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Polymerization of Methyl Methacrylate Using β-Picolinium p-Chlorophenacylide as Initiator

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Polymerization of Methyl Methacrylate Using β-Picolinium p-Chlorophenacylide as Initiator

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ABSTRACT

The β-picolinium p-chlorophenacylide-initiated radical polymerization of methyl methacrylate was carried out at 60, 65, and 70°C by employing the dilatometric technique in a nitrogen atmosphere. A master graph of volume contraction vs percentage conversion was used to calculate the rate of polymerization (R_p), which is a direct function of the initiator concentration. The value of the exponent is 1.10 ± 0.10. The molecular weight of the polymer also increases with an increase in ylide concentration. The overall activation energy is calculated as 7.02 kcal/mol. The reaction involves bimolecular termination. Hydroquinone retards the reaction. Polar solvents do not affect R_p whereas the nonpolar solvent CCl_4 favors R_p but decreases the molecular weight of the polymer due to a chain transfer reaction. The value of the chain transfer constant (C_S) is 6.67×10^{-4}.

INTRODUCTION

There have been many studies on polymerization of vinyl monomers using different initiators, but little has been reported regarding hetero-

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cyclic ylides in the polymer field (ylides are zwitterionic compounds in which a carbanion is covalently bonded to a positively charged hetero atom). In the present paper the results of the polymerization of methyl methacrylate (MMA) initiated by β-picolinium p-chlorophenacylide are reported.

EXPERIMENTAL

Purified reagent grade monomer (BDH) and solvents were used. β-Picoline, dried over sodium hydroxide pellets, was distilled under vacuum. Bromine (E. Merck analytical grade) was used without further purification. β-Picolinium p-chlorophenacylide was prepared by the method given by Krohnke [1] and Lumb [2].

The polymerization was carried out in a modified dilatometric apparatus [3, 4] (bulb capacity 3 mL with a 11-cm long capillary of 2.1 mm diameter) under nitrogen atmosphere for 4 h at 60, 65, and 70°C.

The ylide was dissolved in monomer and then taken into the dilatometer which was placed in a water bath maintained at a specific temperature. The progress of the reaction was monitored with the help of a cathetometer. Polymer, precipitated with acidified isopropanol, was dried to constant weight.

The volume contraction was converted into percentage conversion by means of a "master graph" (Fig. 1). The results obtained were used to calculate the rate of polymerization.

The rate of polymerization (R_p) was calculated as follows (Eq. 5).

If W is the weight of polymer obtained from 1 mL of monomer polymerized, then

$$\text{number of moles of polymer} = \frac{W}{100.12} \tag{1}$$

$$\text{percentage conversion (C)} = \frac{W \times 100}{1 \times 0.90} \tag{2}$$

where 100.12 and 0.90 are the molecular weight and the density of MMA, respectively. Then

$$R_p\ (\text{mol/L·s}) = \frac{W \times 10^3}{t \times 60 \times 100.12} \tag{3}$$

by substituting the value of W from Eq. (2) into Eq. (3):

$$R_p = \frac{0.90 \times C \times 10^3}{100 \times t \times 60 \times 100.12} \tag{4}$$

$$= \frac{1.498 \times C \times 10^{-3}}{t} \tag{5}$$

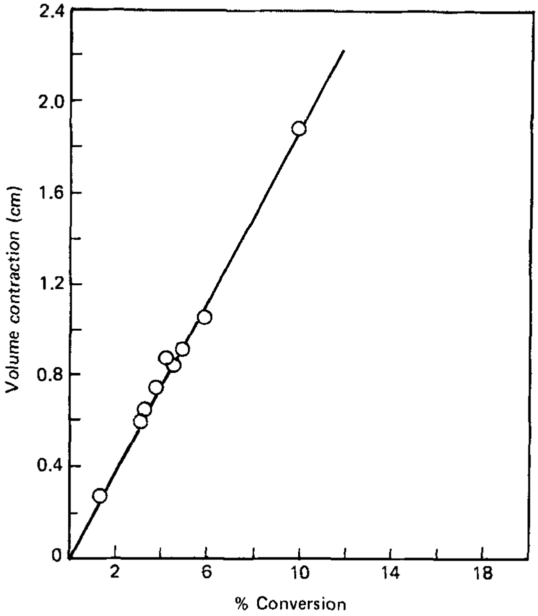

FIG. 1. Master graph showing relationship between volume contraction and percentage conversion of MMA. Time = 4 h.

where t is the polymerization time in minutes.

The intrinsic viscosity $[\eta_{int}]$ of the polymer, determined in benzene at 32°C with a Ubbelohde viscometer, was used to calculate the average degree of polymerization $(\bar{P}_n)$ by [5]

$$\log \bar{P}_n = 3.342 + 1.13 \log [\eta_{int}] \tag{6}$$

The molecular weight $(\bar{M}_v)$ was determined by viscometry using

$$[\eta_{int}]_{32°} = KM^{\alpha} \tag{7}$$

where the values of K and α were taken as 6.46×10^{-5} and 0.75, respectively [6].

The number-average molecular weight $(\bar{M}_n)$ was also calculated from the viscosity data, using benzene as solvent, by [7]

$$[\eta_{int}]_{30°} = 8.69 \times 10^{-5} \bar{M}_n^{0.76} \tag{8}$$

The intrinsic viscosity, also measured in ethyl methyl ketone, was used to calculate the weight-average molecular weight ($\overline{M}_w$) as calculated by Chinai et al. [8]:

$$[\eta_{int}]_{25^\circ} = 7.1 \times 10^{-5}\ \overline{M}_w^{\ 0.72} \tag{9}$$

IR spectrum of the polymer was obtained on a Perkin-Elmer 599B using chloroform as solvent.

RESULTS AND DISCUSSION

The results of the kinetic investigation of the polymerization of MMA with β-picolinium p-chlorophenacylide (changing concentration from 0.5 to 3.25×10^{-3} mol/L) as initiator are presented in Table 1. The polymer is found to be syndiotactic by comparing its IR spectrum (Fig. 2) with the IR spectrum given by Stevens [9]. R_p is a direct function of the concentration of the ylide. The exponent of the initiator is 1.10 ± 0.10 as obtained from a linear graph of log R_p vs the log concentration of the ylide (Figs. 3a and 3b):

$$R_p \propto [\text{ylide}]^{1.10 \pm 0.10} \tag{10}$$

The effect of MMA on R_p was studied by varying the MMA concentration (from 27 to 40.5×10^{-3} mol) as shown in Table 2. It was found that R_p is directly proportional to the monomer concentration. A plot of log R_p vs the log concentration of MMA gives a straight line (Fig. 4), the slope of which gives the following quantitative relationship:

$$R_p \propto [\text{MMA}]^{1.5} \tag{11}$$

Termination was found to be bimolecular in nature as found by the linear plot obtained by plotting the reciprocal degree of polymerization against the square root of the ylide concentration (Fig. 5). The ratio of weight- to number-average molecular weight ($\overline{M}_w/\overline{M}_n$) was found to be 1.54, confirming termination by combination [10].

The value of k_p^2/k_t, determined from the linear slope of a plot of $1/\overline{P}_n$ and $R_p/[M]^2$, was found to be 2×10^{-5} (Fig. 6).

TABLE 1. Polymerization of MMA Initiated by β-Picolinium p-Chlorophenacylide[a]

Run no.	[Ylide] $\times 10^3$ mol/L	$R_p \times 10^5$ mol/L·s	η_{int} (dL/g)	$\overline{M}_v$	$\overline{P}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
1	0.5	0.875	-	-	-	-	-
2	1.0	1.310	-	-	-	-	-
3	1.5	1.750	-	-	-	-	-
4	2.0	2.090	0.033	4,083	46.98	-	-
5	2.5	2.440	0.044	5,994	64.42	-	-
6	3.0	2.810	0.066	10,280	101.90	9528	1.54
7	3.25	3.120	0.078	12,810	123.90	-	-

[a] MMA = 36×10^{-3} mol, 60°C, 4 h.

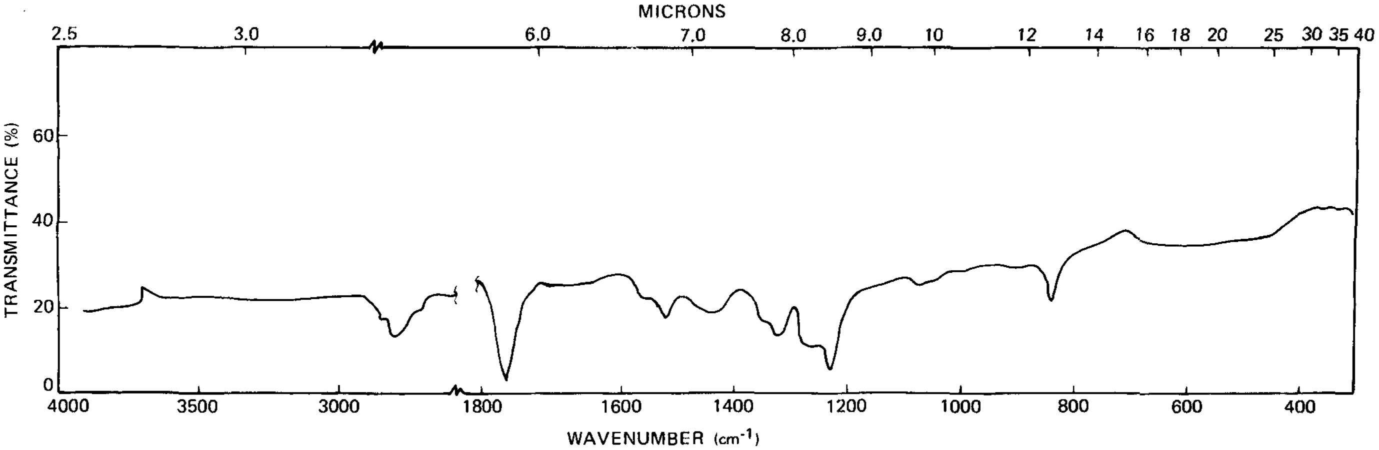

FIG. 2. IR spectrum of poly(methyl methacrylate). Solvent: $CHCl_3$. [Ylide]: 3.25×10^{-3} mol/L. MMA: 36×10^{-3} mol. Polymerization temperature: 60°C.

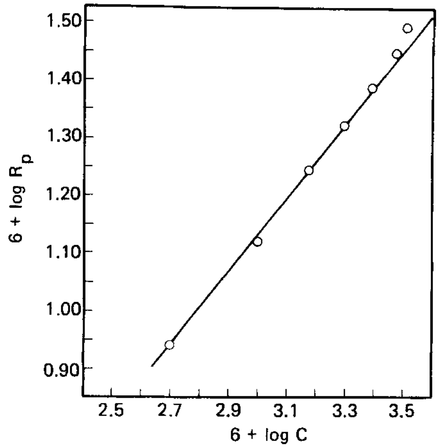

FIG. 3a. Log rate of polymerization vs log concentration of ylide. MMA: 36 × 10^{-3} mol. Time: 4 h. 60°C.

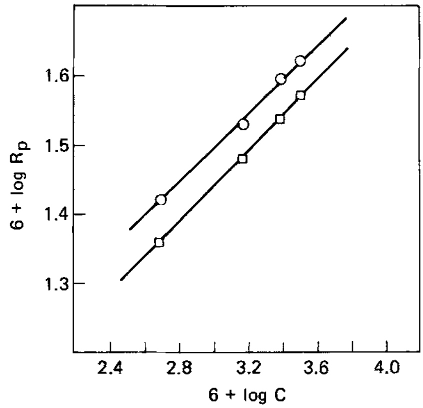

FIG. 3b. Log rate of polymerization vs log concentration of ylide. MMA: 36 × 10^{-3} mol. Time: 4 h. Temperatures (□) 65°C, (○) 70°C.

Effect of Temperature

The rate of polymerization increases with increasing temperature. The overall activation energy was computed to be 7.02 kcal/mol from the slope of an Arrhenius plot of log R_p vs 1/T (Fig. 7).

TABLE 2. Effect of Concentration of MMA on R_p[a]

Run no.	MMA × 10^3 mol	$R_p \times 10^5$ mol/L·s
1	27.0	1.25
2	31.5	2.00
3	36.0	3.12
4	40.5	4.44

[a] [Ylide] = 3.25×10^{-3} mol/L, 60°C, 4 h.

Effect of Retarder

Hydroquinone retards the rate of polymerization as shown in Table 3, which confirms a free radical mechanism of polymerization.

Effect of Solvent

The polymerization of MMA with polar and nonpolar solvents was carried out at a fixed initiator concentration (3.25×10^{-3} mol/L) as listed in Table 3.

It has been found that the nonpolar solvent carbon tetrachloride (CCl_4) favors polymerization but the molecular weight of polymer decreases, whereas the polar solvent acetonitrile (CH_3CN) has no effect on the R_p and on molecular weight; however, dimethylsulfoxide (DMSO) increases R_p. The effect of DMSO can be attributed to the initiating nature of DMSO. The effect of CCl_4 on R_p further confirms a free radical mode of reaction, and the adverse effect of CCl_4 on $\overline{M}_v$ is due to chain transfer reaction. The value of the chain transfer constant (C_S) has been determined from the slope of the linear plot of $1/\overline{P}_n$ vs [S]/[M] (Fig. 8). The value of C_S is 6.67×10^{-4}.

KINETIC SCHEME

In the light of the above discussion, the kinetic scheme shown in Eqs. (12) through (24) is proposed for the present system.

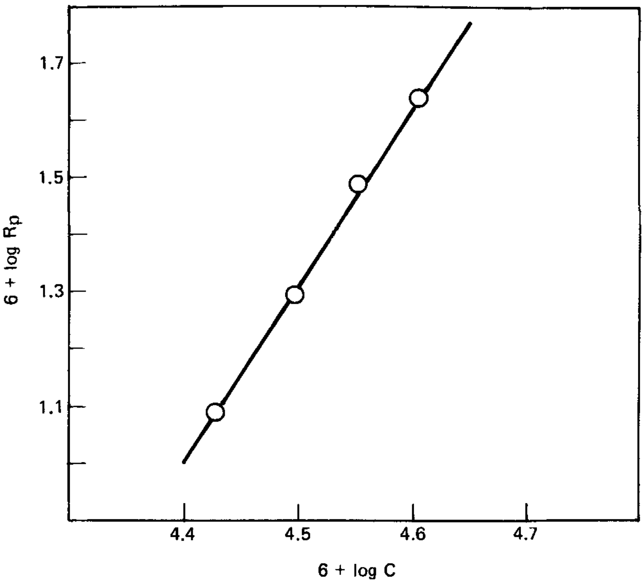

FIG. 4. Log rate of polymerization vs log concentration of MMA. [Ylide]: 3.25×10^{-3} mol/L. Time: 4 h. 60°C.

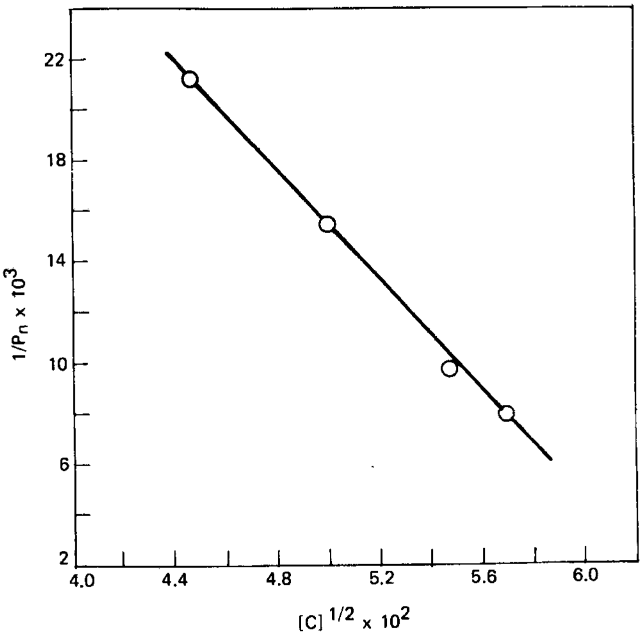

FIG. 5. Reciprocal degree of polymerization vs square root of concentration of ylide. MMA: 36×10^{-3} mol. Time: 4 h. 60°C.

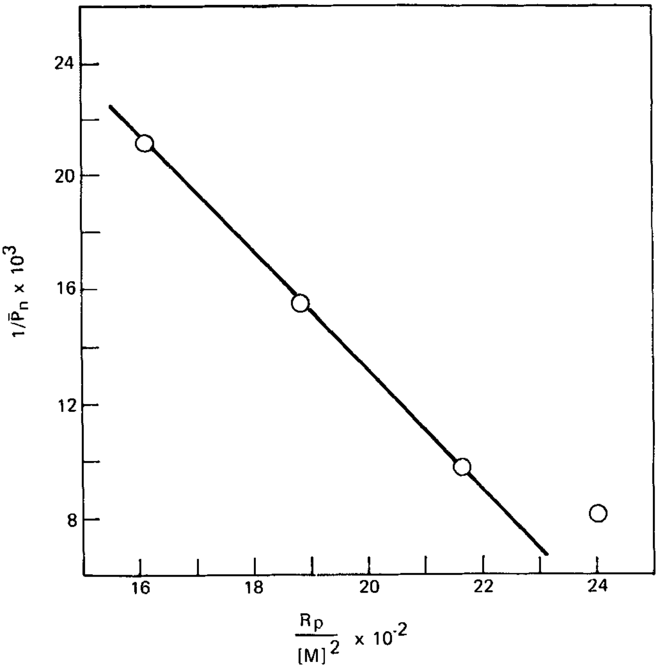

FIG. 6. Reciprocal degree of polymerization vs $R_p/[M]^2$. MMA: 36×10^{-3} mol. Time: 4 h. 60°C.

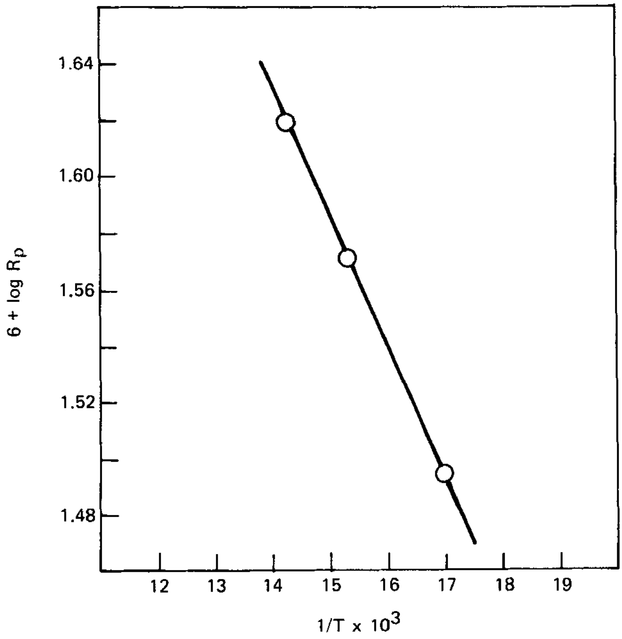

FIG. 7. Log rate of polymerization vs polymerization temperature. MMA: 36×10^{-3} mol. [Ylide]: 3.25×10^{-3} mol/L. Time: 4 h.

TABLE 3. Effect of Hydroquinone, Polar, and Nonpolar Solvents on the Polymerization of MMA[a]

Run no.	Name of additive	Concentration of additive (mol/L)	$R_p \times 10^5$ mol/L·s	η_{int} (dL/g)	$\overline{M}_v$	$\overline{P}_n$
1	Hydroquinone	3×10^{-2}	0.87	-	-	-
2	"	4×10^{-2}	No polymer	-	-	-
3	CCl_4	1	3.25	0.055	8063	82.90
4	"	2	4.12	0.023	2523	30.95
5	"	3	6.25	0.016	1556	20.54
6	DMSO	2.91	7.62	-	-	-
7	"	5.83	8.25	-	-	-
8	CH_3CN	10	3.19	-	-	-

[a] [Ylide] = 3.25×10^{-3} mol/L, MMA = 36×10^{-3} mol, 60°C, 4 h.

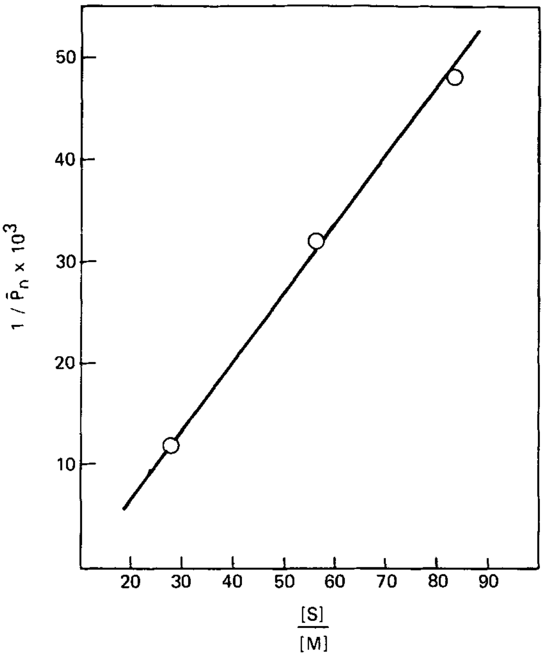

FIG. 8. Reciprocal degree of polymerization vs [S]/[M]. MMA: 36×10^{-3} mol. [Ylide]: 3.25×10^{-3} mol/L. Time: 4 h. 60°C.

Initiation:

$$2Y \xrightarrow{k_d} R^{\cdot} \qquad (12)$$

$$R^{\cdot} + M \xrightarrow{k_i} M^{\cdot} \qquad (13)$$

Propagation:

$$M^{\cdot} + M \xrightarrow{k_p} \sim\sim\sim M^{\cdot} \quad \text{(propagating chain)} \qquad (14)$$

Termination:

$$2\sim\sim\sim M^{\cdot} \xrightarrow{k_t} \text{polymer} \qquad (15)$$

where Y is the initiator molecule, $R^{\cdot}$ is the initiating radical formed, and M and $M^{\cdot}$ are the monomer molecule and monomer radical, respectively. Accordingly, the rate of initiation (R_i), rate of termination (R_t), and rate of propagation ($R_p{}'$) may be derived as follows:

$$R_i = -\frac{d[M^\cdot]}{dt} = k_i[R^\cdot][M] \tag{16}$$

$$[R^\cdot] = k_d[Y]^2 \tag{17}$$

Thus

$$R_i = k_ik_d[M][Y]^2 \tag{18}$$

$$R_t = 2k_t[M^\cdot]^2 \qquad \text{(bimolecular termination)} \tag{19}$$

Assuming steady-state conditions:

$$R_i = R_t$$

$$2k_t[M^\cdot]^2 = k_ik_d[M][Y]^2$$

$$[M^\cdot] = \left[\frac{k_ik_d}{2k_t}\right]^{0.5}[M]^{0.5}[Y] \tag{20}$$

The rate of propagation R_p' (overall rate of polymerization R_p) may be written as

$$R_p = R_p' = k_p[M^\cdot][M] \tag{21}$$

Applying the value of $[M^\cdot]$ from Eq. (20) to Eq. (21):

$$R_p = k_p\left[\frac{k_ik_d}{2k_t}\right]^{0.5}[M]^{1.5}[Y]^{1.0} \tag{22}$$

When the monomer concentration is constant, then

$$R_p \propto [Y]^{1.0} \tag{23}$$

and when the ylide concentration is constant,

$$R_p \propto [M]^{1.5} \tag{24}$$

Thus this kinetic scheme is in good agreement with the experimental data obtained.

Thus β-picolinium p-chlorophenacylide acts as a free radical initiator for preparing syndiotactic polymer (PMMA).

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