by $\text{PhCO}(\text{PPh}_3)_3$ -polyamine- CCl_4 , and in this system [CCl_4] had a great influence on the yield of polymers. Unfortunately Fe^{3+} and Cu^{2+} get precipitated when aliphatic amines are used as nitrogen donor compounds and the system became heterogeneous.² However, the precipitation can be avoided if melamine, malononitrile, sodium cyanide, urea, sodium azide, etc., are used in the presence of the amine.⁴ Although the effect of changing the ligand of the various transition metal complexes on the polymerization of acrylic and vinyl monomers initiated by charge-transfer mechanism is well established, no investigation is reported for the charge-transfer polymerization with the transition metal complex of the type $\text{M}[\text{M}(\text{C}_2\text{O}_4)_n] \cdot x\text{H}_2\text{O}$. In this article,

polymerization of butyl methacrylate (BuMA) is studied using 2,4-dinitrophenylhydrazine (DNPH) as the donor compound in the presence of CBr_4 in dimethyl sulfoxide (DMSO) medium at 60°C.

EXPERIMENTAL

BUMA,¹⁰ and DMSO¹¹ were purified as in the literature. CBr_4 (Fluka) and DNPH (BDH) were used without further purification. The complex $\text{Fe}[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 4\text{H}_2\text{O}$, (A) was prepared as before.¹²

The rate of polymerization was determined dilatometrically as before.²

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

RESULTS AND DISCUSSION

Experimentally it was found that the polymerization of BuMA by DNPB- CBr_4 donor-acceptor system was too slow to be followed dilatometrically. The plot of percent conversion of BuMA against reaction time with DNPB as the donor compound in the presence of CBr_4 is shown in line 1 of Figure 1. The polymerization due to the charge-transfer complex formed between DNPB and the monomer was very slow because the charge-transfer complex was very weak.² However, by the addition of the complex A to the system definite induction periods were observed and after the induction period a rapid rise in the rate of polymerization was observed (Fig. 1). At a constant concentration of DNPB, the induction periods increased as the concentration of A was gradually increased (Fig. 1, curves 2-4). Experimentally it was found that the induction period

reached a maximum value when the molar ratio of A to DNPB was approximately 1 : 6. This indicates that the charge-transfer complex was partially formed till the molar ratio became 1 : 6. If the concentration of A to DNPB was further increased, decrease in induction periods were observed. This may be due to the accelerative effect of excess A (Fe^{3+}) present in the system. However, the rate curve after the induction period during which the rate of polymerization is zero, is followed by a transitional region when the rate of polymerization increases; finally it attains a steady rate of polymerization. This suggested that the charge-transfer complex formed between complex A and DNPB (at 1 : 6 molar ratio) behaved as an ideal retarder.^{13,14} Typical results, in excellent agreement with those of Bamford et al.¹³⁻¹⁵ are shown in Figure 1. This might be due to the reaction between growing poly-BuMA radicals with the A-DNPB charge-transfer complex to give prod-

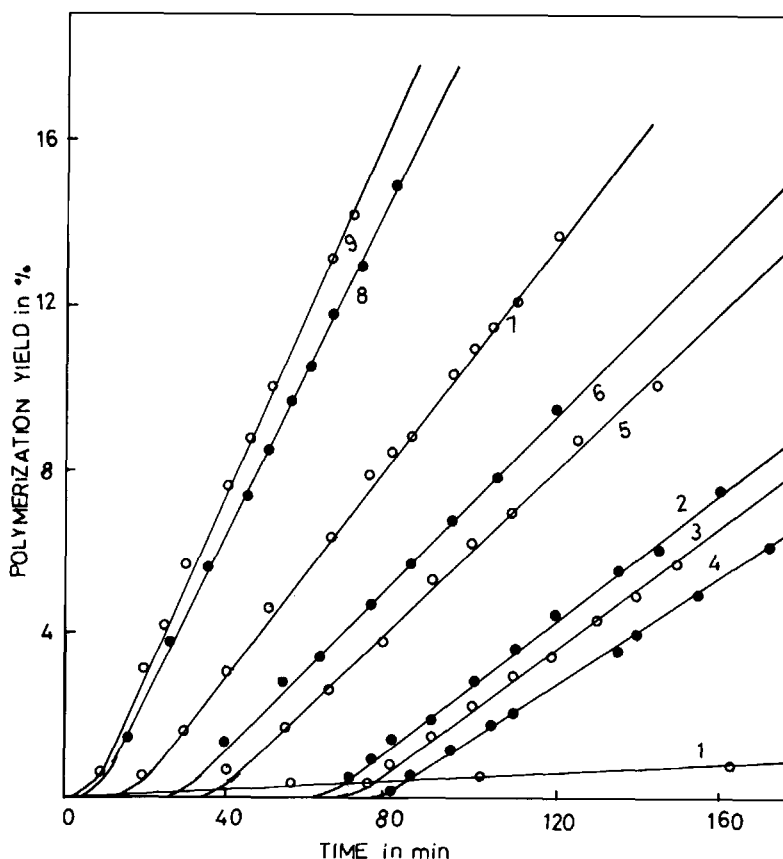


Figure 1 Polymerization of BuMA in DMSO initiated by a charge-transfer complex formed by the interaction of DNPB and CBr_4 with complex A at 60°C . $[\text{BuMA}] = 1.25 \text{ mol/L}$; $[\text{CBr}_4] = 1.01 \times 10^{-1} \text{ mol/L}$; $[\text{DNPB}] = 1.02 \times 10^{-3} \text{ mol/L}$; $[\text{DMSO}] = 11.26 \text{ mol/L}$; curve 1 without complex A (Fe^{3+}); $[\text{A}]$ (in mol/L) = 1.21×10^{-4} for 2, 1.56×10^{-4} for 3, 1.69×10^{-4} for 4, 2.41×10^{-4} for 5, 4.83×10^{-4} for 6, 9.05×10^{-4} for 7, 1.20×10^{-3} for 8, 1.99×10^{-3} for 9.

ucts incapable of further reactions. During the induction period Fe^{3+} ions of A react with a free radical to undergo a one electron transfer reaction:¹⁴



Although, the Fe^{2+} which is formed might undergo an electron transfer reaction to regenerate Fe^{3+} :



Any free radical which is sufficiently nucleophilic to react with Fe^{3+} ions will not be sufficiently electrophilic to undergo any appreciable reaction with Fe^{2+} ions.¹⁴

In a polymerization system containing a powerful ideal retarder (an ideal retarder is a compound which reacts with a polymer radical directly to give an inert product incapable of further reaction), the rate of polymerization during the induction period will be negligible until concentration of the retarder is markedly reduced. These conditions will prevail until sufficient amount of ideal retarder has been consumed so that the retarder can no longer effectively compete with monomer for all active radicals.¹⁵ From this it is apparent that the ideal retarder must be almost completely consumed before the monomer can be polymerized.

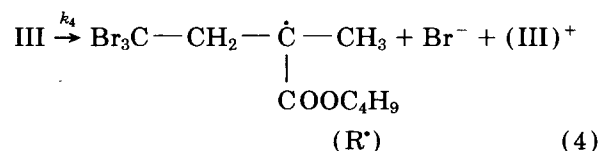
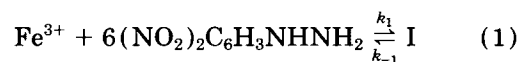
As in the case of earlier studies²⁻⁴ with CCl_4 , the rate of polymerization (R_p) was found to be very sensitive to the presence of CBr_4 .¹⁶ R_p increases rapidly with $[\text{CBr}_4]$ up to 0.090 mol/L, but at a higher concentration it is independent of $[\text{CBr}_4]$. In the present study, therefore, the conditions were so chosen that CBr_4 was always present in excess of the donor compound (DNPH), so that any effect due to concentration variation of $[\text{CBr}_4] : [\text{DNPH}]$ does not come into picture.

Li et al.¹⁷ studied the influence of solvent polarity on photopolymerization of vinyl monomers initiated by the excited charge-transfer complex of benzophenone and amine system. In a medium of high polarity, the rate of polymerization decreases because of the dissociation of the excited charge-transfer complex into solvated radical ions. The effect of polarity of solvents on the charge-transfer photopolymerization of vinyl monomers was also studied by Suzuki et al.¹⁸ It was suggested that both cationic and radical mechanisms coexist in the polymerization system and the reaction course depends on the polarity of the system.

Matsuda et al.¹⁹ studied the accelerative property of SO_2 for charge-transfer polymerization of MMA. They assumed that the liquid SO_2 -nicotine charge-

transfer complex (C) reacts with monomer to form an associated complex which later reacts with CCl_4 to form another associated complex and the latter then decomposes, yielding a primary free radical and ionic species. The similar effect of DNPH,² sodium cyanide, and melamine⁴ with $[\text{Fe}(\text{DMSO})_6](\text{ClO}_4)_3$ as the source of Fe^{3+} ions on the polymerization of MMA were also reported. In the light of such a mechanism, the formation of a charge-transfer complex with DNPH, complex A, CBr_4 and BuMA may be predicted to explain the accelerative property of A (Fe^{3+}) present in the system. The following scheme may explain the mechanism of the reaction:

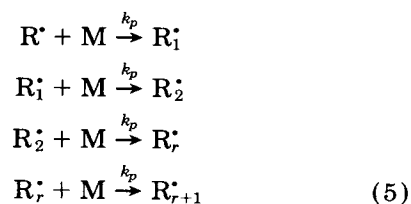
Initiation



where k represents the respective rate constants.

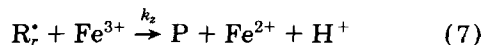
In this scheme (I) represents the associated charge-transfer complex between A and DNPH at the molar ratio of 1 : 6. It is suggested that for the polymerization of BuMA (M) in the presence of A-DNPH donor-acceptor complex (I) and CBr_4 , the complex I reacts with M to form an associated charge-transfer complex II. The formation of an associated charge-transfer complex II consisting of electron donor-acceptor complex and monomer could not be confirmed experimentally. The associated charge-transfer complex II enters into a reaction with CBr_4 to form another complex III, which then decomposes to yield both a primary free radical (R') and ionic species (Br^- and III^+).

Propagation



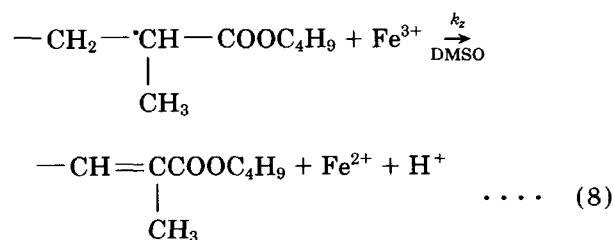
Termination

Termination includes mutual termination of polymer radicals by combination [eq. (6)] and via an oxidation step [eq. (7)]:



where R^{\cdot} , R_1^{\cdot} , R_2^{\cdot} , R_r^{\cdot} , R_{r+1}^{\cdot} , R_s^{\cdot} etc are all growing radicals, k_p is the propagation rate constant, k_t is the termination rate constant, k_z is the rate constant for the interaction of polymer radical with the ideal retarder, and P represents the dead polymer molecule.

The interaction between poly-BuMA radical and A (Fe^{3+}) may be represented as:



Since DNPH is a relatively weak donor compound in comparison with an aliphatic amine^{2,20} the polymerization of BuMA by the DNPH- CBr_4 donor-acceptor system would be slower than an aliphatic amine- CBr_4 system. This is due to the electron withdrawing inductive effect of the benzene ring and due to the fact that the free electrons in the unsubstituted nitrogen atom of DNPH are less reactive in comparison to an aliphatic amine for the charge-transfer interaction with the monomer.² In the presence of Lewis acids which are good electron acceptors the electron donating capacity of DNPH was increased, resulting in increased rate of formation of free radicals.² The rapid electron transfer from the poly-BuMA radical to the central Fe^{3+} of A is likely, since the oxidation potential for $Fe^{3+} + e \rightleftharpoons Fe^{2+}$ system is as high as +0.77 V.²¹

Bamford et al.⁸ studied the polymerization of MMA by using metallic carbonyls in the presence of CBr_4 . They assumed that two types of initiating radicals are generated from CBr_4 (i.e., $\dot{C}Br_3$ and $\dot{B}r$). By incorporating radioactive ^{13}C -labelled CBr_3 to the polymer chain end they have established that the initiating radicals are $\dot{C}Br_3$. CBr_4 is an active chain transfer agent and since transfer also gives rise to terminal CBr_3 groups in the polymer, it is necessary to use low concentration of CBr_4 .⁸ For this reason, low concentrations of CBr_4 were used in the present work. Based on the kinetic analysis of polymerization of MMA by free radicals generated

from the oxidation of $Mo(CO)_6$ with CBr_4 Bamford et al.^{7,8} also demonstrated that the generation of free radicals is a two stage process. It produces Mo^I derivative in the primary oxidation and Mo^V in the secondary oxidation process. CBr_4 is a very reactive halide and with CBr_4 the rate of secondary radical formation is much higher and the two processes can not be separated. They also reported that both stages yield $\dot{C}Br_3$ radicals for initiation.⁸

Assuming the steady-state approximation during the initial stages of polymerization of vinyl monomers retarded by an ideal retarder, Z, Bamford et al. showed that:¹³⁻¹⁵

$$R_i = k_z[R^{\cdot}][Z] + 2k_t[R^{\cdot}]^2 \quad (9)$$

where R_i is the rate of initiation.

When the inhibitor is completely exhausted then $[Z]$ is zero and the concentration of the polymer radical attains a maximum value, $[R^{\cdot}]_s$, given by,

$$R_i = 2k_t[R^{\cdot}]_s^2 \quad (10)$$

The fraction of total termination occurring by mutual reactions of polymer radicals during the induction period is sufficiently small to be neglected and a stationary state treatment leads to eq. (11).

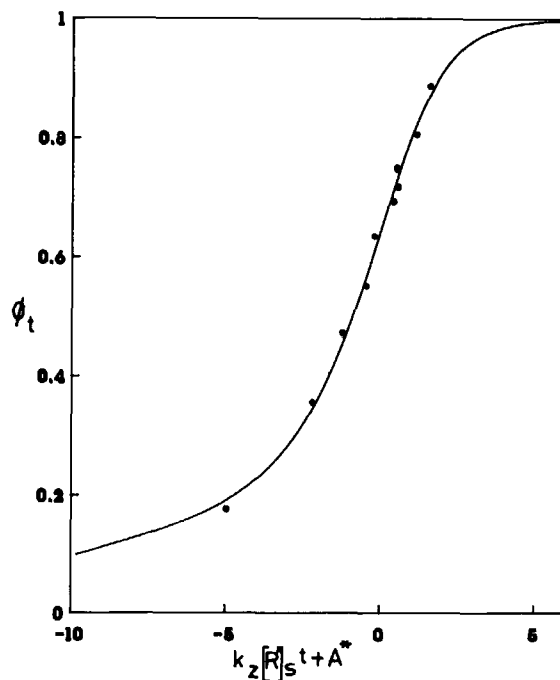


Figure 2 Reduced rate ϕ_t as a function of time t expressed as $k_z[R^{\cdot}]_s t + A^*$, experimental points (O), calculated curve (---), temperature = 60°C. $[BuMA] = 1.25$ mol/L; $[CBr_4] = 1.01 \times 10^{-1}$ mol/L; $[DNPH] = 1.02 \times 10^{-3}$ mol/L; $[DMSO] = 11.26$ mol/L; $[A] = 1.69 \times 10^{-4}$ mol/L.

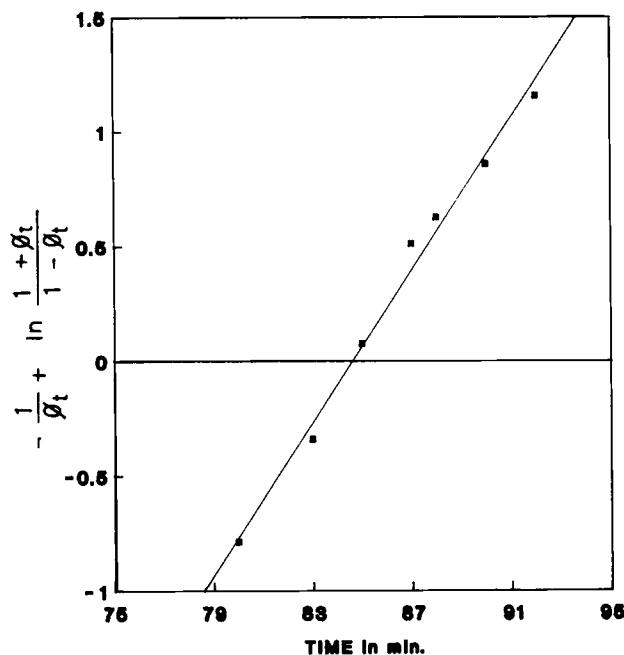


Figure 3 Analysis of the results for the polymerization of BuMA initiated by a charge-transfer complex at 60°C. Where $\phi_t = R_p/R_{ps}$ and k_z is the rate constant for the interaction of poly-BuMA with A. [BuMA] = 1.25 mol/L; [CBr₄] = 1.01×10^{-1} mol/L; [DNPH] = 1.02×10^{-3} mol/L; [DMSO] = 11.26 mol/L; [A] = 1.69×10^{-4} mol/L.

$$-\left(1/\phi_t\right) + \ln\left[\frac{1 + \phi_t}{1 - \phi_t}\right] = k_z[R^*]_s t + C^* \quad (11)$$

where ϕ_t is the reduced rate, equal to 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 retarder 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 C^* is the integration constant.

The theoretical curve was obtained by plotting ϕ_t vs. $-\left(1/\phi_t\right) + \ln\left[\frac{1 + \phi_t}{1 - \phi_t}\right]$ and the experimental one by plotting ϕ_t vs. $k_z[R^*]_s t + C^*$. Reasonable agreement was found between the experimental and theoretical plots when $k_z[R^*]_s$ and C^* were $2.50 \times 10^{-3}/s$ and -12.4 , respectively (Fig. 2). Since the final maximum rate of polymerization, R_{ps} , is given by,

$$R_{ps} = -d[M]/dt = k_p[M][R^*]_s \quad (12)$$

it follows that

$$k_z[R^*]_s[M]/R_{ps} = k_z/k_p \quad (13)$$

Bengough et al.^{22,23} have suggested other methods of analysis for retardation caused by ideal retarding

species. For a range of ϕ_t value equal to 0.15–0.8, the plot of the left hand side of eq. (11) vs. t should produce a straight line of slope $k_z[R^*]_s$, and k_z can be evaluated from eq. (13) with a measured value of R_{ps} at a known monomer concentration $[M]$. This method is known as Bengough's method I, and analysis of the rate curve by Bengough's method I is shown in Figure 3.

By an alternative method for the determination of k_z/k_p Bengough et al.^{22,23} showed that for $0.8 > \phi_t > 0.15$:

$$k_z = \frac{(1 - \phi_t^2)}{\phi_t} \times \frac{(2R_i k_t)^{1/2}}{[Z]} \quad (14)$$

and deduced the relation:

$$\log \frac{(1 - \phi_t^2)}{\phi_t} = \log \frac{k_z[Z]_0}{(2R_i k_t)^{1/2}} + \frac{k_z}{k_p} \log(1 - F) \quad (15)$$

where F is the fraction conversion of monomer to polymer i.e. $F = ([M]_0 - [M])/[M]_0$ and $[Z]_0$ rep-

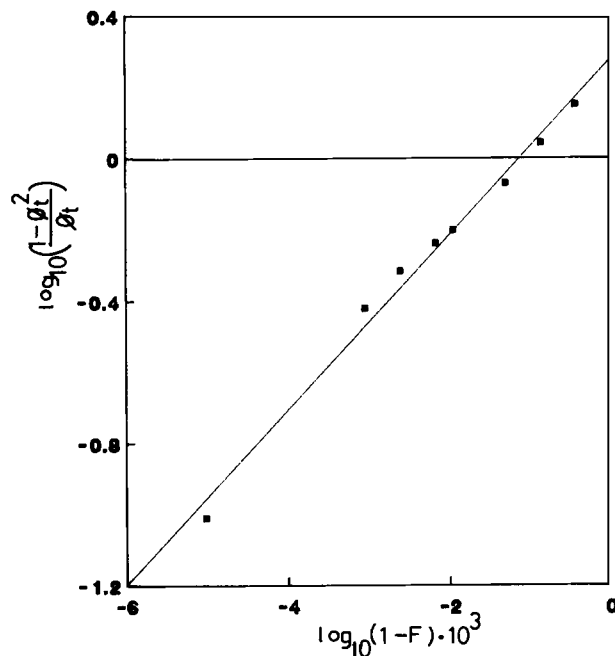


Figure 4 Analysis of the results for the polymerization of BuMA initiated by a charge-transfer complex at 60°C. Where $\phi_t = R_p/R_{ps}$ and F is the fraction conversion of the monomer to polymer (i.e., $F = ([M]_0 - [M])/[M]_0$) and k_z is the rate constant for the interaction of poly-BuMA with A. [BuMA] = 1.25 mol/L; [CBr₄] = 1.01×10^{-1} mol/L; [DNPH] = 1.02×10^{-3} mol/L; [DMSO] = 11.26 mol/L; [A] = 1.69×10^{-4} mol/L.

Table I Effect of $[\text{Fe}(\text{Fe}(\text{C}_2\text{O}_4) \cdot 4\text{H}_2\text{O}) (\text{A})]$ on the Molecular Weights of Poly-BuMA Prepared by the Charge-Transfer Initiation Mechanism

$[\text{A}] \times 10^4$ mol L ⁻¹	$[\text{A}] : [\text{DNPH}]$	$\bar{M}_n \times 10^{-3}$	(\bar{M}_w/\bar{M}_n)
1.56	1.00 : 6.50	12.10	1.9
1.69	1.00 : 6.00	8.50	2.4
2.41	1.00 : 4.20	8.10	2.6
4.83	1.00 : 2.10	7.20	2.7
9.05	1.00 : 1.10	6.90	2.9
12.00	1.00 : 0.85	6.50	2.8

$[\text{BuMA}] = 1.25 \text{ mol L}^{-1}$; $[\text{CBr}_4] = 1.01 \times 10^{-1} \text{ mol L}^{-1}$; $[\text{DNPH}] = 1.02 \times 10^{-3} \text{ mol L}^{-1}$; Solvent = DMSO; Temperature = 60°C; Reaction time = 5 h.

resents the initial concentration of the ideal retarder. For a fixed value of R_i and $[\text{Z}]_0$, the plot of the left hand side of eq. (15) vs. $\log(1 - F)$ should produce a straight line with slope k_z/k_p (Bengough's method II). The analysis of the rate curve by Bengough's method II is shown in Figure 4.

Experimental values of the concentration of monomer $[M]$ and the maximum rate of polymerization, R_{ps} , were 1.25 mol/L and $1.45 \times 10^{-5} \text{ mol/L s}^{-1}$, respectively, for the 1 : 6 molar ratio of $[\text{A}] : [\text{DNPH}]$. Using the Arrhenius expression for BuMA,²⁴ k_p at 60°C was calculated to be 761 L/mol s⁻¹.

The values of k_z at 60°C calculated by Bamford's and Bengough's I and II methods were 1.64×10^5 , 1.82×10^5 , and $1.63 \times 10^5 \text{ L/mol s}^{-1}$, respectively. Hence the average value of k_z was $1.70 \times 10^5 \text{ L/mol s}^{-1}$ at 60°C. This agrees well with the rate constants at 60°C for the interaction of poly-MMA radical with different Fe^{3+} ions.⁴

The effect of variations of $[\text{A}]$ on the molecular weights of polymers obtained with the DNPH-CBr₄ charge-transfer initiator system is shown in Table I. It was found that the molecular weight decreased with the increase of $[\text{A}]$. This is expected since the increase in $[\text{A}]$ increases the growing chain population, which in turn enhances the polymerization rate and simultaneously lowers the molecular weight of the polymer formed.

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