1-(Bromoacetyl)pyrene and Its Arsonium Salt as Novel Photoinitiators for Styrene Polymerization

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ABSTRACT: The photopolymerization of styrene (Sty) in DMSO induced by pyrene (Py), 1-Acetylpyrene (AP), 1-(Bromoacetyl) pyrene (BP), and 1-Acetylpyrene triphenyl arsonium bromide (APAS) has been investigated. Under all conditions employed, Py was completely ineffective. Incorporation of a chromophoric (—$COCH_3$) moiety introduces photoinitiating activity into Py. It was observed that introduction of Br into AP markedly accelerated the rate of UV irradiation-induced polymerization. BP was further modified to its arsonium salt (APAS). The kinetics and mechanism of polymerization using BP and APAS as initiators have been investigated in detail. The polymerization with BP followed nonideal kinetics ($R_p \propto [BP]^{0.8} [Sty]^{1.1}$) with respect to initiator concentration whereas ideal kinetics ($R_p \propto [APAS]^{0.48} [Sty]^{1.1}$) was observed when APAS was used as initiator. Degradative transfer is thought to be mainly responsible for this unusual kinetic behavior for BP–Sty system. The kinetic data proved that BP was more effective and faster initiator than APAS. In both the cases, the mechanism of polymerization was free radical as evident by inhibiting the effect of hydroquinone and ESR studies. IR and NMR spectra showed the atactic nature of polystyrene. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 1793–1798, 2006

Key words: photopolymerization; 1-(bromoacetyl)pyrene; nonideal kinetics; ESR

INTRODUCTION

Photopolymerization is widely used in the areas of radiation curing and imaging technologies, e.g., photoresists, laser imaging, holography, and stereography.[1] A vast majority of photoinduced polymerization and crosslinking reactions involve a free radical mechanism.[2] A wide range of free radical photoinitiating systems, fulfilling requirements for industrial applications, e.g., wavelength selectivity, solubility, are now available and their chemistry is well established.[3] Photoinitiators for radical polymerization[3–7] generally function by intramolecular cleavage, notably of aryl alkyl ketones, or intermolecular H abstraction from a H donor, notably by diaryl ketones. The development of materials in the field of photopolymerization requires researchers to discover more efficient photoinitiator systems.

Colorants make up a large class of molecules extensively used to sensitize or start the polymerization of monomers.[8–14] Pyrene (Py), an aromatic hydrocarbon dye, has been reported as a photosensitizer/photoinitiator in a few communications.[15,16] Introduction of chromophoric groups in Py can enhance its photoefficiency. Moreover, heavy atoms like Br and Cl are also known to cause a significant rise in the photoinitiation ability of the dyes.[10] Present study was undertaken with a view to evaluate the photoinitiating ability of Py by introduction of —$COCH_3$ group into Py nucleus [1-Acetylpyrene (AP)] in the first step and then replacing α-H by —Br [1-(Bromoacetyl) pyrene (BP)]. In the third step, an onium salt [1-Acetylpyrene triphenyl arsonium bromide (APAS)] of BP was prepared by reacting it with triphenylarsine. The initiation time and the extent of percent conversion of styrene (Sty) by Py, AP, BP, and APAS have been reported. A detailed polymerization kinetics and mechanism with BP and APAS as initiators are discussed.

EXPERIMENTAL

Materials

Reagent grade Styrene (Merck-Schuchardt) and other solvents were purified by the usual methods[17,18] and distilled under vacuum before use. Py [M = 202.26 g/mol, m.p. = 149–151°C], AP [M = 244.3 g/mol, m.p = 86–89°C], and BP [M = 323.2 g/mol, m.p = 129–131°C] (Aldrich) were used as received. Hydroquinone was recrystallized twice from methanol. APAS was prepared according to the method given in literature.[19]

Polymerization procedure

Appropriate solutions of monomer in DMSO containing BP or APAS in quartz tube were degassed with nitrogen and then they were irradiated in a merry-go-round type photoreactor equipped with eight Philips tubes (8W each, path length = 10 cm) emitting light nominally at 253 nm at room temperature. The incident light intensity as measured by Lutron Lux Meter Model No. LX-101 was found to be 3.68×10^3 Lux. After a given time, the polymer was isolated with acidified methanol. The resulting polymer was then purified by reprecipitation and dried to constant weight under vacuum at 50°C. Conversions were determined gravimetrically and were independently confirmed using replicate runs. The rates of polymerization (R_p) were calculated by the following equation:[20]

$$R_p \text{ (mol l}^{-1}\text{ s}^{-1}) = \frac{1.451 \times C \times 10^{-3}}{t}$$

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

Characterization

UV spectrum was recorded on Perkin–Elmer Lambda 40 spectrophotometer. The Fourier transform infrared and NMR (^{1}H and ^{13}C) spectra were recorded on a Perkin–Elmer Model 599 B (KBr pellets) and Jeol JNM LA 400 Lambda spectrophotometer using $CDCl_3$ as a solvent and TMS as an internal reference, respectively. The ESR spectrum was recorded on an X-band Bruker EMX-EPR Spectrophotometer (Model 1444) at liquid N_2 temperature (Center Field: 3300 G, sweep width: 1000 G, Mod. Amplitude: 10G, sweep time: 167.77 s, Microwave power 0.201 mW). 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:[21]

$$\text{Log } \bar{P}_n = 3.248 + 1.4 \log [\eta]$$

RESULTS AND DISCUSSION

APAS showed m.p. = 102–104 °C and yield = 75%, and its NMR spectrum (Fig. 1) gave characteristic peaks at 7.2–8.6 δ because of aromatic H and at 2.8 δ because of acetyl H. UV spectra of BP and APAS (Fig. 2) shows λ_{max} = 288 nm, 366 nm, and λ_{max} = 278 nm, 348 nm, respectively

Polymerization kinetics

In Py–Sty system, no polymer formation was observed within 15 h whereas in AP–Sty system, a very low %
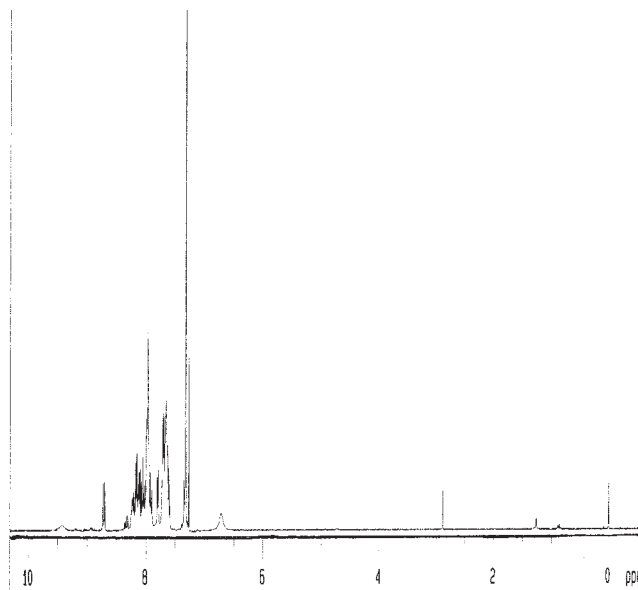

Figure 1   NMR spectrum of APAS.

conversion was observed after 15 h. However, the introduction of bromine in the acetyl moiety (BP–Sty system) significantly reduced the induction period, enhanced the percent conversion, and consequently the polymerization rate. In case of APAS–Sty system, the percent conversion was 3.27% at 0.39×10^{-4} mol l^{-1} in 6 h while BP–Sty system under similar conditions gave 6.4% conversion. Table I shows the data obtained for all the polymerization systems studied. The polymerization time, chosen for BP–Sty system, is 4 h to limit conversions to low percentage to study kinetics.

The results obtained for BP–Sty and APAS–Sty systems proved that BP and APAS were efficient photoinitiators, although APAS was found to be less effective than BP. AP did not seem to be a good initiator while Py–Sty system was not workable.

The results of kinetic investigations of the photopolymerization of Sty at 30°C using varying initiator concentrations at fixed intensity of light source are presented in Table I. The data in Table I present % conversion after having deducted the yield for blank experiments since Sty is polymerized to 0.2–0.4% conversion even in absence of initiator. The initiator exponent values calculated from the slopes of the plots of log Rp vs. log [BP] and log Rp vs. log [APAS] (Fig. 3) were 0.8 and 0.48, respectively. The plot of reciprocal average degree of polymerization ($\bar{P}_n$) against the square root of the initiator concentration [Fig. 4(a)] gave a straight line passing through the origin in case of APAS–Sty system, suggesting ideal radical polymerization with bimolecular termination. The value of k_p^2/kt obtained from the plot of $1/\bar{P}_n$ vs. $R_p/[\text{Sty}]^2$ [Fig. 4(b)] was found to be 0.24×10^{-2} L mol^{-1} s^{-1}. The deviation in the exponent value of BP [Fig. 3(a)]
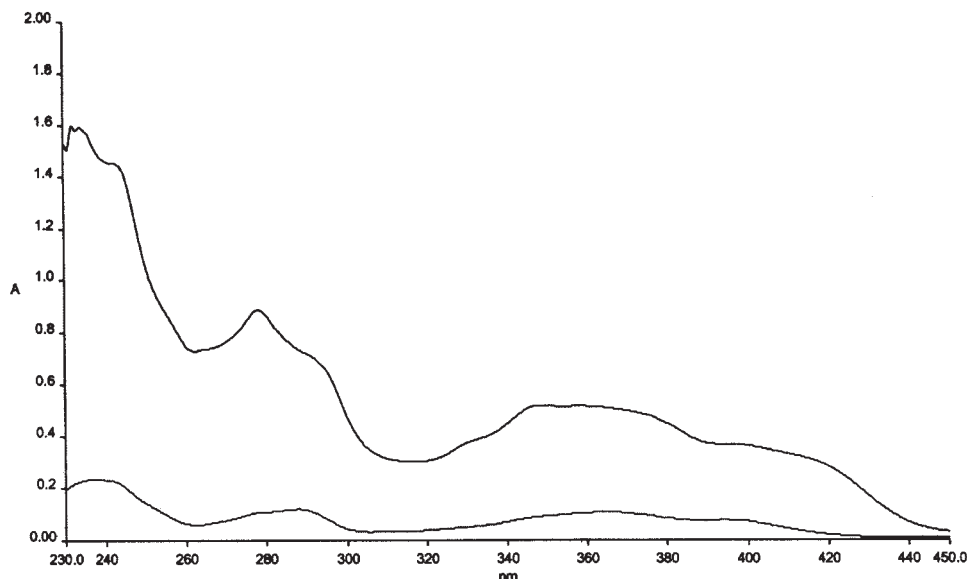
Figure 2 UV spectra of APAS and BP in DCM (3×10^{-5} mol/L).

and an intercept in the plot of $1/\bar{P}_n$ vs. $R_p/[\text{Sty}]^2$ [Fig. 5(a)] suggested that BP–Sty system followed nonideal kinetics. To explain this unusual behavior and to ascertain the nature of the transfer reactions involved, plots of $R_p^2/([\text{BP}][\text{Sty}]^2)$ vs. $R_p/[\text{Sty}]^2$ [Fig. 5(b)] following the equation of Deb[22] were plotted. The positive slope obtained suggested that degradative solvent transfer is mostly operative in the main termination process instead of degradative initiator transfer or primary radical termination.[23]

The data obtained to see the effect of monomer concentration on R_p are shown in Table II. The monomer exponent value, calculated from the slope of the linear plot of log R_p vs. log [Sty], was 1.1 for both

BP–Sty and APAS–Sty system (Fig. 6), suggesting that the systems followed ideal kinetics with respect to monomer concentration.

TABLE I
Effect of Initiator on Rp

S. No.	Initiator (I)	$[\text{I}] \times 10^4$ (mol/L)	% conversion	$Rp \times 10^5$ (mol/L/s)
1.	APAS	0.397	3.27	1.321
2.		0.794	4.52	1.823
3.		1.190	5.54	2.233
4.		1.580	6.31	2.546
5.		1.980	7.08	2.857
6.	BP	0.386	0.92	0.557
7.		0.773	1.73	1.049
8.		1.547	2.95	1.782
9.		2.320	3.84	2.322
10.		3.094	4.80	2.904
11.		3.860	6.29	3.802
12.	Py	5.00	–	–
13.	AP	1.800	–	–
14.		3.500	0.88	0.141

Styrene = 2.18 mol/L; polymerization temperature = 30 $\pm$ 0.2°C; polymerization time = 4 h (for BP); 6 h (for APAS); 15 h (for Py and AP).

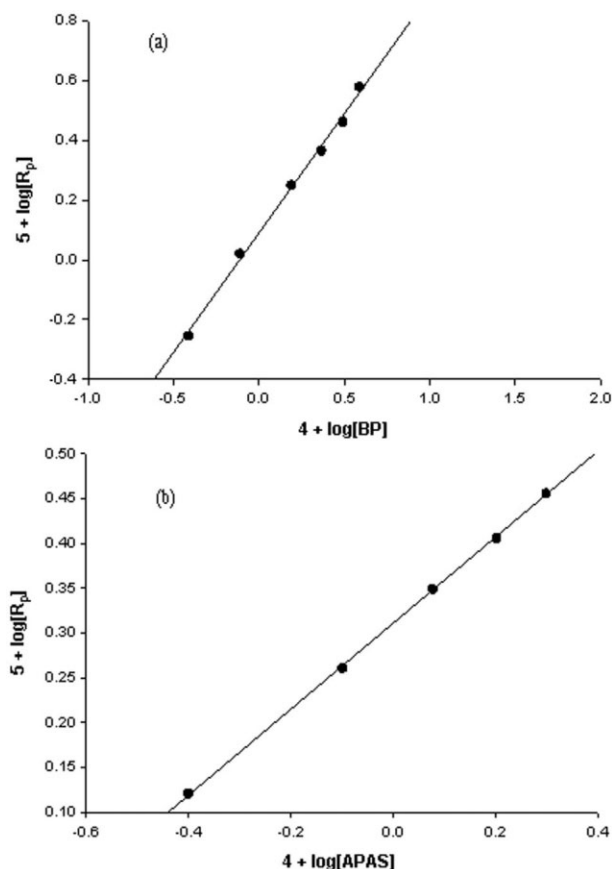**Figure 3** (a) Plot of log [BP] versus log Rp. t = 4 h; (b) Plot of log [APAS] versus log Rp. t = 6 h. [Sty]= 2.18 mol/L; polymerization temperature = 30 $\pm$ 0.2°C.
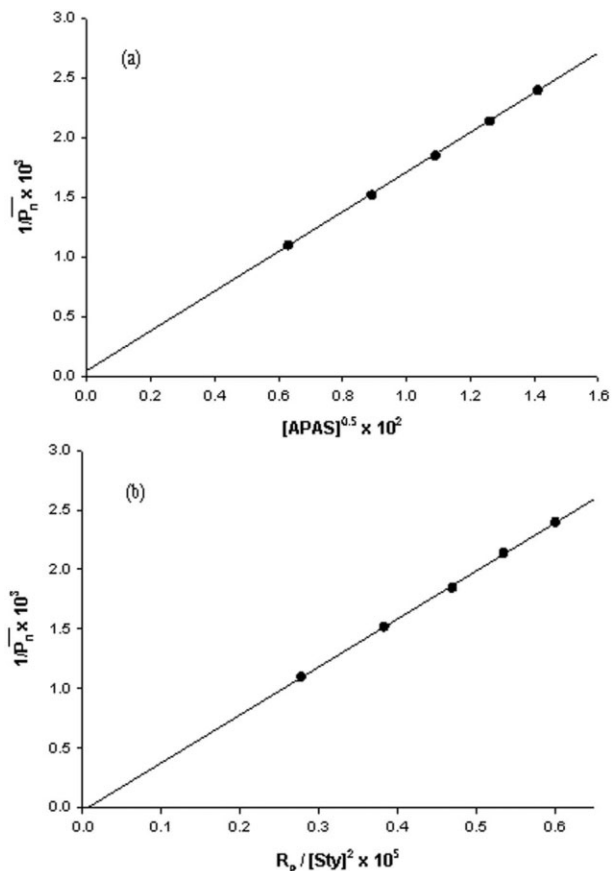
Figure 4 (a) Plot of $1/\bar{P}n$ versus $[\text{APAS}]^{0.5}$; (b) Plot of $1/\bar{P}n$ versus $Rp/[\text{Sty}]^2$ and $1/\bar{P}n$ versus Rp. $[\text{Sty}] = 2.18$ mol/L; $t = 6$ h; polymerization temperature $= 30 \pm 0.2°C$.
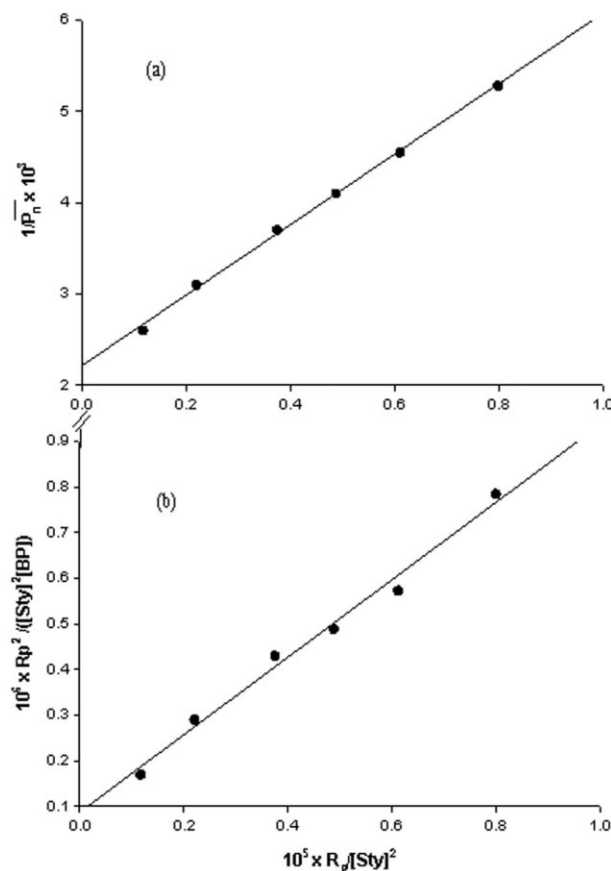

Figure 5 (a) Plot of $1/\bar{P}n$ versus $[\text{BP}]^{0.5}$; (b) Plot of $Rp^2/[\text{Sty}]^2[\text{BP}]$ versus $Rp/[\text{Sty}]^2$. $[\text{Sty}] = 2.18$ mol/L; $t = 4$ h; polymerization temperature $= 30 \pm 0.2°C$.

Characterization of polymer

FTIR spectroscopy and and ^{1}H-NMR spectroscopy

In the ^{1}H-NMR spectrum (Fig. 7), the peaks due to the phenyl protons appear between 6.5 and 7.1 δ. Both, the methylene and methine protons, appear as broad peak at 1.43 δ and 1.83 δ, respectively, indicating atactic nature of the polymer. The atactic polymer exhibits seemingly poorly resolved multiplets but have a syndiotactic preference, supporting free radical mechanism of polymerization.[24]

^{13}C-NMR spectroscopy

The spectrum (Fig. 8) shows a series of peak between 125 and 127 ppm owing to the unsaturated carbons of phenyl rings.[25] The methylene and methine carbons resonate at 30 and 40 ppm, respectively. A band of resonances between 145 and 146 ppm is strong evidence in support of the atacticity of the polymer.[24] These bands of resonances are consistent with a syndiotactic bias in free radical propagations. The syndiotactic bias characterizes the free radical polymerization of all vinyl monomers.

E.S.R. spectroscopy

The spectrum (Fig. 9) shows characterstic free radical absorption at 3370 G for both BP–Sty and APAS–Sty systems. A sharp peak with a "g" value 2.00, which may be conveniently assigned to the Py—CO—CH$_2$· (I) radical formed by the homolytic cleavage of BP, is

TABLE II
Effect of styrene on Rp

S. No.	Styrene (mol/L)	Initiator	% conversion	$Rp \times 10^5$ (mol/L/s)
1.	2.18	APAS	3.27	1.321
2.		BP	1.73	1.049
3.	2.91	APAS	4.53	1.828
4.		BP	2.39	1.445
5.	3.49	APAS	5.60	2.259
6.		BP	2.93	1.770
7.	3.97	APAS	9.83	3.962
8.		BP	3.38	2.041
9.	4.37	APAS	10.83	4.365
10.		BP	3.74	2.264

BP $= 7.735 \times 10^{-5}$ mol/L; $t = 4$ h; APAS $= 3.97 \times 10^{-5}$ mol/L; $t = 6$ h; polymerization temperature $= 30 \pm 0.2°C$.
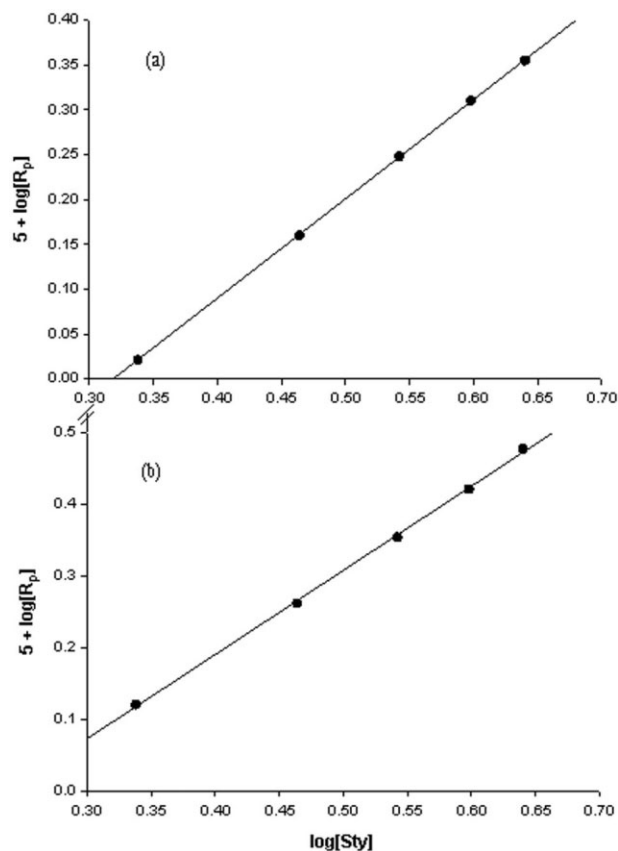
Figure 6 (a) Plot of log [Sty] versus log Rp. [BP] = 7.735 × 10^{-5} mol/L; t = 4 h; (b) Plot of log [Sty] versus log Rp. [APAS] = 3.97 × 10^{-5} mol/L; t = 6 h. Polymerization temperature = 30 ± 0.2°C.

prominent in Figure 9(a). Remaining peaks may be assigned to the Br˙ radical formed simultaneously. A few peaks owing to Br radical seem to have been overlapped by the peak at "g" value 2.00. Figure 9(b) shows a number of peaks in addition to a sharp peak
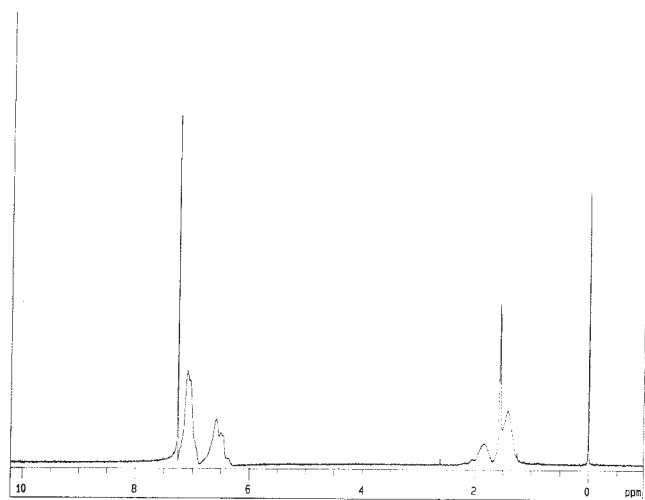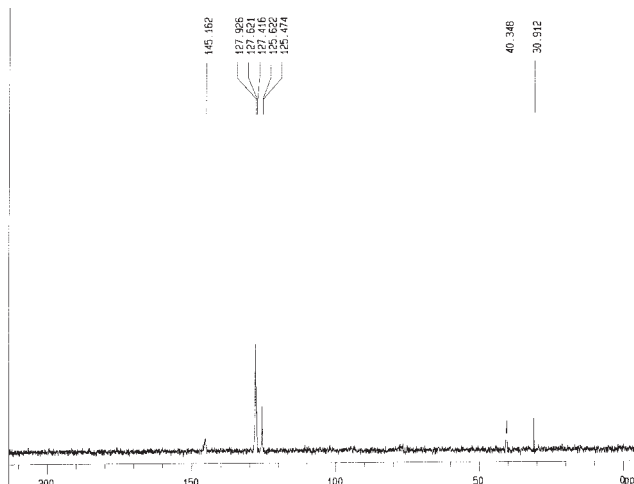

Figure 7 ^{1}H-NMR Spectrum.

Figure 8 ^{13}C-NMR Spectrum.

again at 2.00 "g," which may quite probably be due to triphenyl arsonium cation radical. Hence, ESR studies further confirm free radical initiation by both the photoinitaitors.

Mechanism

The inhibition to polymerization in the presence of a small quantity of hydroquinone, ESR studies, and the
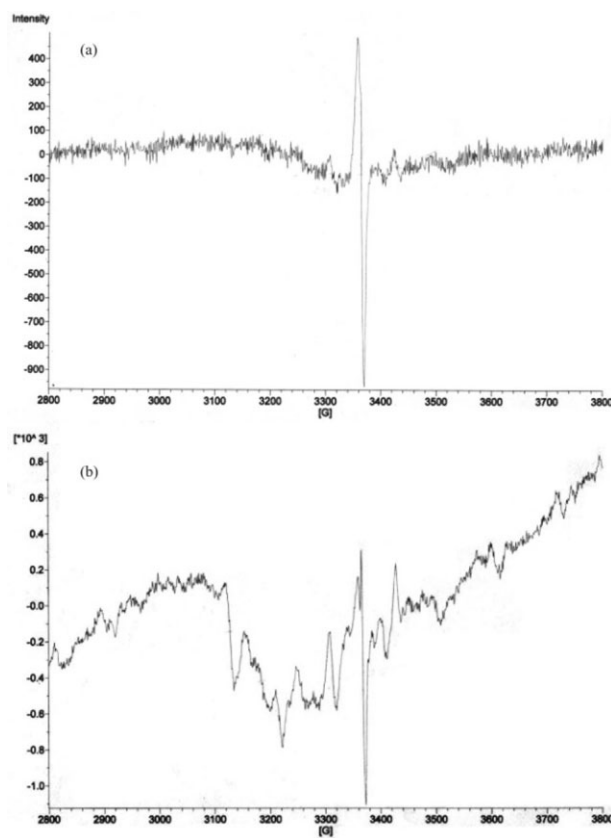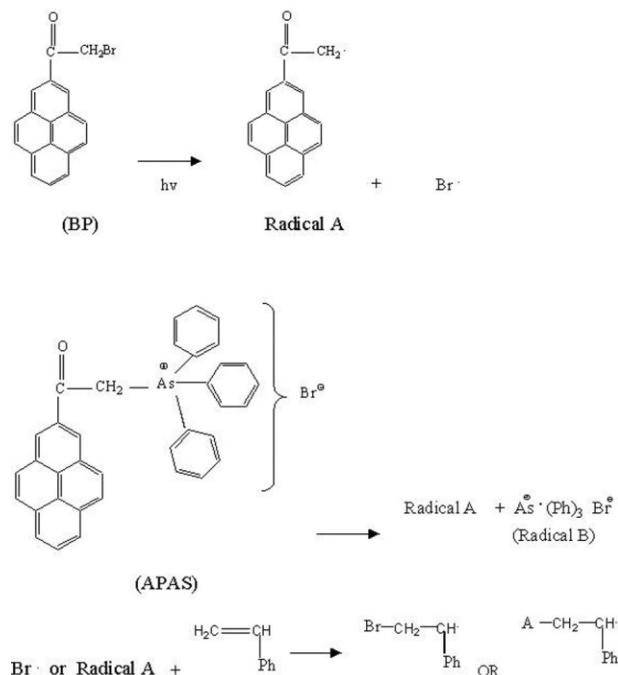

Figure 9 ESR Spectra (a) BP, (b) APAS.

Initiation

Scheme 1

kinetics suggest a radical mechanism for both BP–Sty and APAS–Sty systems. The possible radicals generated by the initiator, BP, are radical A and bromine and from APAS are radical A and triphenylarsonium cation radical (B) as evident by ESR studies. Recent studies on flash photolysis of dialkylphenacyl sulfonium salts[26] report the formation of phenacyl radicals formed as a result of cleavage of C—S bond. On the basis of structural similarity of these salts with APAS and ESR studies, arsonium salt (APAS) may be satisfactorily cleaved homolytically into the above-mentioned radicals.

The greater polymerization efficiency of BP than that of APAS, suggested from kinetics, could also be explained by the propagation of Sty by both bromine and radical A formed from BP. In case of APAS as initiator, the cation radical (B) formed is probably too reactive to participate in polymerization. Hence, only radical A might be involved in polymerization for the APAS–Sty system. A proposed mechanism is as given in Scheme 1.

CONCLUSIONS

A comparative study on photopolymerization of Sty in DMSO induced by Py, AP, BP, and APAS proved

that incorporation of a chromophoric (—COCH$_3$) moiety introduces photoinitiating activity into Py and Br markedly accelerated the rate of polymerization. The kinetic data suggested that BP was more effective and faster initiator than APAS. The polymerization with BP followed nonideal kinetics with respect to initiator concentration because of degradative chain transfer whereas ideal kinetics was observed when APAS was used as initiator. Free radical mechanism was confirmed by ESR spectra.

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