

Polymerization of Methyl Methacrylate by Charge–Transfer Mechanism with Sodium Azide and Iron(III) Complex

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ABSTRACT: Polymerization of methyl methacrylate (MMA) by the charge–transfer complex formed by the interaction of sodium azide (NaN_3), MMA, and carbon tetrachloride (CCl_4) has been studied in dimethylsulfoxide (DMSO) medium at 60°C . The polymerization can be vastly accelerated by Lewis acids like Fe^{3+} . This paper reports the polymerization of MMA initiated by NaN_3 and CCl_4 and accelerated with hexakis(dimethylsulfoxide)iron (III) perchlorate $[\text{Fe}(\text{DMSO})_6](\text{ClO}_4)_3$ at 60°C . The rate of polymerization, R_p , was found to vary as $[\text{NaN}_3]^{0.53}$ and $[\text{MMA}]^{1.43}$. The presence of $\text{Fe}(\text{N}_3)_3$ in the polymerization system produced well defined induction periods. The rate constant at 60°C for the interaction of poly(MMA) radical towards $\text{Fe}(\text{N}_3)_3$ was calculated to be $1.09 \times 10^5 \text{ l mol}^{-1} \text{ s}^{-1}$.

KEY WORDS Charge–Transfer / Lewis Acids / Nitrogen Donor Compounds
/ Free Radical / Induction Period / Ideal Retarder / Electron Transfer /

Polymerization of vinyl monomers by a compound containing a donor nitrogen atom in the presence of CCl_4 is now well established.^{1–7} For a number of years the initiation of polymerization by charge–transfer complexes in the presence of various metal salts and complexes has been an active research field.^{8–11} The main goal on ongoing studies in charge–transfer initiated polymerization of acrylic and vinyl monomers is to design the polymer to maximize their desirable chemical and physical properties. Studies^{8–11} reveal that transition metal complexes play a significant role in vinyl polymerization initiated by charge–transfer mechanism. Bamford *et al.*^{12,13} showed that with metal carbonyl–halide charge–transfer complex system the rate of polymerization with CBr_4 was considerably higher than with CCl_4 . Recently, it was reported¹⁴ that the polymerization of methyl

methacrylate (MMA) can be initiated by $\text{PhCO}(\text{PPh}_3)_3$ –polyamine– CCl_4 and in this system $[\text{CCl}_4]$ has a great influence on the yield of polymers. Taninaka and Minoura¹⁵ also reported the accelerative effect of triphenylphosphine (TPP) for the polymerization of acrylonitrile by a complex involving TPP and monomer. Unfortunately Fe^{3+} and Cu^{2+} get precipitated when aliphatic amines are used as donor compounds and the system became heterogeneous.¹⁰ However, the precipitation can be avoided if melamine, malononitrile, sodium cyanide, urea, etc. are used in presence of amine.⁴ In the present study sodium azide (NaN_3) was used as a donor compound for the polymerization of MMA. Since N_3^- contains a donor nitrogen atom, it may be expected to initiate the polymerization of MMA in the presence of CCl_4 . The complex formed between Fe^{3+} and N_3^- was well characterized.

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EXPERIMENTAL

MMA, CCl_4 and DMSO were purified by the standard methods. NaN_3 (BDH) was used without further purification. The complex $[\text{Fe}(\text{DMSO})_6](\text{ClO}_4)_3$, (A) was prepared as before.¹⁶

The rate of polymerization was determined dilatometrically as before.¹⁰

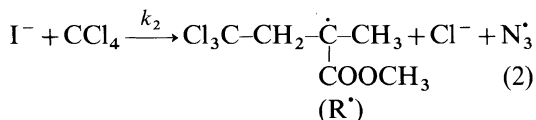
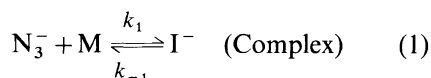
Gel permeation chromatography was performed using a Waters model 510 solvent delivery system at a flow rate of 1.0 ml min^{-1} through a set of four ultrastyrigel columns of exclusion sizes 10^6 , 10^5 , 10^4 , and 500 \AA . The analysis was performed at room temperature using purified HPLC grade THF 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 $50 \mu\text{l}$. The GPC curves were analyzed with the calibration curve obtained by 9 narrow-MWD polystyrene samples.

RESULTS AND DISCUSSION

Rate Measurement with NaN_3 and CCl_4

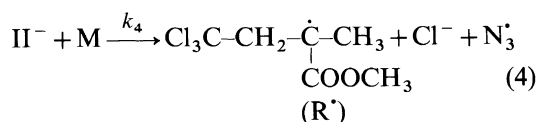
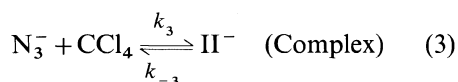
It was found that MMA could be polymerized by NaN_3 which contains a donor nitrogen atom in the presence of CCl_4 at 60°C in a solvent like DMSO and DMF. The mechanism for initiation of vinyl monomers by charge-transfer associated complex is not certain. According to Matsuda *et al.*,¹ the charge-transfer complex (1:1 associated complex) formed between a nitrogen donor compound and monomer (M) interacts with CCl_4 to produce primary free radical and ionic species. In the present study involving NaN_3 as nitrogen donor compound the following mechanism may be proposed for the polymerization of MMA:

Initiation:



where M is MMA, I^- is the 1:1 associated ionic species formed between N_3^- and MMA, R^* is the primary free radical formed and all the k 's are the respective rate constants.

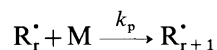
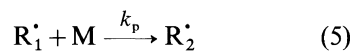
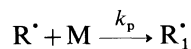
Again, according to Vofsi *et al.*⁹ and Lautenberger *et al.*,¹⁷ initiation is due to the charge-transfer complex formed between a compound containing a donor nitrogen atom and CCl_4 , which interacts with monomer and produces primary free radical. Similarly for the present system the mechanism may be postulated as:



where II^- is the charge-transfer complex formed between N_3^- and CCl_4 .

Presumably, both mechanisms are possible.³⁻⁵

Propagation



Mutual termination of polymer radicals by combination:



where R^* , R_1^* , R_r^* , R_s^* , etc. are all growing radicals, k_p is the propagation rate constant, k_t is the termination rate constant and P represent

the dead polymer molecule.

Applying steady state approximation it can be shown that:

$$[I^-] = \frac{k_1[N_3^-][M]}{k_{-1} + k_2[CCl_4]} \quad (7)$$

and

$$[II^-] = \frac{k_3[N_3^-][CCl_4]}{k_{-3} + k_4[M]} \quad (8)$$

Spectroscopic identification of charge-transfer complex formed between aliphatic amine (donor) and CCl_4 (acceptor) was reported by Lautenberger *et al.*¹⁷ It is presumed that the associated charge-transfer complexes consisting of N_3^-M and $N_3^-CCl_4$ are reversible, but these could not be detected in the polymerization system.

Assuming bimolecular termination, we can deduce certain mathematical expression for rate of polymerization, R_p . Investigations on the polymerization of MMA with aliphatic amines as donor compound³⁻⁵ established that when $[CCl_4]/[N_3^-] \leq 1$, then mechanism (3) predominates and R_p may be written as:

$$R_p = \frac{k_p k_3^{1/2}}{(2k_t)^{1/2}} [M]^{1.0} [N_3^-]^{0.5} [CCl_4]^{0.5},$$

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

$$= k [M]^{1.0} [N_3^-]^{0.5} [CCl_4]^{0.5} \quad (9)$$

Again, when $[CCl_4]/[N_3^-] \gg 1$, mechanism (1) predominates and R_p became independent of $[CCl_4]$, and the rate expression becomes:

$$R_p = \frac{k_p k_1^{1/2}}{(2k_t)^{1/2}} [M]^{1.5} [N_3^-]^{0.5},$$

(assuming $k_2[CCl_4] \gg k_{-1}$)

$$= k [M]^{1.5} [N_3^-]^{0.5} \quad (10)$$

The relationship between R_p and $[CCl_4]$ given in eq 9 and 10 are in good agreement with the experimental results (Figure 1) *i.e.*, R_p increases rapidly with $[CCl_4]$ up to a concentration of 0.60 mol l^{-1} , but beyond

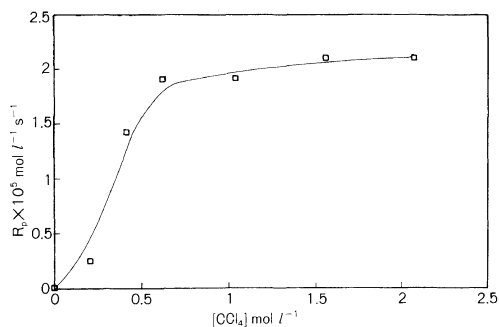


Figure 1. Plot of R_p vs. $[CCl_4]$ at 60°C . $[MMA] = 1.87 \text{ mol l}^{-1}$; $[N_3^-] = 0.177 \text{ mol l}^{-1}$.

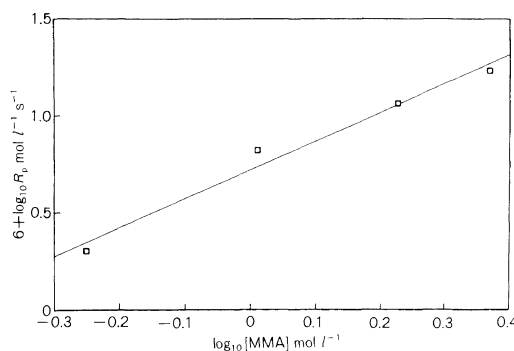


Figure 2. Relationship between $\log R_p$ and $\log [MMA]$ at 60°C . $[N_3^-] = 0.183 \text{ mol l}^{-1}$; $[CCl_4] = 0.829 \text{ mol l}^{-1}$.

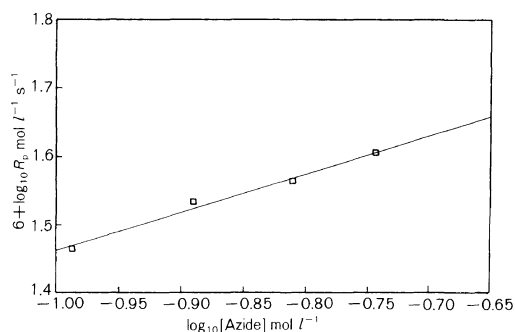


Figure 3. Plot of $\log R_p$ vs. $\log [N_3^-]$ at 60°C . $[MMA] = 1.87 \text{ mol l}^{-1}$; $[CCl_4] = 0.829 \text{ mol l}^{-1}$.

that R_p is independent of $[CCl_4]$.

Experimentally R_p was found to vary as $[MMA]^{1.43}$ (Figure 2) and $[N_3^-]^{0.53}$ (Figure 3). The average rate constant k was found to be $1.26 \times 10^{-5} \text{ l mol}^{-1} \text{ s}^{-1}$.

The effect of variation of N_3^- , monomer, and

Table I. Dependence of molecular weight (\bar{M}_n) and polydispersity index on MMA, NaN_3 , and CCl_4 concentrations

Solvent = DMSO; temperature = 60°C; time = 4 h.

[MMA]	$[\text{N}_3^-]$	$[\text{CCl}_4]$	\bar{M}_n	Polydispersity index
mol l^{-1}	mol l^{-1}	mol l^{-1}		
0.46	0.177	0.829	31500	2.4
0.93	0.177	0.829	34800	2.2
1.40	0.177	0.829	38900	2.2
1.87	0.177	0.829	43500	2.3
1.87	0.212	0.829	32200	2.1
1.87	0.109	0.829	49000	3.0
1.87	0.058	0.829	63300	3.5
1.87	0.029	0.829	82300	2.0
1.87	0.177	0.417	38500	1.8
1.87	0.177	1.550	38300	2.5
1.87	0.177	2.070	39500	2.8

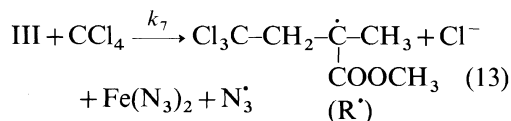
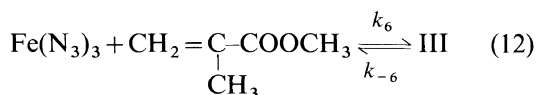
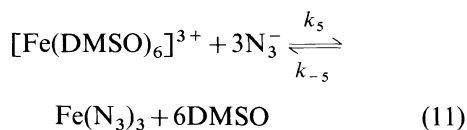
CCl_4 concentrations on the molecular weight of poly(MMA) obtained with N_3^- - CCl_4 charge-transfer initiator system is shown in Table I. It was found that the molecular weight increases with increase of [MMA] but decreases with increase of $[\text{N}_3^-]$. This is expected as there is the possibility of termination by N_3^- also. It was also found that the molecular weight of poly(MMA) obtained is independent of $[\text{CCl}_4]$ even at relatively high concentration of CCl_4 .

Effect of Adding Complex A to NaN_3 on the Rate of Polymerization

In the polymerization of MMA initiated by liquid SO_2 -nicotine complex (C_1) and CCl_4 , Matsuda *et al.*² suggested that the complex C_1 reacts with the monomer to form an associated complex which enters into a reaction with CCl_4 to form another complex and the latter then decomposes to yield a primary free radical and ionic species. Similar effect of 2,4-dinitrophenylhydrazine (DNPH),¹⁰ sodium cyanide and melamine⁴ with Fe^{3+} ions for the polymerization of MMA were also reported. In the polymerization of MMA initiated by DNPH- CCl_4 donor-acceptor system, it was found that due to the electron withdrawing inductive effect of the benzene ring, the free

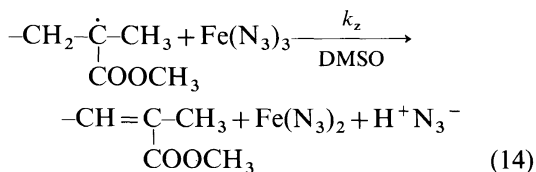
electrons in the unsubstituted nitrogen atom of DNPH are less available than those of an aliphatic amine for charge-transfer interaction with MMA. The process was vastly accelerated by Lewis acids like Fe^{3+} . Experimentally it was found that the rate became maximum when $[\text{A}]:[\text{DNPH}]$ was 1:6 and beyond this limit induction periods were observed. In the light of such a mechanism the formation of a charge-transfer complex with MMA, $[\text{Fe}(\text{DMSO})_6](\text{ClO}_4)_3$ (A) and N_3^- may thus be predicted and the accelerative effect of A in the polymerization of MMA may also be similarly explained. The following scheme may explain the mechanism of the reaction:

Initiation:



Termination:

Termination includes mutual termination of polymer radicals by combination (eq 6) and also an additional step (eq 14):



In this scheme, III represents $\text{Fe}(\text{N}_3)_3$ -MMA associated charge-transfer complex and k_z is the rate constant for the interaction of polymer radical with ideal retarder $\text{Fe}(\text{N}_3)_3$.

The rates of polymerization of MMA were recorded at 60°C by adding different amounts of N_3^- to a constant composition of MMA,

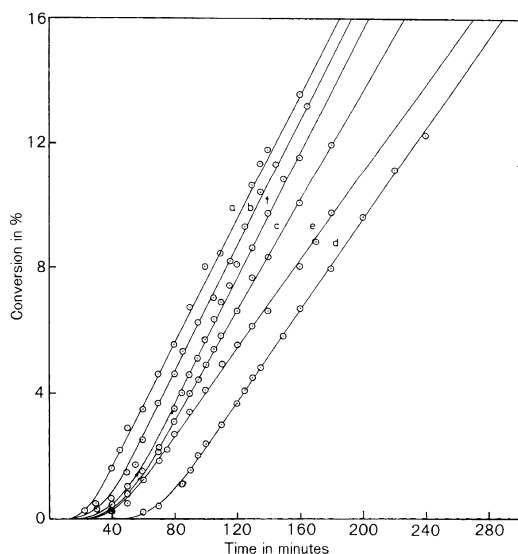


Figure 4. Polymerization of MMA in DMSO initiated by a charge-transfer complex formed by the interaction of sodium azide and MMA in presence of CCl_4 with hexakis(dimethylsulfoxide)iron(III)perchlorate (A) at 60°C . $[\text{MMA}] = 1.87 \text{ mol l}^{-1}$; $[\text{CCl}_4] = 1.03 \text{ mol l}^{-1}$; $[\text{A}] = 7.87 \times 10^{-3} \text{ mol l}^{-1}$; $[\text{DMSO}] = 9.87 \text{ mol l}^{-1}$. Molar ratio of $[\text{A}]:[\text{N}_3^-]$ corresponding to curves: (a) = 1:0.5; (b) = 1:1; (c) = 1:2; (d) = 1:3; (e) = 1:4; (f) = 1:6.

CCl_4 , and complex A in DMSO. A few of the rate curves obtained from dilatometric experiments are shown in Figure 4. In the free radical polymerization of styrene, it was found that, NaN_3 alone over the concentration range used in the experiments produced no retardation or inhibition.¹⁸ Addition of NaN_3 to a fixed composition of styrene, AIBN and complex A in a non-aqueous medium produced well defined induction periods at 60°C and at the end of which the rate always rapidly attained the value expected in the absence of the complex A. The composition of the 1:3 compound formed between complex A and NaN_3 *in situ* was well established.¹⁸ $\text{Fe}(\text{N}_3)_3$ prepared *in situ* produced an induction period proportional to the concentration of the complex formed. The experiment was repeated keeping $[\text{A}]$ constant and varying $[\text{N}_3^-]$. It was found that the induction periods were reduced when the molar ratio of $[\text{A}]:[\text{N}_3^-]$ was less

than 1:3, indicating that $\text{Fe}(\text{N}_3)_3$ was partially formed till the molar ratio became 1:3. When this occurred all the Fe^{3+} present in the system was converted into $\text{Fe}(\text{N}_3)_3$. It was also found that the induction periods were less when $[\text{A}]:[\text{N}_3^-]$ exceeded 1:3. This may be due to the charge-transfer initiation of excess N_3^- ions present in the system. However, the rate curves after the induction periods became parallel to the rate curves of polymerization with 1:3 molar ratio of $[\text{A}]:[\text{N}_3^-]$. During the induction period, interaction between the poly(MMA) radical and $\text{Fe}(\text{N}_3)_3$ took place; after the induction period *i.e.*, after complete oxidation of poly(MMA) radical, the rate curves became parallel to the polymerization rate curve without the ideal retarder.

The rapid electron transfer from poly(MMA) radical to Fe^{3+} is likely, since the oxidation potential for $\text{Fe}^{3+} + e \rightleftharpoons \text{Fe}^{2+}$ system is as high as $+0.77 \text{ V}$.¹⁹

Assuming the steady state approximation during the initial stages of polymerization of vinyl monomers retarded by an ideal retarder, Z, Bamford *et al.*^{20,21} derived the following expression:

$$-(1/\phi_t) + \ln[(1 + \phi_t)/(1 - \phi_t)] = k_z[\text{R}'_s]t + A^* \quad (15)$$

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 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 A^* is the integration constant.

A detailed analysis of the rate curve measured with 1:3 molar ratio of $[\text{A}]:[\text{N}_3^-]$ was made by the methods of Bamford *et al.*^{20,21} and a plot of ϕ_t vs. $k_z[\text{R}'_s]t + A^*$ is shown in Figure 5. Reasonable agreement was found between the experimental and theoretical plots when $k_z[\text{R}'_s]$ and A^* were $1.70 \times 10^{-3} \text{ s}^{-1}$ and -6.1 respectively for Bamford's method, where k_z is the rate constant for the interaction of poly(MMA) radical with $\text{Fe}(\text{N}_3)_3$ (eq 14).

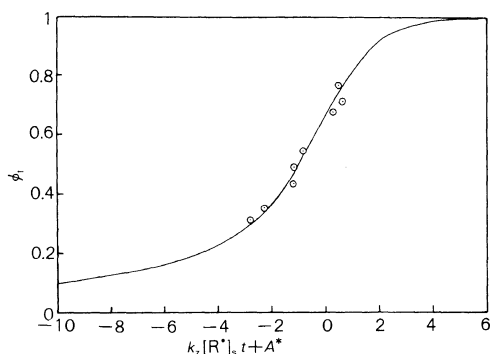


Figure 5. Reduced rate ϕ_t as a function of time t expressed as $k_z[R^*]_s t + A^*$, experimental points (o), calculated curve (---); temperature = 60°C, ϕ_t is the ratio of the rate at any time, t , R_p , in the presence of the retarder to the final maximum rate, R_{ps} , when the retarder has disappeared, i.e., $\phi_t = R_p/R_{ps}$; k_z is the rate constant for the interaction of poly(MMA) radical with $\text{Fe}(\text{N}_3)_3$, prepared *in situ*, and A^* is the integration constant. Molar ratio of $[\text{A}]:[\text{N}_3^-] = 1:3$; $[\text{MMA}] = 1.87 \text{ mol l}^{-1}$; $[\text{CCl}_4] = 1.03 \text{ mol l}^{-1}$; $[\text{DMSO}] = 9.87 \text{ mol l}^{-1}$; $[\text{A}] = 7.87 \times 10^{-3} \text{ mol l}^{-1}$.

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. $k_z [R^*]_s t + A^*$.

Bengough *et al.*²² has 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 left hand side of eq 15 vs. t should produce a straight line of slope $k_z [R^*]_s$. With a measured value of R_{ps} at a known monomer concentration $[\text{M}]$, k_z can be evaluated from eq 16.

$$\frac{k_z [R^*]_s [\text{M}]}{R_{ps}} = \frac{k_z}{k_p} \quad (16)$$

This method is known as Bengough's method I and analysis of the rate curve by Bengough's method I is shown in Figure 6.

By an alternative method for the determination of k_z/k_p Bengough *et al.*²² showed that for $0.8 > \phi_t > 0.15$

$$\log \frac{(1 - \phi_t^2)}{\phi_t} = \log \frac{k_z [\text{Z}]_0}{(2R_i k_t)^{1/2}} + \frac{k_z}{k_p} \log(1 - F) \quad (17)$$

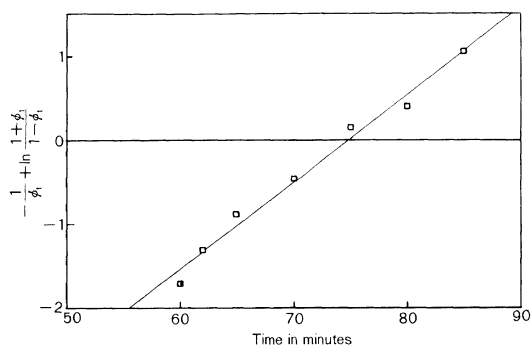


Figure 6. Analysis of the results for the polymerization of MMA initiated by a charge-transfer complex at 60°C, where $\phi_t = R_p/R_{ps}$ and k_z is the rate constant for the interaction of poly(MMA) with $\text{Fe}(\text{N}_3)_3$, prepared *in situ*. Molar ratio $[\text{A}]:[\text{N}_3^-] = 1:3$; $[\text{MMA}] = 1.87 \text{ mol l}^{-1}$; $[\text{CCl}_4] = 1.03 \text{ mol l}^{-1}$; $[\text{DMSO}] = 9.87 \text{ mol l}^{-1}$; $[\text{A}] = 7.87 \times 10^{-3} \text{ mol l}^{-1}$.

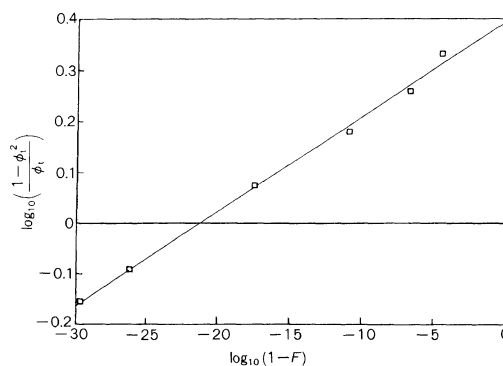


Figure 7. Analysis of the results for the polymerization of MMA initiated by a charge-transfer complex at 60°C, where $\phi_t = R_p/R_{ps}$ and F is the fraction conversion of the monomer to polymer i.e., $F = ([\text{M}]_0 - [\text{M}])/[\text{M}]_0$ and k_z is the rate constant for the interaction of poly(MMA) with $\text{Fe}(\text{N}_3)_3$, prepared *in situ*. Molar ratio $[\text{A}]:[\text{N}_3^-] = 1:3$; $[\text{MMA}] = 1.87 \text{ mol l}^{-1}$; $[\text{CCl}_4] = 1.03 \text{ mol l}^{-1}$; $[\text{DMSO}] = 9.87 \text{ mol l}^{-1}$; $[\text{A}] = 7.87 \times 10^{-3} \text{ mol l}^{-1}$.

where F is the fraction conversion of monomer to polymer i.e., $F = ([\text{M}]_0 - [\text{M}])/[\text{M}]_0$, R_i is the rate of initiation and $[\text{Z}]_0$ represents the initial concentration of $\text{Fe}(\text{N}_3)_3$. For a fixed value of R_i and $[\text{Z}]_0$, the plot of the left hand side of eq 17 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 7.

Experimental values of concentration of monomer $[M]$ and maximum rate of polymerization R_{ps} were 2.00 mol l^{-1} and $2.50 \times 10^{-5} \text{ mol l}^{-1} \text{ s}^{-1}$ respectively for the 1:3 molar ratio of $[A]:[N_3^-]$. Assuming k_p to be $734 \text{ l mol}^{-1} \text{ s}^{-1}$ at 60°C ,²³ the values of k_z calculated by Bamford's and Bengough's I and II methods were 1.00×10^5 , 1.23×10^5 , and $1.04 \times 10^5 \text{ l mol}^{-1} \text{ s}^{-1}$, respectively. Hence, the average value of k_z was $1.09 \times 10^5 \text{ l mol}^{-1} \text{ s}^{-1}$ 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 mechanism of interaction of poly(MMA) radical with $\text{Fe}(\text{N}_3)_3$ remains uncertain, but there is the possibility that electron transfer between Fe^{3+} and Fe^{2+} is facilitated by a bridge activated complex mechanism.²⁴ It was assumed that azide ion may act as a conductor during the electron transfer process and in azide an ion pair is available on each end nitrogen atom,²⁵ and the occurrence of azide bridge intermediate in redox processes of metal complexes involving a group transfer is widely accepted.²⁴ For azide ion generally accepted bridging medium is thorough end to end linkage, though alternative bridging mode *via* one nitrogen atom must also be considered.²⁵ The rate of electron transfer reaction will be high since the ligand is unsaturated and π bonded. The type of possible metal ligand interaction may be $p\pi-d\pi$.²⁶ Back donation from the metal d-orbital to the p-orbital of nitrogen may also occur. An extended π bond may be formed by the interaction of the appropriate metal d-orbital, π orbital of azide and $2p$ -orbital of the polymer radical end carbon atom. The 'nephelauxetic effect' caused by the formation of an extended π bond of this type in the transition state should facilitate rapid electron transfer between Fe^{3+} and Fe^{2+} to produce an induction period.¹⁸

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