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Sulphur Ylide Initiated Photopolymerization of Methyl Methacrylate

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Solution polymerization of methyl methacrylate was carried out in the presence of visible light (440 nm) using 3-nitrophenacyl dimethyl sulfonium ylide as a photoinitiator at 30°C. The initiator and monomer exponent values were calculated to be 0.49 and 1.0 respectively. An average value of K_P^2/K_T was 2.0×10^{-2}. The polymerization was restarted in the presence of benzoquinone. Kinetic data and ESR studies indicate that the overall polymerization takes place by radical mechanism.

INTRODUCTION

Polymerization of vinyl monomers by ylide has attracted attention in recent years. The phosphonium ylides[1], picolinium ylides[2–7] and sulfonium ylides[8,9] have been used as thermal and photoinitiator in homo and copolymerization of some vinyl monomers. We have already reported[10] the thermal polymerization of styrene initiated by 3-nitrophenacyl dimethyl sulfonium ylide. This article describes the photoinitiated polymerization of methyl methacrylate (MMA) using 3-nitrophenacyl dimethyl sulfonium ylide.

EXPERIMENTAL

Purified reagent grade MMA and solvents were used. Dimethyl sulfonium-*m*-nitrophenacylide was prepared by the method given in literature[11].

The polymerization was carried out in glass ampoules of 50 ml capacity filled with the monomer and the solution of ylide in tetrahydrofuran was flushed with purified nitrogen, stoppered and illuminated with visible light of 440 nm wavelength using a high pressure mercury vapour lamp (Hanovia Make). Polymers formed at low conversions (< 8%), were precipitated with excess of acidified methanol and then dried to constant weight. The steady polymerization rates (R_P) were calculated as follows:

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

where C is the percentage conversion and t is the polymerization time in minutes.

The intrinsic viscosity $[\eta_{int}]$ of polymers were determined in benzene at 30°C using an ubbelohde viscometer. The average degree of polymerization was calculated by equation[12]

$$\log P_n = 3.342 + 1.13 \log [\eta_{int}]$$

The ESR spectrum was recorded on an X—band EPR—109 E—line century series spectrometer at 30°C.

RESULTS AND DISCUSSION

The results of kinetic investigations of the photopolymerization of MMA at 30°C in varying ylide concentrations (4.44×10^{-3} mol l^{-1} to 8.0×10^{-3} mol l^{-1}) and at fixed intensity of light source are presented in Table 1 and in Figs. 1–3. No polymerization was observed when MMA with 4.44×10^{-3} mol l^{-1} of ylide was kept in dark at 30°C, however a negligible amount of polymer was formed when MMA alone was exposed to light at 30°C. No induction period was observed in the polymerization reaction.

TABLE 1

PHOTOPOLYMERIZATION OF METHYL METHACRYLATE USING 3-NITROPHENACYL DIMETHYL SULFONIUM YLIDE AS INITIATOR

$[Y]\times10^4$ mol l^{-1}	[MMA] mol l^{-1}	$R_P\times10^6$ mol $l^{-1}S^{-1}$	$R_P/[M]^{-2}\times10^6$	$\bar{P}_n$	[Benzoquinone] $\times10^2$ mol l^{-1}
44.4	5.45	41.68	1.40	449.77	—
53.2	4.45	45.71	1.54	400.00	—
62.2	5.45	50.12	1.68	384.61	—
71.0	5.45	53.70	1.80	344.82	—
80.0	5.45	60.90	2.05	322.58	—
44.4	3.63	28.84	—	—	—
44.4	4.54	35.89	—	—	—
44.4	6.36	48.42	—	—	—
44.4	5.45	—	—	—	1

Polymerization time = 5 hrs., Polymerization temperature = 30°C.

Fig. 1 shows a plot of log R_P vs log [Y], the initiator exponent, determined from the slope of this plot is found to be 0.49. The plot of reciprocal average degree of polymerization against the square root of the initiator concentration gives a straight line passing through the origin (Fig. 2b). These two observations indicate that ylide initiated polymerization of MMA brought about by a radical mechanism. The value of k_p^2/k_t, calculated from the slope of the linear plot of $1/p_n$ vs $R_p/[M]^2$ (Fig. 3a) is found to be 2.0×10^{-2} which is close to the data available in literature for photopolymerization of MMA using radical initiator.

The absence of an intercept on the $1/\bar{P}_n$ in the plot of $1/\bar{P}_n$ vs R_p (Fig. 2a) indicates negligible initiator transfer and monomer transfer.

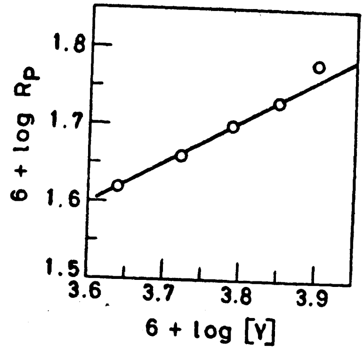

Fig. 1 Plot of log rate of polymerization versus log concentration of ylide

[MMA] = 5.45 mol l^{-1}
Polymerization time = 5 hrs
Polymerization temperature = 30°C

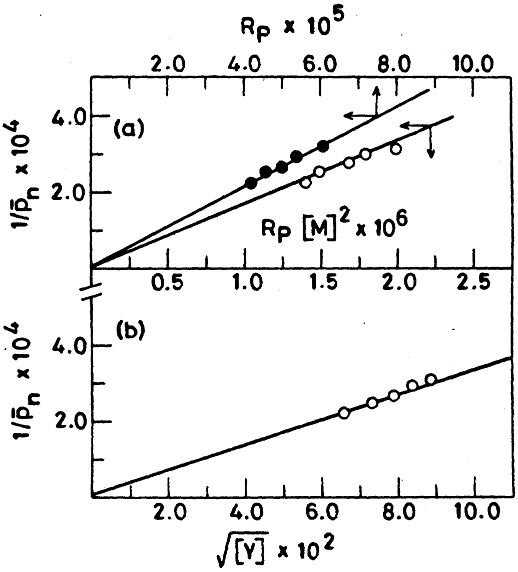

Fig. 2 (a) Plot of $(1/P_n)$ versus R_p and $(1/P_n)$ versus $R_p/[M]^2$
(b) Plot of $(1/P_n)$ versus $[\text{Ylide})^{0.5}$

[MMA] = 5.45 mol l^{-1}
Polymerization time = 5 hrs
Polymerization temperature = 30°C

Photopolymerization of MMA was also carried out at 30°C by varying monomer concentration (3.63 to 6.36 moles l^{-1}) at fixed ylide concentration (4.44 $\times 10^{-3}$ moles l^{-1}). The results are summarized in Table 1. The monomer exponent, calculated from the slope of the linear plot of log R_p against log [MMA] is 1.0 (Fig. 3).

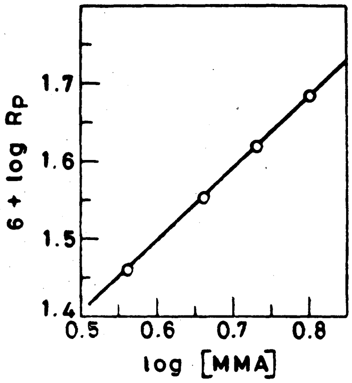

Fig. 3 Plot of log R_p versus log concentration of MMA

[Ylide] = 44.4×10^{-4} mol l^{-1}
Polymerization time = 5 hrs
Polymerization temperature = 30°C

The effect of free radical inhibitor (benzoquinone) on the photopolymerization of MMA was also observed. Polymerization completely inhibits in presence of benzoquinone.

The ESR spectrum shows characteristic free radical absorption of 3350 G. The value of gyromagnetic ratio (g) calculated is 2.0324. Kinetic data, inhibitory effect of benzoquinone and the ESR spectrum show that photopolymerization of MMA initiated by ylide proceeds by a radical mechanism.

The radical generation process can be explained on the basis of the fact that sulfonium ylide of decomposition gives triplet carbene[13,14], which acts as a source of radicals[10].

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