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Heterocyclic Ylide-Initiated Polymerization of Methyl Acrylate

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ABSTRACT

β-Picolinium-p-chlorophenacylide initiates radical polymerization of methyl acrylate (MA) up to 19.5% conversion without gelation due to autoacceleration. The average rate of polymerization (R_p) increases as [ylide] is raised from 1.02 to 3.06 mmol/L, the order of reaction being 0.5 ± 0.02. However, at higher concentrations (>3.06 mmol/L), R_p decreases. The monomer exponent is 1.40 when benzene is used as diluent. The overall energy of activation is computed to be 28.8 kJ/mol. A polar solvent like dimethylsulfoxide and a radical scavenger like hydroquinone retard the reaction. The kinetic data and ESR studies indicate that the polymerization proceeds via a free-radical mechanism. Chain termination by degradative chain (initiator) transfer appears to be significant.

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INTRODUCTION

Despite the large amount of data accumulated for polymerization of vinyl monomers, relatively little quantitative kinetic information has been published on the polymerization of methyl acrylate (MA). Advances in this area have been hampered by the autoacceleration problem. Walling [1] found a gradual increase in the rate of polymerization throughout the reaction. Bagdasarayan [2] showed that autoacceleration disappeared when polymerization was carried out in ethyl acetate solution containing less than 50% monomer. Mahadevan and Santhappa [3] found a maximum conversion of 10%. Rizzardo and Solomon [4] investigated a new mechanism of initiation using di-t-butyl peroxalate as radical initiator. Recently, Rubio et al. [5] polymerized MA in aqueous hydrochloric acid solution in the presence of $TiCl_3$-NH_2OH as the redox system.

The present work reveals that β-picolinium-p-chlorophenacylide could be used to obtain 19.5% conversion of MA without gelation due to autoacceleration, which is nearly double the conversion obtained by using the conventional free-radical initiator α,α'-azobisisobutyronitrile (AIBN).

EXPERIMENTAL

Purified reagent-grade monomer (Burgoyne) and solvents were used. β-Picoline, dried over NaOH, was distilled under vacuum. Bromine (E. Merck) and p-chloroacetophenone (SRL) were used without further purification. β-Picolinium-p-chlorophenacylide was prepared by the method of Krohnke [6, 7] and Lumb [8].

The polymerization was carried out in a modified dilatometric apparatus [9]. The requisite amount of ylide was dissolved in monomer and introduced into the dilatometer, flushed with purified N_2, stoppered, and placed in a water bath at the required temperature. The polymer, precipitated by acidified methanol, was dried to constant weight.

The percentage conversion (C) was calculated from the volume contraction (monitored with the help of a cathetometer) in the calibrated dilatometers. Then the rate of polymerization was calculated [10] from the conversion data using

$$R_p \ (\text{mol}/(\text{L}\cdot\text{s})) = \frac{1.851 \times C \times 10^{-3}}{t}, \tag{1}$$

where t is the polymerization time in minutes.

The intrinsic viscosity $[\eta]$ of poly-MA was determined in benzene at 30°C using an Ostwald viscometer. The average degree of polymerization ($\overline{P}_n$) was calculated [11] by

$$\overline{P}_n = 11.2([\eta] \times 100)^{1.22}. \tag{2}$$

The ESR spectrum was recorded on an x-band EPR-109 E-line Century series spectrometer at room temperature.

RESULTS AND DISCUSSION

The results of the kinetic investigation of the polymerization of MA with β-picolinium-p-chlorophenacylide as initiator are presented in Tables 1 to 3 and Figs. 1 to 5. When MA was polymerized at 60°C with 7.62 mmol/L of AIBN, the polymerization accelerated continuously up to 7.0% conversion, and gelation took place at 9.45% conversion.

Effect of Ylide Concentration

The influence of [ylide] on R_p was studied over a concentration range of 1.02-30.60 mmol/L (Table 1) at 60, 65, and 70°C. The rate of polymerization increased consistently with increasing [ylide] in the range 1.02-3.06 mmol/L. The order of reaction, determined from the slope of the plot (Fig. 1) of log R_p vs log [ylide], was found to be 0.5 ± 0.02. At higher concentrations of ylide (>3.06 mmol/L), the rate decreased, probably due to lowering of initiator efficiency, which might be a consequence of high concentrations of primary radicals, leading to their mutual annihilation to a certain extent.

The presence of an intercept on the $1/\overline{P}_n$ axis in the plot of $1/\overline{P}_n$ vs $[\text{ylide}]^{0.5}$ (Fig. 2) indicates that some additional termination mechanism occurs along with the usual bimolecular termination. A plot of $1/\overline{P}_n$ against R_p (Fig. 2) shows upward deviation from linearity. The nature of the plot is also indicative of a prominent initiator transfer effect, which appears to become degradative in nature. This brings about the observed delay in the onset of gelation.

An equation derived by Deb [12], simplified by Ghosh and Mitra [13], was used to analyze degradative chain (initiator) transfer with reinitiation:

$$\ln \frac{R_p^{\,2}}{[Y][M]^2} = \ln \frac{2f_k k_d k_p^{\,2}}{k_t} - \frac{k_p^{\,2} k_{rty}}{k_t k_{iy} k_p} C_y \frac{[Y]}{[M]} \tag{3}$$

TABLE 1. Polymerization of Methyl Acrylate with β-Picolinium-p-Chlorophenacylide as Initiator at 60°C for 8 h

Run no.	[Ylide], mmol/L	Percentage conversion	R_p, mmol/(L·s)	$\overline{P}_n$
1	1.02	9.5	0.037	351
2	1.53	11.5	0.044	304
3	2.04	13.3	0.051	247
4	2.55	14.5	0.056	226
5	3.06[a]	15.1	0.058	198
6	3.31	13.3	0.051	-
7	5.10	12.3	0.047	-
8	7.65	11.8	0.046	-
9	12.75	11.2	0.043	-
10	17.85	10.8	0.042	-
11	22.95	10.5	0.041	-
12	28.06	10.2	0.039	-
13	30.60	9.8	0.038	-

[a] 19.5% conversion at 70°C.

or

$$\log \frac{R_p^2}{[Y][M]^2} = \log \frac{2f_k k_d k_p^2}{k_t} - 0.434 \frac{k_p^2 k_{rty}}{k_t k_{iy} k_p} C_Y \frac{[Y]}{[M]}. \tag{4}$$

The plot of the left side of Eq. (4) against [Y]/[M] (Fig. 3) is linear with a negative slope, indicating significant degradative initiator transfer.

Effect of Methyl Acrylate Concentration

Polymerization of MA was studied at several monomer concentrations (2 780-6 250 mmol/L) and at fixed [ylide] (3.06 mmol/L) with benzene as solvent, which does not have any effect on the R_p in this system

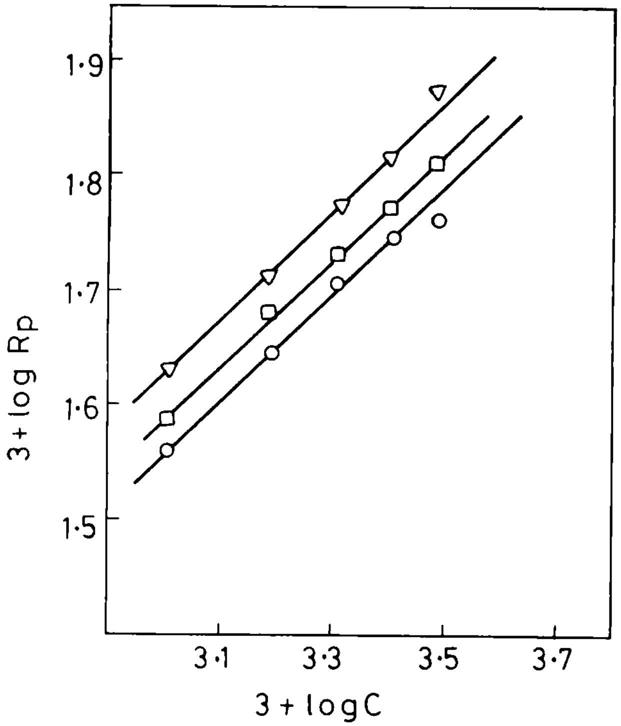


FIG. 1. Rate of polymerization as a function of ylide concentration. Polymerization time = 8 h. Temperature (○) 60°C, (□) 65°C, (▽) 70°C.

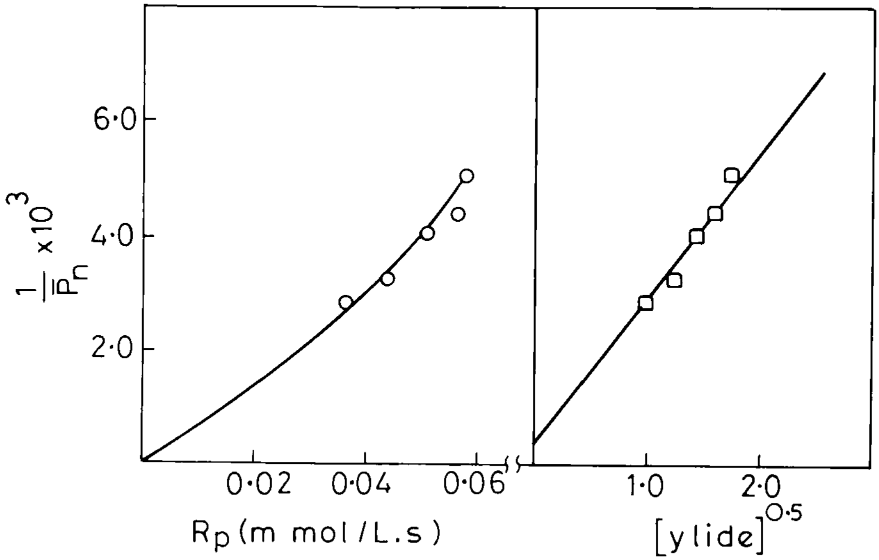


FIG. 2. Plot of reciprocal average degree of polymerization vs (○) the rate of polymerization and the (□) square root of ylide concentration. Polymerization time = 8 h. Temperature = 60°C.

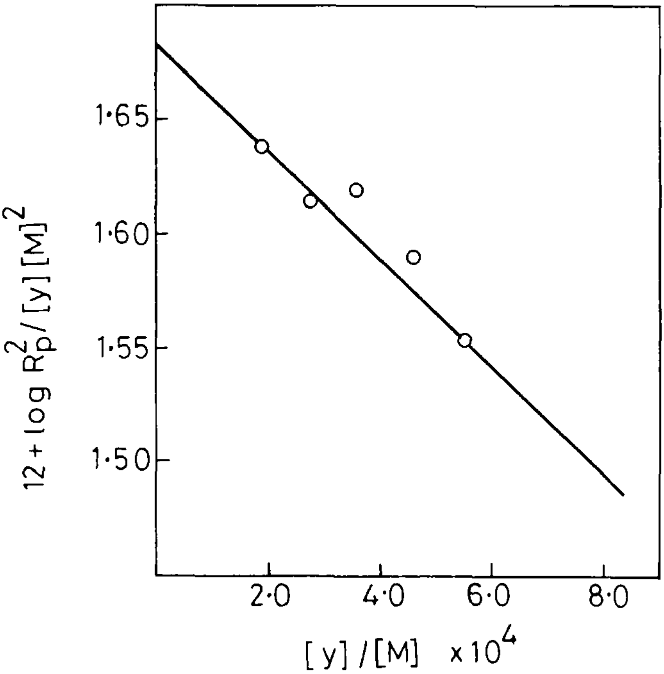


FIG. 3. Plot of log $R_p^2/[Y][M]^2$ vs $[Y]/[M]$ for the polymerization of MA to analyze degradative initiator transfer. Polymerization time = 8 h. Temperature = 60°C.

and acts merely as inert diluent. The monomer exponent, calculated from the slope of the linear plot of log R_p vs log [MA], was 1.40. The results are summarized in Table 2.

Effect of Temperature

The rate of polymerization was studied within the temperature range 60-70°C. The increase in temperature causes an enhancement in R_p. The overall energy of activation, calculated from the Arrhenius plot (Fig. 4), was found to be 28.8 kJ/mol.

Effect of Additives

The polymerization of MA was carried out at 60°C with 3.06 mmol/L of ylide (Table 3) in the presence of low concentrations of the polar solvent dimethylsulfoxide (DMSO), which decreased R_p.

TABLE 2. Effect of [MA] on R_p[a]

Run no.	[MA], mmol/L	R_p, mmol/(L·s)
1	2 780	0.021
2	3 470	0.030
3	4 260	0.040
4	4 860	0.051
5	5 550	0.058
6	6 250	0.068

[a] [Ylide] = 3.06 mmol/L. Polymerization time = 8 h. Polymerization temperature = 60°C.

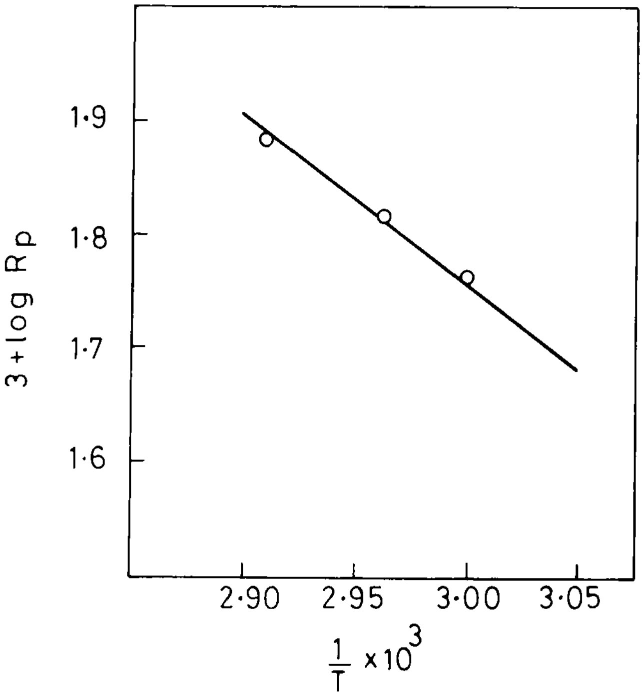


FIG. 4. Arrhenius plot of polymerization rate. Polymerization time = 8 h, [ylide] = 3.06 mmol/L.

TABLE 3. Effect of Hydroquinone and Polar Solvent (DMSO) on R_p[a]

Run no.	Additive	Concentration of additive, mmol/L	R_p, mmol/(L·s)
1	Hydroquinone	0.00	0.058
		30	0.034
		40	0.032
2	DMSO	0.00	0.058
		10	0.036
		20	0.030
		30	0.020

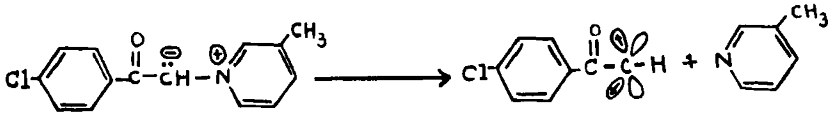
[a] [Ylide] = 3.06 mmol/L. Polymerization time = 8 h. Polymerization temperature = 60°C.

Polymerization of MA exhibited strong inhibition in the presence of hydroquinone, a free-radical inhibitor (Table 3).

MECHANISM

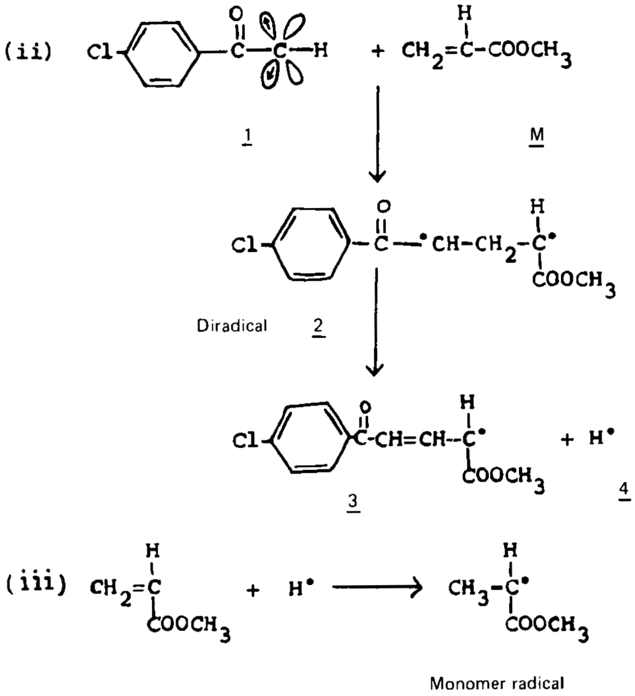
The ESR spectrum (Fig. 5) shows characteristic free-radical absorption at 3300 G. The gyromagnetic ratio (g) was calculated to be 2.0324, which is very close to the value given for the DPPH radical (g = 2.0036 ± 0.03). This confirms that the present system follows the free-radical mode of polymerization. This can be explained on the assumption that β-picolinium-p-chlorophenacylide (Y) dissociates to a triplet carbene (1) [14], which acts as a source of radicals. The triplet carbene reacts with monomer (M) to form Diradical 2 [15, 16], which further decomposes into two radicals (3 and 4). Radical 3 would be resonance stabilized, and therefore, polymerization takes place in one direction by means of Radical 4. The propagation and termination steps are the same as for conventional radical polymerization.

(i)



Y

Triplet carbene 1



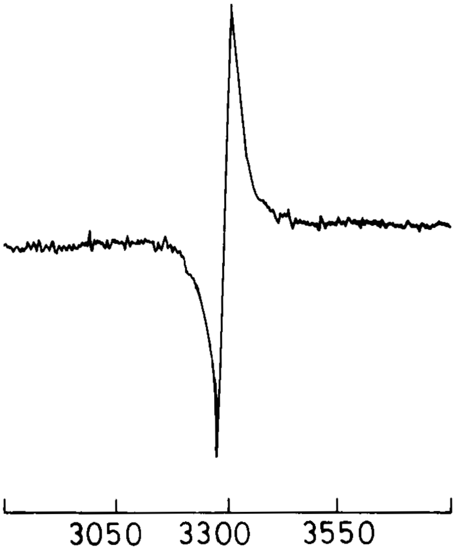


FIG. 5. ESR spectrum of polymerization mixture (methyl acrylate and ylide). Scan range = 5 kG, field set = 3300 G, modulation amplitude = 4×1 G, modulation frequency = 100 kHz, room temperature = 20°C, microwave frequency = 9.387 GHz.

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