

Methylmethacrylate Polymerization Photoinitiated by 1-(Bromoacetyl)pyrene

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ABSTRACT: The photopolymerization of methylmethacrylate induced by pyrene, 1-acetylpyrene (AP), and 1-(bromoacetyl)pyrene (BP) has been investigated. Under all conditions employed, pyrene was completely ineffective. Introduction of a carbonyl and a bromo group in pyrene enhanced the polymerization efficiencies. Efficiency of AP as photoinitiator was very low; however, BP was proved to be a good photoinitiator. The polymerization with BP follows first-order kinetics with respect to monomer conversion, with a shorter induction period as compared with that of

AP. The value of the initiator exponent (0.5) and the linear dependence of reciprocal average degree of polymerization on the square root of the initiator concentration suggest radical polymerization with bimolecular termination. IR and NMR spectra showed the atactic nature of polymethylmethacrylate. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 920–926, 2006

Key words: photopolymerization; pyrene; 1-(bromoacetyl)pyrene; kinetics; bimolecular termination

INTRODUCTION

There have been a number of studies on the photoinitiated polymerization of vinyl monomers using excited carbonyl or aromatic hydrocarbon compounds.^{1,2} Colorants make up a large class of molecules extensively used to sensitize or start the polymerization of monomers.^{3–8} The panchromatic sensitization of polymerization requires the presence of a suitable dye as a light absorber. For such a case, photophysical energy transfer from dye molecule to an acceptor molecule that yields free radicals to initiate polymerization takes place. This process is usually very slow and initiation may take several hours.⁶ Dyes can be made fast photoinitiators by introducing such groups that produce free radicals either by intramolecular α -cleavage or by hydrogen-transfer process.^{9–12} Thus, introduction of photocleavable groups in the aromatic hydrocarbon dyes is expected to make them better photoinitiators. Moreover, heavy atoms like Br and Cl are also known to cause a significant rise in the photoinitiation ability of the dyes.⁶ Pyrene, an aromatic hydrocarbon dye, has been reported as a photoinitiator in the presence of triethylamine.^{1,13}

Present study was undertaken with a view to see a change in the photo-initiating ability of pyrene, to polymerize methylmethacrylate (MMA), by introduction of $-\text{COCH}_3$ group in the ring at first step and then replacing α -H by $-\text{Br}$. The initiation time and the extent of percent conversion of MMA by pyrene (P), 1-acetylpyrene (AP), and 1-(bromoacetyl)pyrene (BP) have been reported. A detailed polymerization kinetics and mechanism with only BP as initiator are discussed.

EXPERIMENTAL

Materials

Reagent-grade MMA (Merck-Schuchardt) and other solvents were purified by the usual methods^{14,15} and distilled under vacuum before use. Pyrene [$M = 202.26 \text{ g mol}^{-1}$, mp = 149–151°C], 1-acetylpyrene (AP) [$M = 244.3 \text{ g mol}^{-1}$, mp = 86–89°C], and 1-(bromoacetyl)pyrene [$M = 323.2 \text{ g mol}^{-1}$, mp = 129–131°C] (Aldrich, Milwaukee, WI) were used as received. Hydroquinone was recrystallized twice from methanol.

Polymerization procedure

The required amounts of monomer, initiator, and DMSO were charged into a quartz tube. This tube was degassed under vacuum by the conventional freeze and thaw technique and sealed off under vacuum. This reaction mixture was irradiated in a photochem-

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TABLE I
Effect of [BP] on R_p ^a

Sample no.	[BP] (10^4 mol L ⁻¹)	% Conversion	R_p (10^5 mol L ⁻¹ s ⁻¹)	\bar{P}_n
1	1.54	4.81	2.403	781
2	2.32	5.77	2.880	609
3	3.09	6.80	3.396	537
4	4.64	8.31	4.146	431
5	6.18	9.59	4.780	386

^a [MMA] = 2.35 mol/L; polymerization time, 5h; polymerization temp., (30 ± 0.2)°C.

ical reactor containing eight 253-nm UV tubes (8 W each, path length = 10 cm), arranged in a circular fashion, for known periods of time at 30°C. After irradiation, the contents were poured into excess methanol, and the precipitated polymer was washed with acidified methanol. After two reprecipitations from methanol, the polymers were dried in vacuum oven at 60°C for 24 h. The rates of polymerization (R_p) were calculated by the following equation:¹⁶

$$R_p(\text{mol l}^{-1} \text{s}^{-1}) = \frac{1.498 \times C \times 10^{-3}}{t}$$

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

Characterization

The FTIR and NMR (¹H and ¹³C) spectra were recorded on a PerkinElmer Model 599 B (KBr pellets)

and Jeol JNM LA 400 Lambda spectrophotometer using CDCl₃ as a solvent and TMS as an internal reference, respectively. The intrinsic viscosity (η) of the polymers was determined in benzene at 30°C using an Ubbelohde viscometer. The average degree of polymerization \bar{P}_n was calculated by the following equation:¹⁷

$$\log \bar{P}_n = 3.342 + 1.13 \log [\eta]$$

RESULTS AND DISCUSSION

Photoinitiation ability of initiators used was compared on the basis of the data obtained for P-MMA, AP-MMA, and BP-MMA systems. In P-MMA system no polymer formation was observed within 15 h, whereas in AP-MMA system, 2% conversion was observed after 15 h. However, the introduction of bromine in the acetyl moiety significantly reduced the induction period and enhanced the polymerization rate, and 12% conversion was observed in BP-MMA system in 5 h.

Polymerization kinetics

The effect of [BP] on R_p has been studied by varying [BP] from 1.54×10^{-4} mol L⁻¹ to 6.18×10^{-4} mol L⁻¹, keeping [MMA] constant at 2.35 mol L⁻¹ (Table I). The R_p increases with increase in concentration of BP. The initiator exponent calculated from the slope of the plot of $\log R_p$ versus \log [BP] is 0.5 (Fig. 1). The value of the initiator exponent and the observation that the plot of

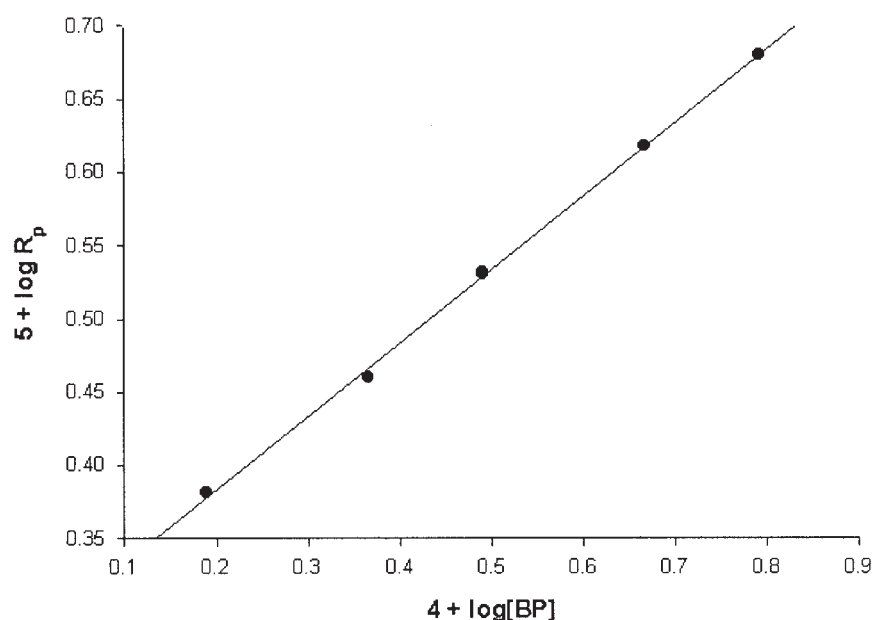


Figure 1 Plot between \log [BP] versus $\log R_p$. [MMA] = 2.35 mol L⁻¹; polymerization time, 5 h; polymerization temperature, (30 ± 0.2)°C.

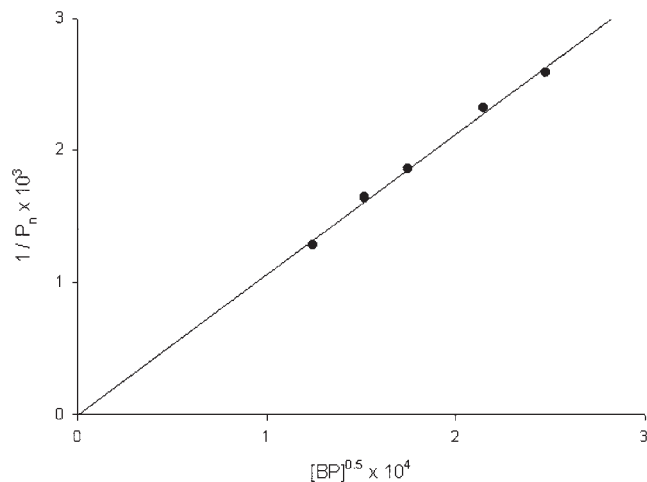


Figure 2 Plot of $1/P_n$ versus $[BP]^{0.5}$. $[MMA] = 2.35 \text{ mol L}^{-1}$; polymerization time, 5 h; polymerization temperature, $(30 \pm 0.2)^\circ\text{C}$.

reciprocal average degree of polymerization (\bar{P}_n) against the square root of the initiator concentration give a straight line passing through the origin (Fig. 2), suggesting radical polymerization with bimolecular termination. The dependence of the average molecular weight of polymer upon $[BP]$ is as expected for radical polymerization.

The effect of monomer concentration on R_p is studied by varying $[MMA]$ from 2.35 to 5.87 mol L^{-1} , keeping $[BP]$ constant at $1.54 \times 10^{-4} \text{ mol L}^{-1}$. The respective data are shown in Table II. The monomer

TABLE II
Effect of $[MMA]$ on R_p ^a

Sample no.	$[MMA]$ (mol L^{-1})	% Conversion	R_p ($10^5 \text{ mol L}^{-1} \text{ s}^{-1}$)
1	2.35	4.81	2.403
2	3.52	7.11	3.548
3	4.7	9.15	4.56
4	5.87	12.07	6.02

^a $[BP] = 1.54 \times 10^{-4} \text{ mol/L}$; polymerization time, 5 h; polymerization temp., $(30 \pm 0.2)^\circ\text{C}$.

exponent value calculated from the slope of the linear plot of $\log R_p$ versus $\log [MMA]$ is 0.98 (Fig. 3), suggesting that the system follows ideal kinetics.

Characterization of polymer

FTIR spectroscopy

The FTIR spectrum (Fig. 4) of polymer consists of the following group of bands: —C—H str vibrations of methyl and methylene group at 2951 and 2843 cm^{-1} respectively; >C=O str vibrations of ester carbonyl at 1731 cm^{-1} ; the C—H deformation bands in the region of 1387–1480 cm^{-1} ; C—O str bands in the region of 1150–1250 cm^{-1} ; characteristic band at 1060, 988, 482 cm^{-1} are supportive of the atactic nature of the polymer.¹⁸

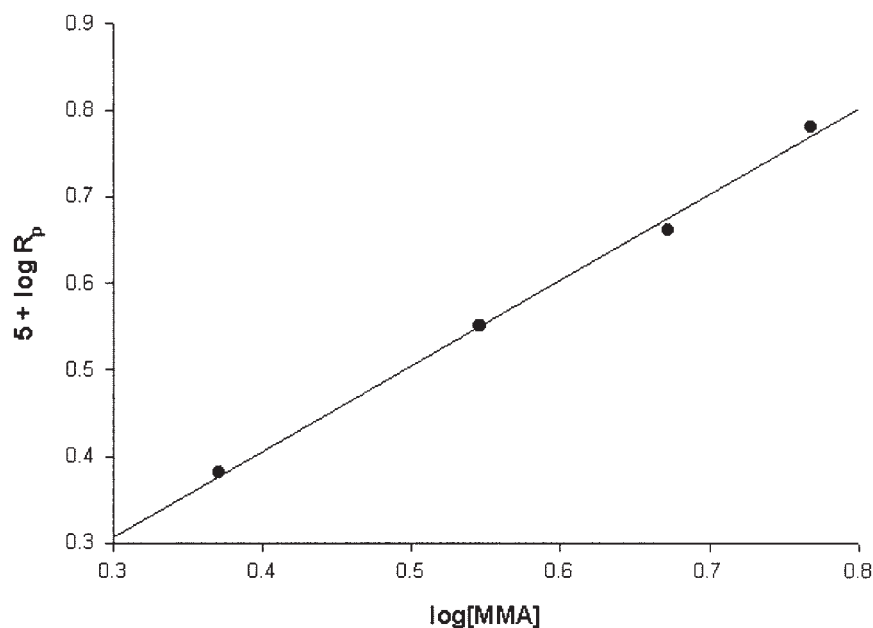


Figure 3 Plot of $\log [MMA]$ versus $\log R_p$. $[BP] = 1.54 \times 10^{-4} \text{ mol L}^{-1}$; polymerization time, 5 h; polymerization temperature, $(30 \pm 0.2)^\circ\text{C}$.

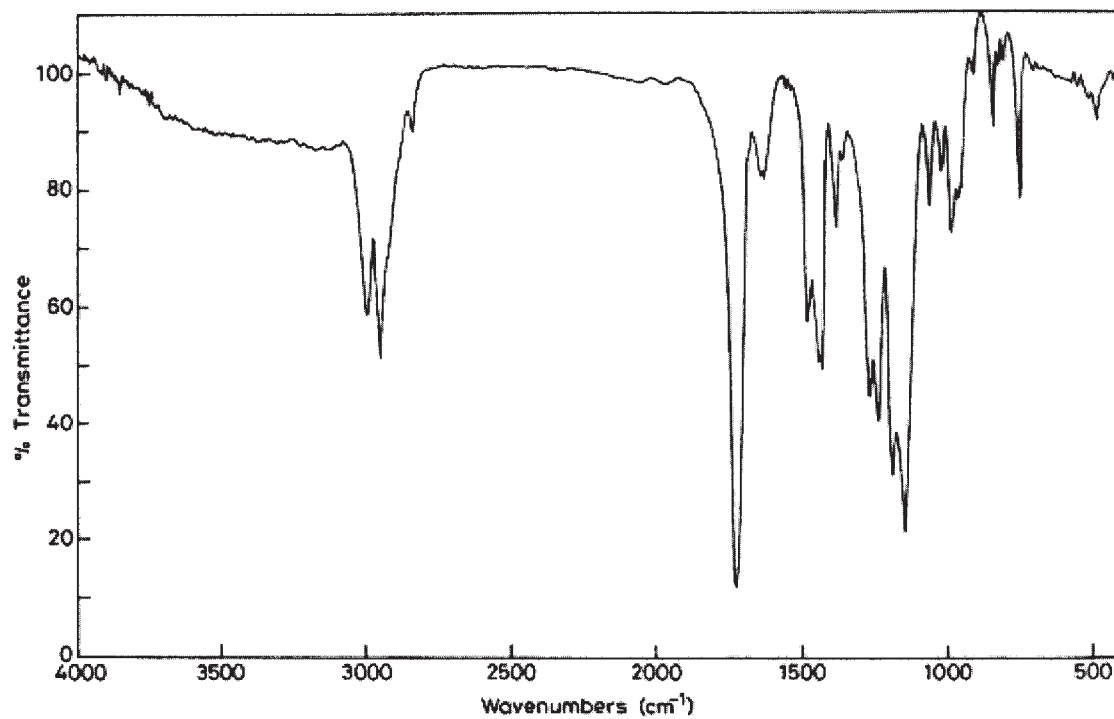
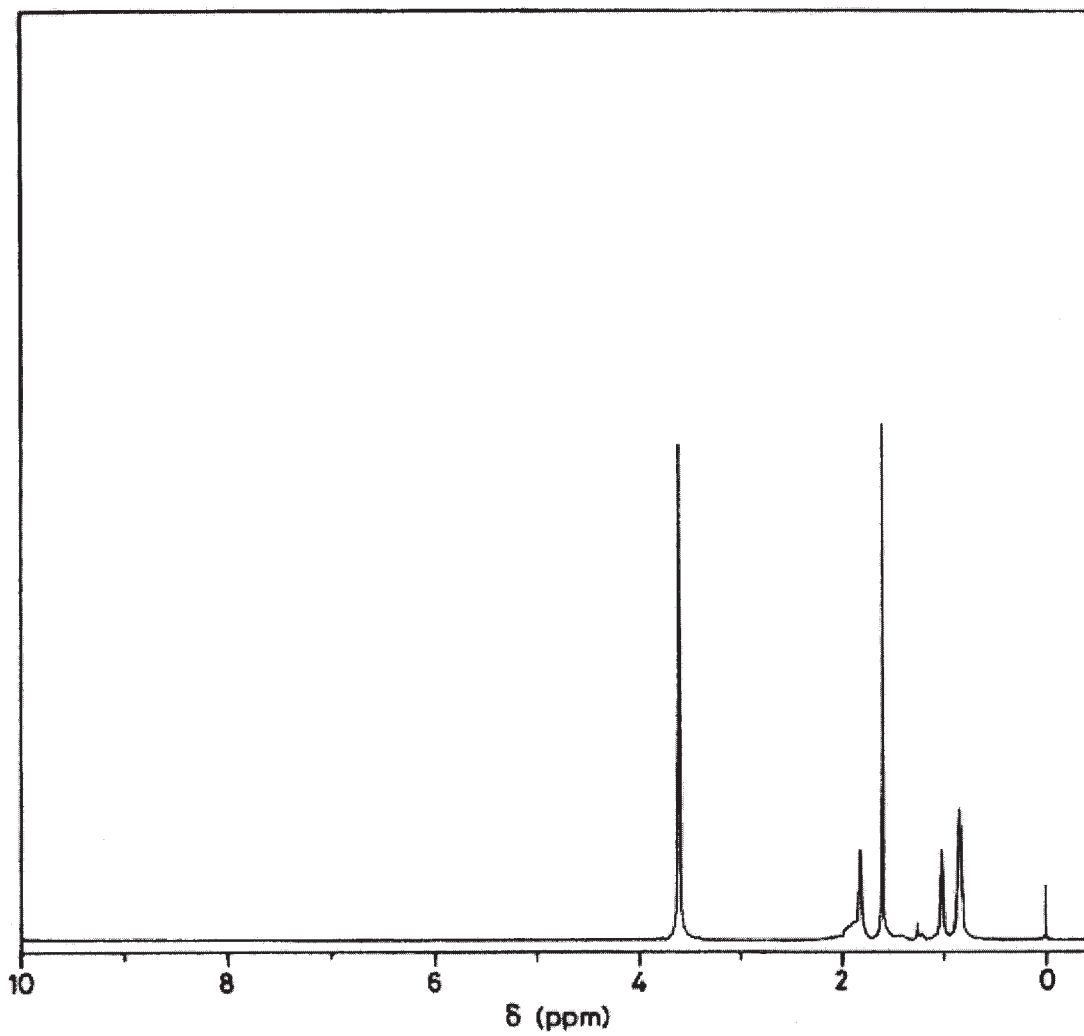


Figure 4 FTIR Spectrum.

Figure 5 ¹H NMR Spectrum.

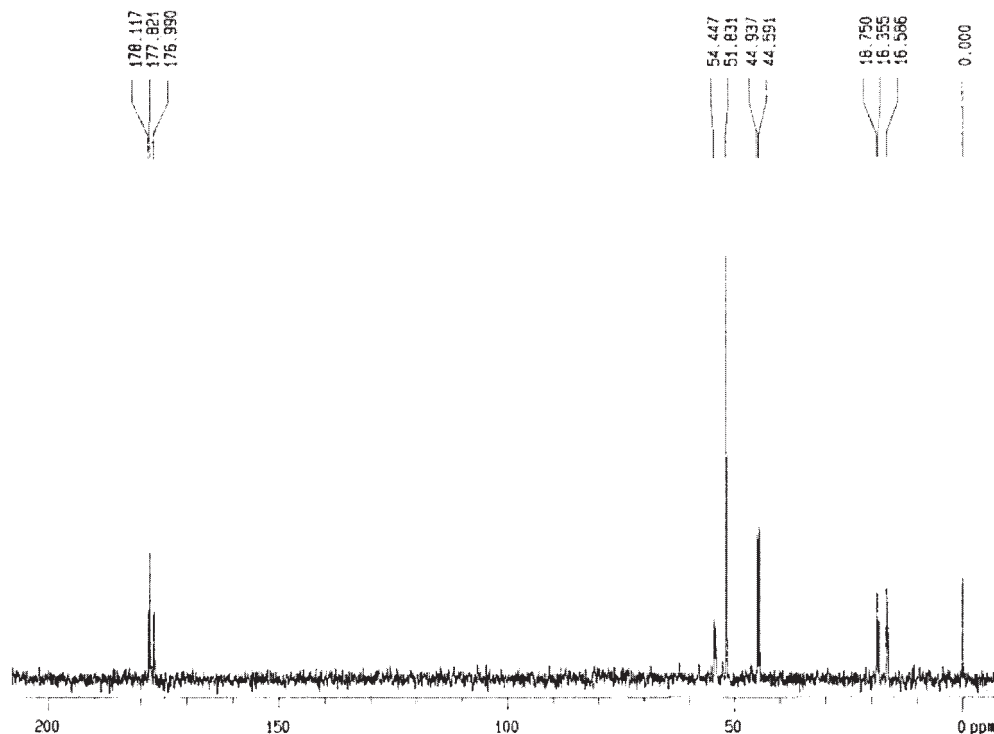


Figure 6 ^{13}C NMR Spectrum.

^1H NMR Spectroscopy

In the ^1H NMR spectrum (Fig. 5) a singlet due to methoxy protons appears at 3.6 δ . Methyl protons appear in the region between 0.9 and 1.02 and methylene protons between 1.62 and 1.81 δ . The methylene protons appear as singlet at 1.83 in syndiotactic polymethylmethacrylate (PMMA), whereas a doublet at 1.62 and 2.33 is observed in isotactic PMMA. In this case neither of these characteristic peaks¹⁹ was observed; therefore, it was concluded that an atactic PMMA was formed by BP-MMA system

^{13}C NMR Spectroscopy

The spectrum (Fig. 6) shows a series of peaks between 176 and 178 ppm owing to the ester carbon,²⁰ further confirming the atactic nature of polymer. The methoxy carbon appears at 51 ppm while the peaks at 44 and 16–18 ppm are attributed to methylene and methyl carbons.

Mechanism

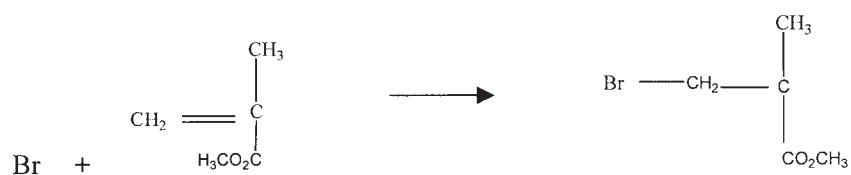
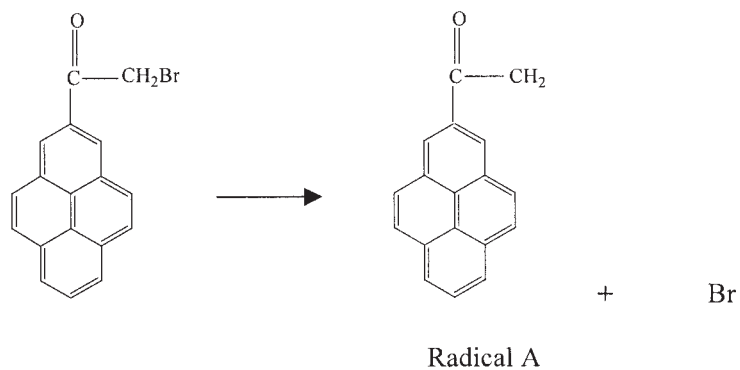
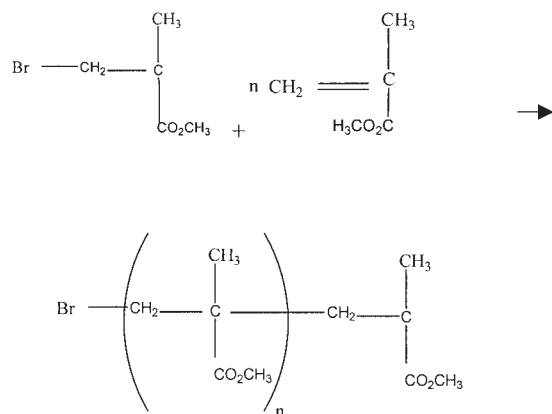
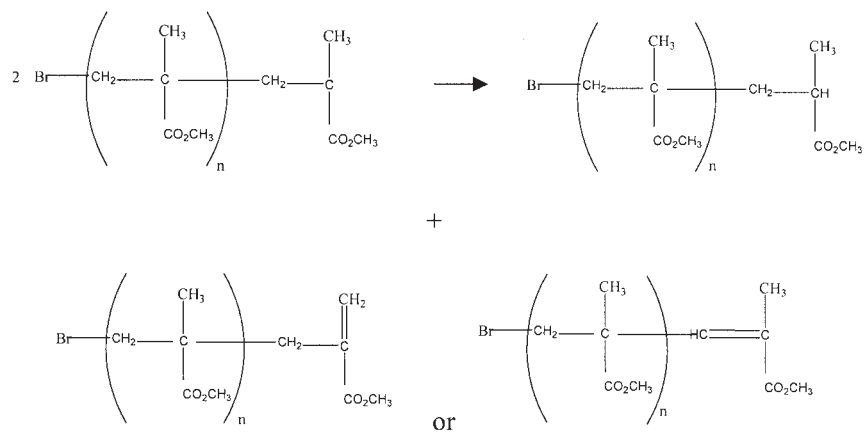
The inhibition of polymerization in the presence of a small quantity of hydroquinone and the kinetics suggest a radical mechanism. The possible radicals generated by the initiator BP are radical A and bromine. It was suggested that the reactive bromine radical would

propagate the chain reaction as radical A was supposed to be a stable species. A shorter induction period in BP-MMA system as compared with that in AP-MMA system suggests the faster generation of radicals for initiation in the former. The easier cleavage of $-\text{CH}_2-\text{Br}$ bond, as compared with that of $-\text{CH}_2-\text{CO}$ bond, was theoretically expected at lower energy levels because of the more polar nature of the former. A proposed mechanism is as given in Scheme I.

CONCLUSIONS

The photoinitiating efficiencies of pyrene, AP, and BP to polymerize MMA were compared. The introduction of $-\text{COCH}_3$ group in the ring at first step and then replacing $\alpha\text{-H}$ by $-\text{Br}$ in an aromatic hydrocarbon dye pyrene made it a much better photoinitiator. A detailed polymerization kinetics and mechanism with BP as initiator suggest a free radical approach for the synthesis of PMMA. The success of the present approach is the use of BP as a new and efficient photoinitiator, which decomposes to give two unsymmetrical free radicals with distinctly different reactivities toward a polymerizable monomer.

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Initiation**Propagation****Termination****Scheme 1**

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