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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

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To cite this Article Lenka, Subasini , Nayak, Padma L. and Nayak, Sanjay K.(1983) 'Photopolymerization Initiated by Charge-Transfer Complex. VII. Photopolymerization of Methyl Methacrylate with the Use of α -Picoline Chlorine Charge-Transfer Complex', Journal of Macromolecular Science, Part A, 20: 8, 835 – 845

To link to this Article: DOI: 10.1080/00222338308061402

URL: <http://dx.doi.org/10.1080/00222338308061402>

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Photopolymerization Initiated by Charge-Transfer Complex. VII. Photopolymerization of Methyl Methacrylate with the Use of α -Picoline Chlorine Charge-Transfer Complex

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ABSTRACT

Polymerization of methyl methacrylate in visible light was studied at 30°C using the α -picoline-chlorine charge-transfer complex as the photoinitiator. Analysis of kinetic and other data indicate that polymerization proceeds via a radical mechanism and that termination is initiator dependent. Chain termination via degradative chain (initiator) transfer appears to be significant.

INTRODUCTION

Recently we have reported the photopolymerization of methyl methacrylate using the lutidine-bromine and quinaldine-bromine [1], lepidine-bromine [2], and γ -picoline-bromine [3] charge-transfer complex as photoinitiators. α -Picoline-chlorine (α -Pi-Cl₂) easily forms an isolable charge-transfer complex when reacted with chlorine. The α -picoline-chlorine charge-transfer complex was found to be a better photoinitiator for polymerization of certain vinyl monomers than chlo-

rine itself. In the present studies, we have examined the suitability of the α -Pi-chlorine charge-transfer complex (1:1) as a photoinitiator for the polymerization of methyl methacrylate.

EXPERIMENTAL

Preparation of α -Pi-Chlorine (α -Pi-Cl₂) Charge-Transfer Complex

Five milliliters of reagent grade α -picoline (freshly distilled after being dried over NaOH pellets) was dissolved in an equal volume of purified chloroform in a wide test tube which was cooled to 0-5°C in an ice-bath. Purified chlorine gas, prepared in the laboratory from the reaction between reagent grade KMnO₄ and concentrated HCl and purified by passing the gas through two successive scrubbers containing water and concentrated H₂SO₄, was then gently bubbled through the cold α -picoline solution. Brownish yellow crystals of the α -picoline-chlorine complex gradually precipitated out. The passage of chlorine was stopped when no further absorption of the gas was apparent. The crystalline precipitate was then filtered off, washed with purified chloroform, and finally dried under vacuum at 30°C. The assayed chlorine content of the prepared complex was 20.89% against a theoretical chlorine content of 21.28% for the 1:1 complex of α -picoline and chlorine.

Polymerization

The polymerization was carried out according to our previous procedure. The intrinsic viscosities $[\eta]$ of the polymers were measured in benzene solution at 30 ± 0.05°C in an Ubbelohde viscometer. The results are expressed in deciliters per gram. The molecular weights of the poly(methyl methacrylate) were calculated from the viscosity data by using the equation [4]

$$[\eta] = 8.69 \times 10^{-5} \bar{M}_w^{0.76} \text{ (dL/g)}$$

RESULTS AND DISCUSSION

It was observed that the rate of polymerization of MMA with the use of the α -picoline-chlorine charge-transfer complex as initiator at 30 ± 0.1°C was faster in the presence of light (wavelength 440 nm) than in the dark. The process of photopolymerization is associated with a smaller induction period than in case of thermal polymerization using the same

initiator. No polymerization, however, was observed when MMA was exposed to light of the same wavelength either alone or in the presence of a small amount of α -picoline at 30°C.

A few of the polymer samples prepared by using the α -picoline- Cl_2 complex were characterized for the chlorine endgroup by the dye partition technique developed by Palit et al. [5]. The test was positive in all cases, indicating the incorporation of chlorine atom endgroups in these cases.

Initiator Exponent, Monomer Exponent, and Activation Energy

The results of the photopolymerization of MMA at 30°C using various concentrations of α -Pi- Cl_2 complexes have been studied. A plot of $\log R_p$ versus $\log [\alpha\text{-Pi-Cl}_2]$ is shown in Fig. 1. From the slope of the plot, the initiator exponent was determined to be 0.60. The polymerization remains uninhibited in the presence of air, but hydroquinone strongly inhibited the polymerization process. The polymerization

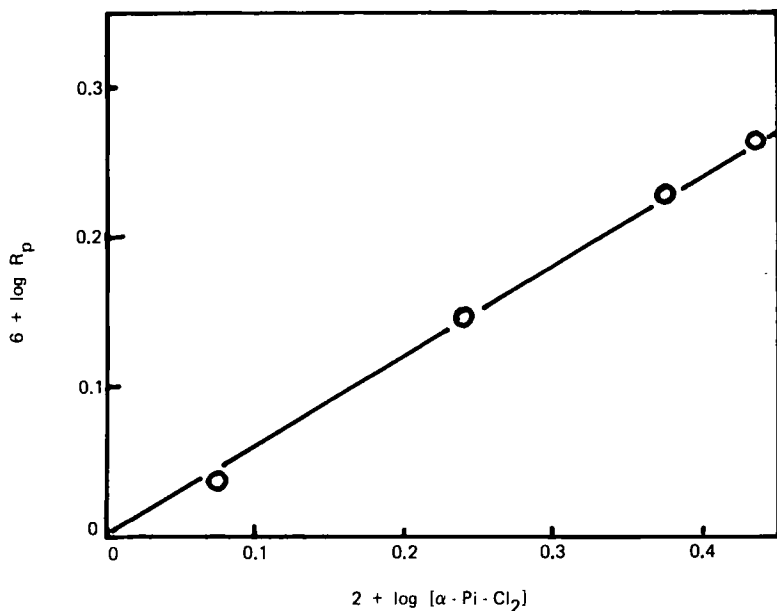


FIG. 1. Plot of $\log R_p$ vs $\log [\alpha\text{-Pi-Cl}_2]$: $[\text{MMA}] \times 10^2 = 46.92 \text{ M}$, 30°C, 6 h.

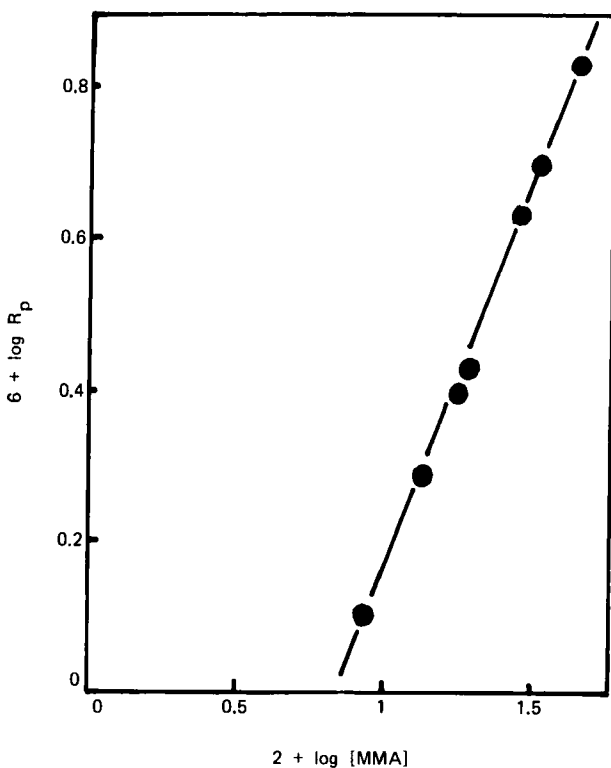


FIG. 2. Plot of $\log R_p$ vs $\log [MMA]$: $[\alpha\text{-Pi-Cl}_2] \times 10^2 = 2.95 \text{ M}$, 30°C , 6 h.

gave a positive response to the dye partition test for chlorine endgroups. All these observations indicate a free radical mechanism for the polymerization.

R_p values were also measured at several monomer concentrations using a fixed value of initiator concentration. A linear plot of $\log R_p$ versus $\log [MMA]$ is shown in Fig. 2. From the slope of this plot, the monomer exponent was calculated to be 1.05.

The rates of polymerizations were measured at three different temperatures at fixed monomer and initiator concentrations. The rate of polymerization increases with increasing temperature. From the slope of the Arrhenius plot of $\log R_p$ versus $1/T$ (Fig. 3), the overall activation energy was computed to be 3.8 ± 0.5 kcal/mol, and this value is close to some reported values of activation energy for the aqueous polymerization of MMA.

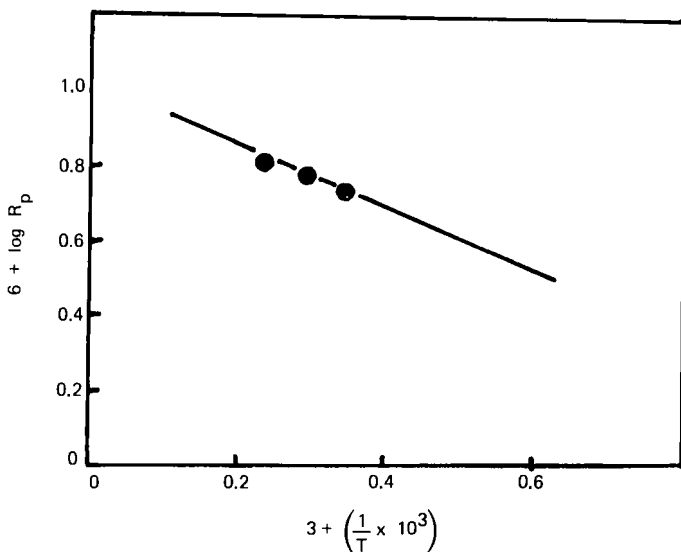
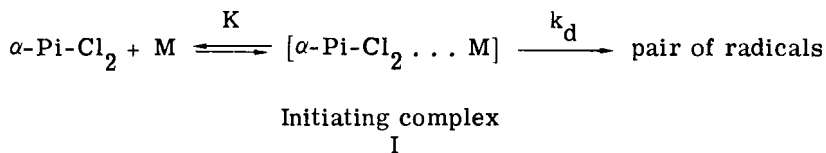


FIG. 3. Plot of $\log R_p$ vs $1/T$.

Mechanism

Kinetic data, the inhibitory effect of hydroquinone, and the results of endgroup analysis indicate a radical mechanism. The radical generation step may be considered to follow an initial complexation reaction between monomer and initiator molecules:



Assuming bimolecular termination, the rate of polymerization, R_p , may be expressed as

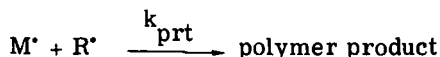
$$R_p = k_p \left(\frac{k_d K}{k_t} \right)^{0.5} [\alpha\text{-pi-Cl}_2]^{0.5} [M]^{1.5}$$

The radical generation process is considered to be preceded by a complexation reaction between monomer and $\alpha\text{-Pi-Cl}_2$ complex molecules

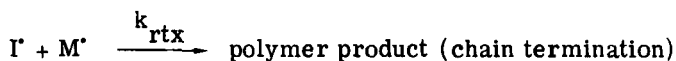
which is characterized by an equilibrium constant K such that the initial concentration of the actual initiating complex I is given by $[I] = K[\alpha\text{-Pi-Cl}_2][M]$ and k_p , k_d , and k_t have their usual significance.

The initiator-dependent termination process may be of two kinds as shown below:

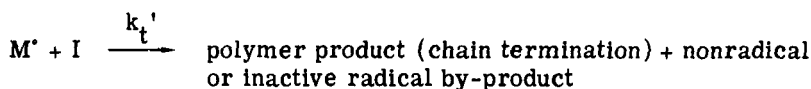
(1) Primary radical termination:



(2) Termination via degradative initiator transfer, either (a) with reinitiation such as:



or, (b) with little reinitiation, such as:



Analysis of Primary Radical Termination and Degradative Initiator Transfer Processes

The equation of Deb and Meyerhoff [6] assumes the following form when the primary radical termination effect as well as degradative chain transfer for the present system are analyzed.

Initiator-dependent termination:

$$\log \frac{R_p^2}{[\alpha\text{-Pi-Cl}_2][M]^3} = \log \frac{Kfk_d R_p^2}{k_t} - 0.8684 \frac{k_{prt}}{k_i k_p} \frac{R_p}{[M]^2}$$

A plot (Fig. 4) of the left-hand side of the above equation against $R_p/[M]^2$ gave a negative slope, indicating measurable primary radical termination for the present system. The value of $k_{prt}/k_i k_p$ calculated from

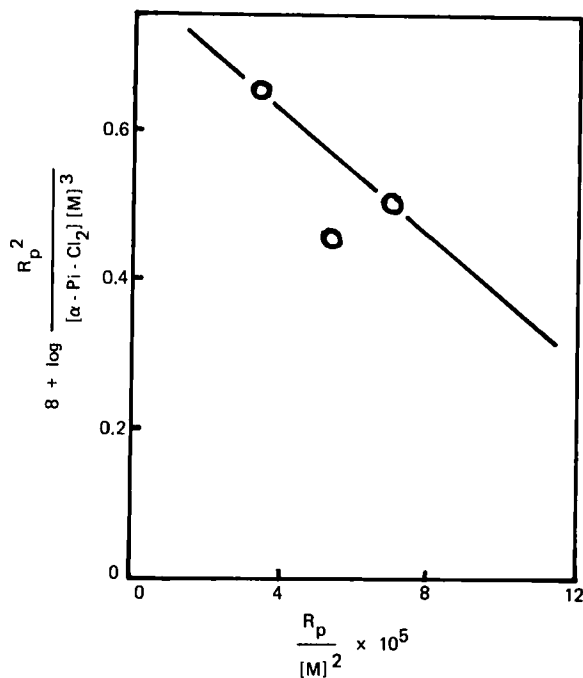


FIG. 4. Plot of $\log R_p^2 / ([\alpha\text{-Pi-Cl}_2][M]^3)$ vs $R_p/[M]^2$.

the slope of this plot is $0.276 \times 10^6 \text{ mol} \cdot \text{s}/\text{L}$. The value of Kfk_d , or more precisely $K\phi\epsilon I_0$, obtained from the intercept of this plot is $5.55 \times 10^{-6} \text{ L}/\text{mol} \cdot \text{s}$.

k_p^2/k_t Value

The value of the kinetic parameter k_p^2/k_t was obtained from the initial slope of the plot of $1/\bar{P}_n$ versus $R_p/[M]^2$ (Fig. 5), following the usual procedures and assumptions, with the help of the Mayo equation.

$$\frac{1}{\bar{P}_n} = 1.85 \frac{k_t}{k_p^2} \frac{R_p}{[M]^2} + \sum \frac{R_{tr}}{R_p}$$

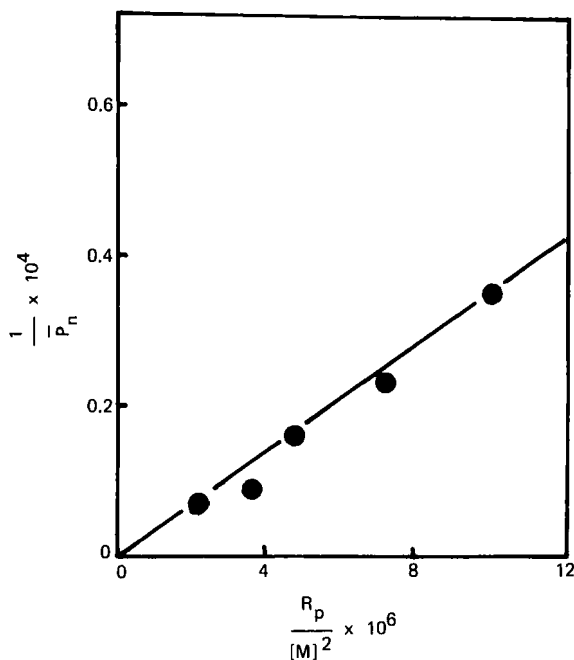


FIG. 5. Plot of $1/\bar{P}_n$ vs $R_p/[M]^2$.

The last term in the right-hand side of the equation was included to account for the chain-transfer effect, assuming that this would not affect the slope of the plot for low initiator concentrations. From the slope, the value of k_p^2/k_t was calculated to be 1.801 L/mol·s.

Degradative Initiator Transfer With Reinitiation Effect

An equation derived by Deb [7] to analyze degradative chain (initiator) transfer with reinitiator was simplified by Ghosh et al. [8] to the following form:

$$\ln \frac{R_p^2}{[I][M]^2} = \ln \frac{fk_d k_p^2}{k_t} - \frac{k_p^2}{k_t} \frac{k_{rtx}}{k_{ix} k_p} C_1 \frac{[I]}{[M]}$$

In the present case, $[I] = K[\alpha\text{-Pi-Cl}_2][M]$, and hence we have

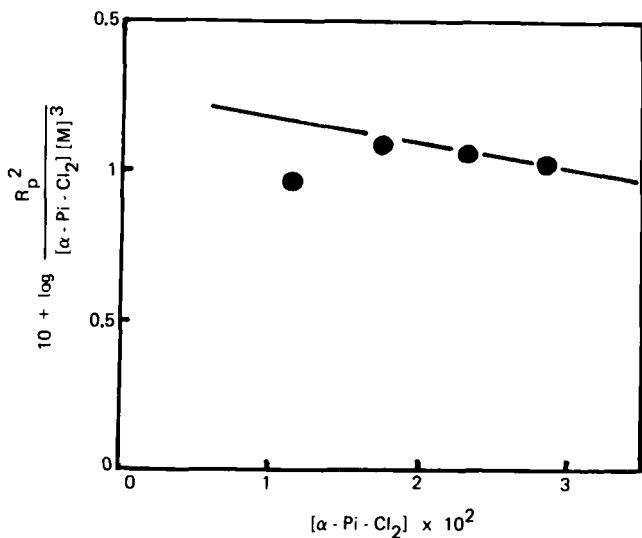


FIG. 6. Plot of $\log R_p^2 / ([\alpha\text{-Pi-Cl}_2][M]^3)$ vs $[\alpha\text{-Pi-Cl}_2]$.

$$\log \frac{R_p^2}{[\alpha\text{-Pi-Cl}_2][M]^3} = \log Kfk_d \frac{k_p^2}{k_t} - 0.434 \frac{k_p^2}{k_t} \frac{k_{rtx}}{k_{ix}k_p} C_1 K [\alpha\text{-Pi-Cl}_2]$$

where C_1 is the initiator transfer constant. The plot of the left-hand side of the above equation against $[\alpha\text{-Pi-Cl}_2]$ (Fig. 6) is linear with a negative slope, indicating degradative initiator transfer. From the plot of the value of the kinetic parameter, Kfk_d , i.e., $K\phi I_0$, is 5.1×10^{-8} L/mol · s.

Degradative Initiator Transfer with Little Reinitiation

The aspect may be expressed as follows. Under steady-state conditions we have

$$\frac{R_i}{R_p} = \frac{R_t}{R_p} = \frac{2k_t[M']^2 + k_t'[I][M']}{R_p}$$

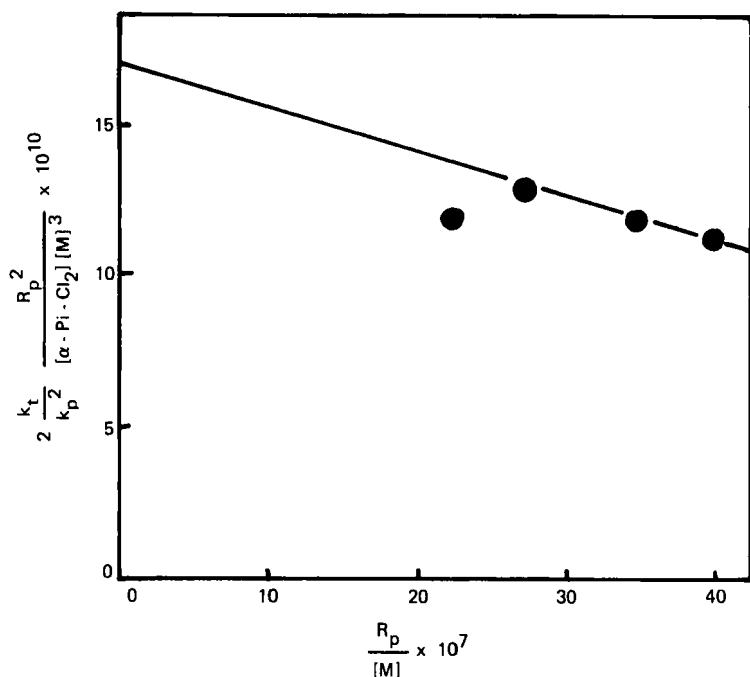


FIG. 7. Plot of $2 k_t/k_p^2 R_p^2/[M]^3 [\alpha\text{-Pi-Cl}_2]$ vs $R_p/[M]$.

$$= \frac{2k_t[M']^2 + k_t'K[\alpha\text{-Pi-Cl}_2][M][M']}{R_p}$$

or

$$R_i = \frac{2k_t}{k_p^2} \frac{R_p^2}{[M]^2} + \frac{k_t'K}{k_p} [\alpha\text{-Pi-Cl}_2] R_p$$

$$= 2\phi\epsilon I_0 K [\alpha\text{-Pi-Cl}_2] [M]$$

or

$$2 \frac{k_t}{k_p^2} \frac{R_p^2}{[M]^3 [\alpha\text{-Pi-Cl}_2]} = 2\phi\epsilon I_0 K - \frac{k_t'K}{R_p} \frac{R_p}{[M]}$$

A plot of the left-hand side of the above equation against $R_p/[M]$, which gives a straight line with a negative slope (Fig. 7), is obtained for the present photopolymerization of MMA. From this plot, the value of $\phi\epsilon I_0 K$ was computed to be 5.9×10^{-6} L/mol·s, which is very close to value obtained from Figs. 5 and 6. Thus, degradative initiator transfer of either kind (with or without reinitiation) can easily account for the nonideal kinetics in the present photopolymerization.

Although we have reasonable indication of primary radical termination as a possible cause for nonideality, consideration of the dependence of R_p on monomer concentration predicts it to be of small consequence. With an observed monomer exponent value of less than 1.5, the nonideality in the present polymerization appears to be due to degradative initiator transfer.

ACKNOWLEDGMENT

The authors are thankful to CSIR, New Delhi, for financial assistance.

REFERENCES

- [1] P. L. Nayak, S. Lenka, and M. K. Mishra, J. Polym. Sci., Polym. Chem. Ed., **19**, 2457 (1981).
- [2] S. Lenka, P. L. Nayak, and M. Dash, J. Appl. Polym. Sci., In Press.
- [3] S. Lenka, P. L. Nayak, and A. K. Tripathy, J. Polym. Sci., Polym. Chem. Ed., **20**, (1982).
- [4] T. G. Fox, J. B. Kinsinger, H. F. Mason, and I. M. Schuele, Polymer, **3**, 71 (1962).
- [5] M. K. Saha, P. Ghosh, and S. R. Palit, J. Polym. Sci., Part A-1, **2**, 1366 (1966).
- [6] P. C. Deb and G. Meyerhoff, Eur. Polym. J., **10**, 709 (1974).
- [7] P. C. Deb, Ibid., **11**, 31 (1975).
- [8] P. Ghosh and P. S. Titra, J. Polym. Sci., Polym. Chem. Ed., **15**, 1743 (1977).

Accepted by editor February 27, 1983

Received for publication April 7, 1983