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CHARGE TRANSFER INITIATION OF METHYLMETHACRYLATE BY ISOPROPYLAMINE

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Abstract—Methylmethacrylate (MMA) can be initiated by charge transfer complexes (i) formed by the interaction of aliphatic amines and MMA and (ii) formed by the interaction of aliphatic amines and carbon tetrachloride in a solvent like N–N dimethylformamide (DMF), dimethyl sulphoxide (DMSO) or chloroform. This paper reports the polymerization of MMA by isopropylamine (IPA) in the presence of CCl_4 in DMSO at 30°. The rate of polymerization, R_p, increases rapidly with CCl_4 up to a concentration of 0.25 mol l^{-1} but, for a higher concentration, it is practically independent of the CCl_4 concentration. R_p is proportional to (IPA concentration)$^{1/2}$ and to power of (MMA concentration)$^{1.30}$ when $[CCl_4] \geq [IPA]$. The average rate constant, k, is 2.1×10^{-6} l mol^{-1} sec^{-1}.

INTRODUCTION

There has been an increasing interest in the initiation of polymerization by charge transfer complexes [1–9]. Recently the polymerization of methylmethacrylate (MMA) by a charge transfer complex formed by the interaction of aliphatic amine with carbon tetrachloride (CCl_4) in a solvent like *N–N* dimethylformamide (DMF), dimethyl sulphoxide (DMSO) or chloroform at 30° or even below 30° was reported [8]. The aliphatic amine acts as a donor and CCl_4 and MMA act as acceptors for the formation of complexes. The existence of charge transfer complex between amine(donor) and CCl_4(acceptor) have been established by Lautenberger *et al.* [10] and Vofsi *et al.* [3] and that between amine(donor) and vinyl monomers(acceptor) have been reported by Matsuda *et al.* [4].

EXPERIMENTAL

MMA [11], DMF [12], DMSO [13] and CCl_4 [6] were purified as in the literature. Isopropylamine (IPA) was twice distilled before use. Polymerization was done in an atmosphere of positive pressure of oxygen-free N_2 in a three necked flask at 30.0 ± 0.01° using DMSO as the solvent. The polymerization was not allowed to proceed beyond 20%, to avoid effects due to increase in the viscosity [14] and to avoid the formation of side products which might affect the rate of polymerization. Poly MMA was precipitated by methanol containing traces of hydroquinone. The polymer was determined gravimetrically and the rate of polymerization was evaluated. i.r. Spectra were recorded with SPECORD 75 IR spectrometer using thin film of the polymer.

RESULTS AND DISCUSSION

It was found that MMA could be polymerized by IPA in the presence of CCl_4 at 30° or below in a solvent like DMF, DMSO or $CHCl_3$. No polymerization took place under experimental condition in the absence of CCl_4 even in $CHCl_3$.

The relationship between R_p and concentration of MMA at constant concentration of amine and CCl_4 is given in Fig. 1. R_p was proportional to (MMA concentration)$^{1.30}$.

Figure 2 shows a linear relationship between R_p and (concentration of IPA)$^{1/2}$ at the constant concentration of MMA and CCl_4. The plot of R_p vs (concentration of IPA)$^{1/2}$ intercepts the axis of amine concentration at 0.6 mol l^{-1} which is the limiting concentration of IPA in the formation of charge transfer complex, i.e. below this concentration of IPA, it is used up for the formation of associated complex with DMSO by hydrogen bonding [15]. Above this concentration of amine, it is available for the formation of charge transfer complex and hence initiation in the process of polymerization of MMA starts when the concentration of IPA exceeds 0.6 mol l^{-1}.

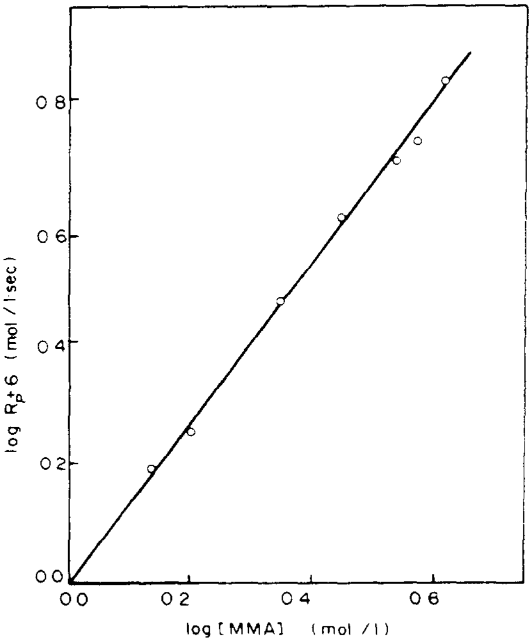

Fig. 1. Relationship between R_p and concentration of methylmethacrylate at 30°. $[CCl_4] = 2.06$ mol l^{-1}; $[IPA] = 1.17$ mol l^{-1}.

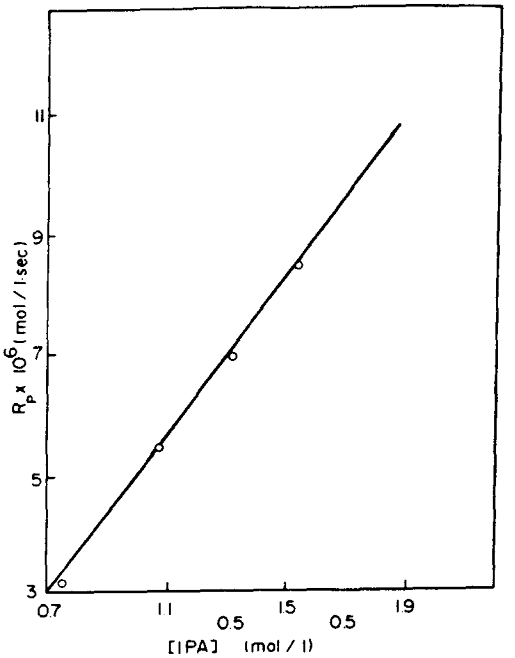

Fig. 2. Plot of R_p vs $[IPA]^{1/2}$ at 30°. $[MMA] = 2.81\ mol\ l^{-1}$; $[CCl_4] = 1.03\ mol\ l^{-1}$.

The relationship between R_p and the concentration of CCl_4 is shown in Fig. 3. R_p increases markedly with CCl_4 concentration up to $0.25\ mol\ l^{-1}$, but at higher concentration R_p is independent of the concentration of CCl_4.

The reaction could be inhibited by oxygen and hydroquinone suggesting a free radical polymerization reaction. Apparently free radicals are formed by decomposition of the charge transfer complexes.

A typical plot of R_p and % conversion of MMA against reaction time with IPA as donor is shown in Fig. 4. The reaction is very sensitive of the composition of reaction mixture. The differential rate of polymerization were computed by the method of ratio variation.

The mechanism for initiation of vinyl esters by donor-acceptor associated complex is confusing. According to one school [4], initiation is due to the donor-acceptor amine/monomer charge transfer complex (1:1), **I**, in the presence of CCl_4. The mechanism may be formulated as follows:

$$RNH_2 + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathbf{I}$$

$$\mathrm{I} + CCl_4 \xrightarrow{k_2} R_i^{\cdot} + RNH_2^{+}Cl^{-} \qquad (1)$$

According to the other group [3, 9], initiation is due to the amine/CCl_4 charge transfer complex, **II**, which decomposes to produce $\cdot CCl_3$. The mechanism may be formulated as:

$$RNH_2 + CCl_4 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathbf{II}$$

$$\mathbf{II} + M \xrightarrow{k_4} R_i^{\cdot} + RNH_2^{+}Cl^{-} \qquad (2)$$

Presumably both mechanisms should be possible. The formation of associated charge transfer complexes **I** and **II** consisting of amine–monomer and amine–CCl_4 are presumed to be reversible, but this could not be confirmed experimentally. If $[A_0]$ is the concentration of added amine, $[A_f]$ is the concentration of unreacted free amine then, at equilibrium, the concentration of amine reacted would be $[A_0] - [A_f]$. Using steady state approximation, we can show that

$$[\mathrm{I}] = k_1\ [A_0][M]/k_{-1} + k_2\ [CCl_4] \qquad (3)$$

and

$$[\mathrm{II}] = k_3\ [A_0][CCl_4]/k_{-3} + k_4\ [M] \qquad (4)$$

If fraction α of the reacted amine is used in mechanism (1) and (1–α) fraction in mechanism (2), then the

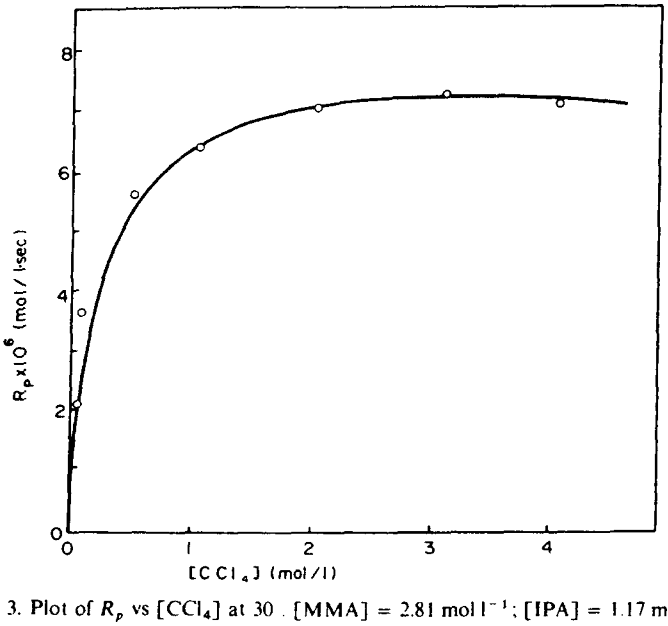

Fig. 3. Plot of R_p vs $[CCl_4]$ at 30°. $[MMA] = 2.81\ mol\ l^{-1}$; $[IPA] = 1.17\ mol\ l^{-1}$

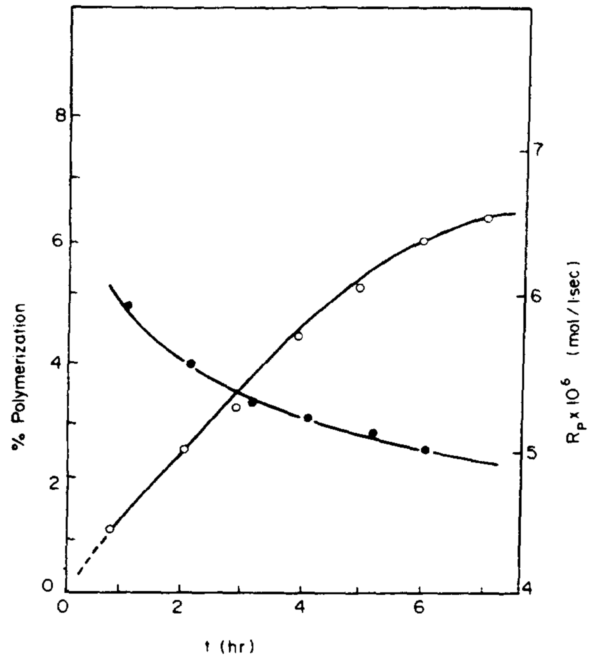

Fig. 4. Double plot of % polymerization ○ and R_p ● against reaction time, t, at 30° in N_2 [MMA] = 1.87 mol l^{-1}; [IPA] = 1.87 mol l^{-1}; [CCl_4] = 1.87 mol l^{-1}; [DMSO] = 6.35 mol l^{-1}.

rate of initiation will be

$$V_i = d[R_i^\cdot]/dt$$

$$= \frac{\alpha k_1 k_2 [A_0][M][CCl_4]}{k_{-1} + k_2[CCl_4]} + \frac{(1-\alpha) k_3 k_4 [A_0][M][CCl_4]}{k_{-3} + k_4[M]}. \quad (5)$$

Assuming bimolecular termination, we may show that

$$[R_i^\cdot] = \frac{1}{k_t^{1/2}} \left\{ \frac{\alpha k_1 k_2 [A_0][M][CCl_4]}{k_{-1} + k_2[CCl_4]} + \frac{(1-\alpha) k_3 k_4 [A_0][M][CCl_4]}{k_{-3} + k_4[M]} \right\}^{1/2}. \quad (6)$$

R_p can be expressed by Eqn. (7)

$$R_p = k_p[M][R_i^\cdot]$$

$$= \frac{k_p}{k_t^{1/2}} [M] \left\{ \frac{\alpha k_1 k_2 [A_0][M][CCl_4]}{k_{-1} + k_2[CCl_4]} + \frac{(1-\alpha) k_3 k_4 [A_0][M][CCl_4]}{k_{-3} + k_4[M]} \right\}. \quad (7)$$

When the concentration of CCl_4 is less than that of amine i.e. $[CCl_4]/[A_0] < 1$, then mechanism (2) predominates. Under that condition $\alpha \approx 0$ and R_p may be derived as:

$$R_p = \frac{k_p}{k_t^{1/2}} [M] \left\{ \frac{k_3 k_4 [A_0][M][CCl_4]}{k_{-3} + k_4[M]} \right\}^{1/2}. \quad (8)$$

Since R_p is always increasing with the increase in concentration of MMA, we may assume that $k_4[M] \gg k_{-3}$; Eqn. (8) may then be further simplified as

$$R_p = \frac{k_p k_3 k_4}{k_t^{1/2}} [M][A_0]^{1/2}[CCl_4]^{1/2}. \quad (9)$$

The relationship between R_p and the concentration of CCl_4 given by Eqn. (9) is also consistent with the experimental results shown in Fig. (3) i.e. the rate increases rapidly with CCl_4 up to a concentration of 0.25 mol l^{-1}. Experimentally we found that, up to that concentration of CCl_4, Eqn. (9) holds good.

When the ratio of the concentration of CCl_4 to amine is > 1 then mechanism (1) predominates. Under this condition $\alpha = 1$ and the rate expression may be formulated as:

$$R_p = \frac{k_p}{k_t^{1/2}} [M] \left\{ \frac{k_1 k_2 [A_0][M][CCl_4]}{k_{-1} + k_2[CCl_4]} \right\}^{1/2} \quad (10)$$

If $k_2[CCl_4] \gg k_{-1}$, then R_p becomes

$$R_p = \frac{k_p k_1 k_2}{k_t^{1/2}} [M]^{3/2}[A_0]^{1/2}. \quad (11)$$

Experimental results suggest that the assumption may be true. Experimentally, R_p was found to vary as $[M]^{1.3}$ and $[A_0]^{0.44}$ and the average rate constant, k, to be 2.1 × 10^{-6} l mol^{-1} sec^{-1} at 30°. Since some monomer units were used in the initiation, the value of order with respect to [M] is less than the theoretical value [4]. Expressions (9) and (11) are in qualitative agreement with the experimental results.

The drop in the rate after 20% conversion might be due to side products like R-NHCH$_2$-CHCH$_3$-COOCH$_3$, RN = CCl$_2$ or RNH$_2^+$Cl$^-$ etc. However, the products could not be identified experimentally.

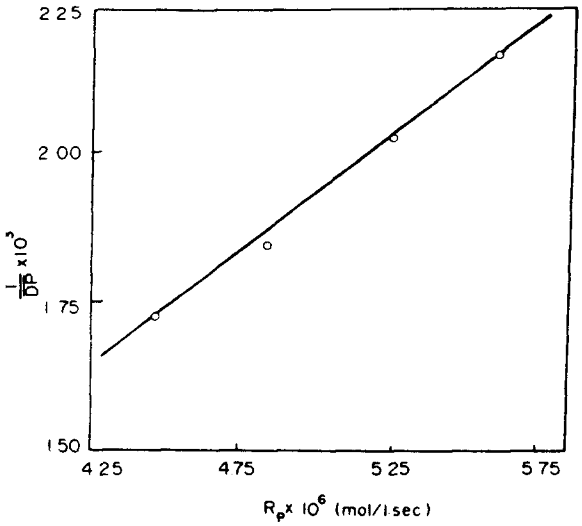

Fig. 5. Plot of 1/DP as a function of R_p in N_2 at 30 : [MMA] = 1.87 mol l^{-1}; [IPA] = 2.34 mol l^{-1}; [CCl_4] = 3.10 mol l^{-1}; [DMSO] = 4.23 mol l^{-1}.

The molecular weight of PMMA in $CHCl_3$ was calculated from viscometric data by the relation [16]

$$[\eta] = 4.3 \times 10^{-5} [\bar{M}_n]^{0.8}$$

This relation may not be valid since molecular weight distribution may not be the same for these charge transfer polymerizations. However, osmotic data [8] showed that the above relation gave reasonable values for such polymers.

The molecular weight of PMMA decreased with increased concentration of amine. This is expected as there is the possibility of termination by amine also. The plot of 1/DP against R_p also was linear (Fig. 5).

The i.r. spectra of the PMMA formed by charge transfer mechanism was exactly the same as that of thermally polymerized MMA. It was observed that films of PMMA prepared by charge transfer mechanism were relatively more transparent and more rigid than those of PMMA prepared thermally or by free radical mechanism. So PMMA prepared by charge transfer mechanism may be conveniently used for standardization of i.r. spectrophotometer. Further work with Lewis acids as catalysts for the charge transfer polymerization of vinyl monomers is in progress.

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