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Anuradha Mishra^a; Swati Daswal^a

^a Department of Chemistry, University Institute of Engineering and Technology, CSJM University, Kanpur, India

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Polymerization of n-Butyl Acrylate Photoinitiated by 1-(Bromoacetyl)pyrene and its Arsonium Salt

ANURADHA MISHRA AND SWATI DASWAL

Department of Chemistry, University Institute of Engineering and Technology, CSJM University, Kanpur, India

A comparative study on the photoinitiating efficiency of pyrene (Py), 1-Acetylpyrene (AP), 1-(Bromoacetyl)pyrene (BP) and 1-Acetylpyrene triphenyl arsonium bromide (APAS) for polymerization of n-butylacrylate (BA) was done. An experimental investigation of the kinetics of free radical solution polymerization at $25 \pm 0.2^\circ\text{C}$ using all four photoinitiators showed that pyrene was completely ineffective in initiating the polymerization of BA under all conditions employed, whereas AP was able to initiate polymerization. Incorporation of bromo group into AP markedly accelerated the rate of UV induced polymerization. Further modification of bromo derivative (BP) to its arsonium salt (APAS) produced a less effective initiator. The kinetics and mechanism of polymerization using BP and APAS as initiators have been investigated in detail. The polymerization with BP followed non-ideal kinetics ($R_p \propto [\text{BP}]^{0.8} [\text{BA}]^{0.98}$) with respect to initiator concentration, whereas ideal kinetics ($R_p \propto [\text{APAS}]^{0.49} [\text{BA}]^{1.07}$) was observed when APAS was used as an initiator. This unusual kinetic behavior for the BP-BA system can be interpreted in light of degradative transfer and the emergence of occlusion. The kinetic data proved that BP was a more effective and faster initiator than APAS.

Keywords photopolymerization, 1-(bromoacetyl)pyrene, non-ideal kinetics, ESR

Introduction

During the last two decades, photoinitiated polymerization has received considerable attention and has been practically applied in a variety of areas, including printing inks, adhesives, surface coatings, microelectronics, and printing plates (1–3). A large proportion of today's relevant research on photoinitiators includes the introduction of new initiators with improved solubility, particularly in commercially important monomers, or modifying the spectral sensitivity of existing ones (4–6). Photoinitiators for radical polymerization (7–10) generally function by intramolecular cleavage, notably α -cleavage of an aromatic ketone group in the photoinitiator, or intermolecular H abstraction from a donor by the photoinitiator.

Dyes make up a large class of molecules used extensively to sensitize or initiate the polymerization of monomers (11–17). Pyrene, an aromatic hydrocarbon dye, has been

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Address correspondence to Anuradha Mishra, Department of Chemistry, University Institute of Engineering and Technology, CSJM University, Kanpur 208 024, India. E-mail: anuradha_mishra@rediffmail.com

reported as a photosensitizer/photoinitiator in several communications (18–20). Introduction of a chromophoric group ($-\text{COCH}_3$) in pyrene is expected to enhance its efficiency. Moreover, heavy atoms such as Br and Cl are also known to cause a significant rise in the photoinitiation ability of the dyes (13). The kinetics of homopolymerization of BA initiated with various types of initiators has been studied and reported by several researchers (21, 22). However, to the best of our knowledge, there has been no report on the use of BP or APAS as sole photoinitiator for polymerization of BA.

Present study was undertaken with a view to evaluate the photoinitiating ability of pyrene and its various derivatives like AP, BP and APAS for polymerization of BA. The initiation time and the extent of percent conversion of BA with each initiator have been reported. The polymerization starts in a homogeneous system but proceeds heterogeneously because of the insolubility of the polymer products in the solvent. A detailed polymerization kinetics and mechanism with BP and APAS as initiators for polymerization of BA are discussed.

Experimental

Materials

Reagent grade n-butylacrylate (Merck-Schuchardt) and other solvents (SD Fine) were purified by the usual methods (22, 23) and distilled under vacuum before use. Pyrene [$M = 202.26 \text{ g/mol}$, m.p. = $149\text{--}151^\circ\text{C}$], 1-Acetylpyrene [$M = 244.3 \text{ g/mol}$, m.p. = $86\text{--}89^\circ\text{C}$] and 1-(bromoacetyl) pyrene [$M = 323.2 \text{ g/mol}$, m.p. = $129\text{--}131^\circ\text{C}$] (Aldrich) were used as received. Hydroquinone was recrystallized twice from methanol. 1-Acetylpyrene triphenyl arsonium bromide was prepared according to the method given in literature (24).

Polymerization procedure

Appropriate solutions of monomer in dimethyl sulphoxide (DMSO) containing BP or APAS (Table 1) in quartz tube were degassed with nitrogen and the tubes were sealed before irradiation. At the end of irradiation in a merry-go-round type photoreactor equipped with eight Philips tubes (8W each, path length = 10cm, 253nm interference filter) and emitting light nominally at 253nm at room temperature, the solutions were poured into methanol. After two reprecipitations from methanol, the polymers were dried in vacuum oven at 50°C for 24h. The incident light intensity as measured by Lutron Lux Meter Model No. LX-101

Experimental

The present study was undertaken with a view to evaluate the photoinitiating ability of pyrene and its various derivatives like AP, BP and APAS for polymerization of BA. The Meter Model No. LX-101 was found to be $3.68 \times 10^3 \text{ Lux}$. Conversions were determined gravimetrically and were independently confirmed using replicate runs. The rates of polymerization (R_p) were calculated by the following equation:

$$R_p \text{ (mol l}^{-1} \text{ s}^{-1}\text{)} = \frac{1.1625 \times C \times 10^{-3}}{t}$$

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

Table 1
Effect of [BP] and [BA] on R_p , polymerization temp. = $25 \pm 0.2^\circ\text{C}$; $t = 3 \text{ h}$

S. no.	[BP] $\times 10^4$ (mol/l)	[BA] (mol/l)	% Conversion	$R_p \times 10^5$ (mol/l/s)	M_v
1	0.38	1.74	5.27	3.404	87,321
2	0.77	1.74	9.11	5.875	69,798
3	1.16	1.74	12.89	8.317	50,504
4	1.54	1.74	9.78	6.309	39,195
5	2.32	1.74	6.92	4.466	30,389
6	0.38	2.32	6.95	4.487	—
7	0.38	2.79	8.34	5.382	—
8	0.38	3.17	9.51	6.137	—
9	0.38	3.48	10.36	6.683	—

Characterization

UV spectra were recorded on a Perkin-Elmer Lambda 40 spectrophotometer. The FTIR and NMR (^1H 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: 10 G, sweep time: 167.77 s, Microwave power 0.201 mW). The intrinsic viscosity $[\eta]$ of the polymers was determined in acetone at 25°C using an Ubbelohde viscometer. The viscosity average molecular weight (M_v) was calculated using the Mark-Houwink-Sakaruda equation:

$$\eta = kM_v^a$$

where 'k' and 'a' are constants with values $6.85 \times 10^{-5} \text{ dl g}^{-1}$ and 0.7, respectively (25). The software Sigma Plot 5.0 has been used to perform statistical analysis of the kinetic data obtained by applying linear regression/curve fitting method.

Results and Discussion

1-Acetylpyrene triphenyl arsonium bromide showed m.p. = $102\text{--}104^\circ\text{C}$, yield = 75% and its NMR spectrum (Figure 1) gave characteristic peaks at $7.2\text{--}8.6 \delta$ due to aromatic H and at 2.8δ due to acetyl H. UV spectra of BP and APAS in dichloromethane (DCM) (Figure 2) shows $\lambda_{\text{max}} = 288 \text{ nm}$, 366 nm and $\lambda_{\text{max}} = 278 \text{ nm}$, 348 nm , respectively.

Polymerization Kinetics

The concentration of Py was varied from 5 to $50 \times 10^{-4} \text{ mol/l}$ but no polymer formation was observed up to 15 h, whereas in the AP-BA system ($[\text{AP}] = 5 \times 10^{-4} \text{ mol/l}$), less than 1% conversion was achieved after 15 h. However, the introduction of bromine in the acetyl moiety (BP-BA system) enhanced the percent conversion to 13% in 3 h. No polymerization was observed for the APAS-BA system when the concentration of

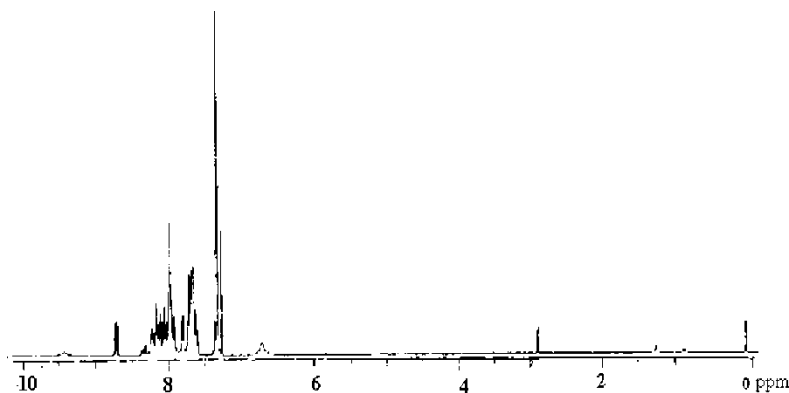


Figure 1. NMR spectrum of APAS.

APAS was $< 1.19 \times 10^{-4}$ mol/l and the time period was < 5 h. The kinetic data proved it to be a less efficient photoinitiator than BP. The results obtained for BP-BA and APAS-BA systems proved that BP and APAS were efficient photoinitiators, whereas AP did not seem to be a good initiator and the Py-BA system was not workable.

The results of kinetic investigations of the photopolymerization of BA at 25°C using varying concentrations of BA and BP at fixed intensity of light source are presented in Table 1. No polymerization was observed in the absence of an initiator. The effect of monomer concentration on R_p is studied by varying [BA] from 1.74 mol/l to 3.48 mol/l, keeping [BP] constant at 3.86×10^{-5} mol/l. The monomer exponent value, calculated from the slope of the linear plot of $\log R_p$ vs. $\log [\text{BA}]$ is 0.98 (Figure 3(a)). Dependence of R_p on [BP] displayed a maximum at [BP] = 1.16×10^{-4} mol/l (Table 1). A further increase in the concentration of BP leads to a

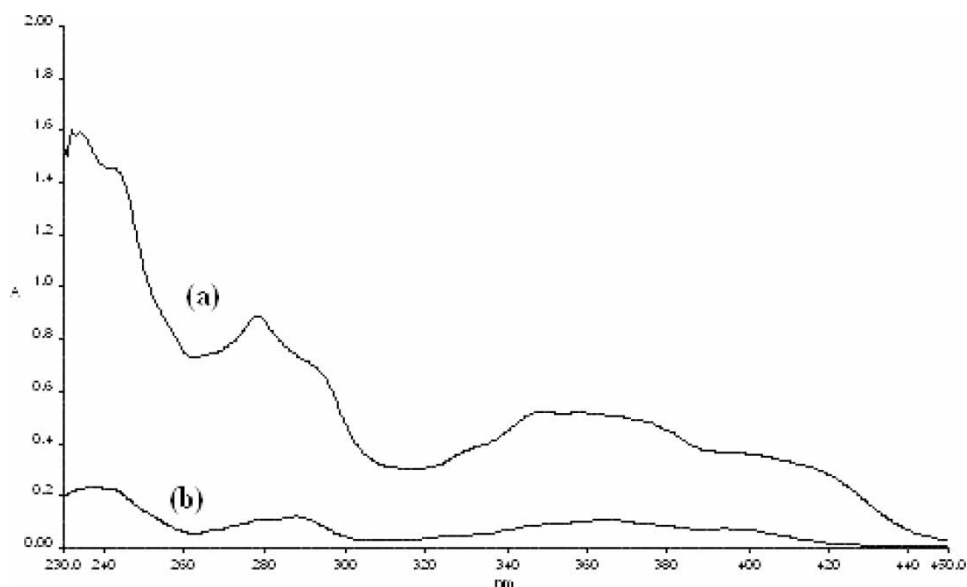


Figure 2. UV spectra, a) APAS and b) BP in dichloromethane (3×10^{-5} mol/l).

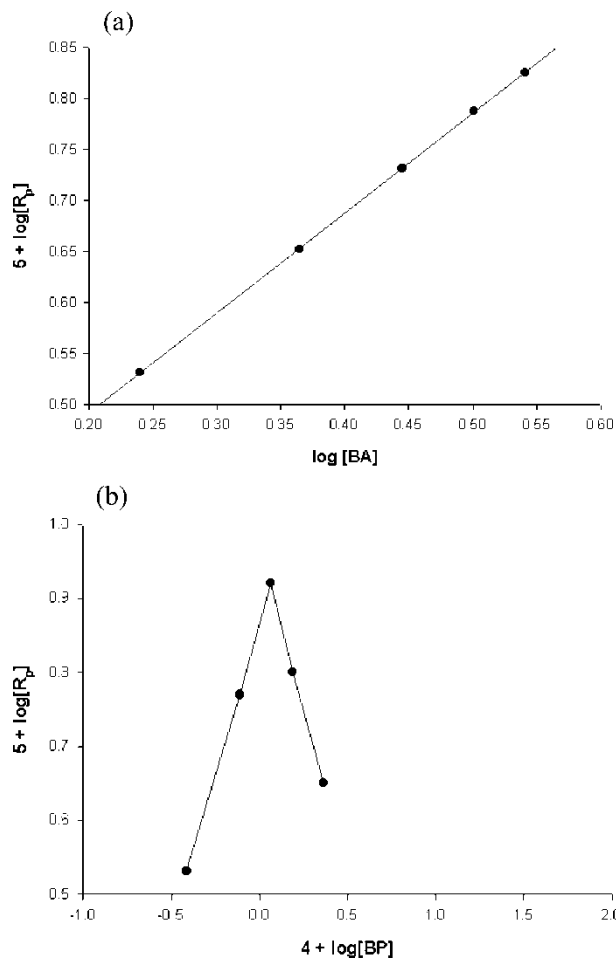


Figure 3. (a) Plot of $\log [BA]$ vs. $\log R_p$, $[BP] = 3.86 \times 10^{-5}$ mol/l; (b) Plot of $\log [BP]$ vs. $\log R_p$, $[BA] = 1.74$ mol/l, polymerization temp. = $25 \pm 0.2^\circ\text{C}$; $t = 3$ h.

decrease in R_p , which can be ascribed to the consumption of $[BP]$ in a fast chain transfer reaction leading to an extremely higher termination rate. The initiator exponent value calculated from the positive slope of the linear plot of $\log R_p$ vs. $\log [BP]$ (Figure 3(b)) is 0.8. The deviation in the exponent value suggests that the system follows non-ideal kinetics. An initiator exponent in a range of 0.5-1 would be the consequence of the co-occurrence of normal bimolecular termination due to propagating radical occlusion. The occlusion theory was first developed by Bamford and Jenkins (26) according to which the growing radical precipitates from the liquid phase before termination occurs and becomes tightly coiled. Although this termination is first order because the radical becomes trapped and inaccessible to the monomer, there seems to be no direct correlation between the extent of occlusion and the initiator exponent (27). Degradative solvent transfer also seems to be a probable cause for the kinetic non-ideality. In order to ascertain the nature of the transfer reactions involved, plots of $R_p^2/([BP][BA]^2)$ vs. $R_p/[BA]^2$ (Figure 4), following the equation of Deb (28) were plotted. The positive slope obtained suggested that degradative solvent transfer was mostly operative in the

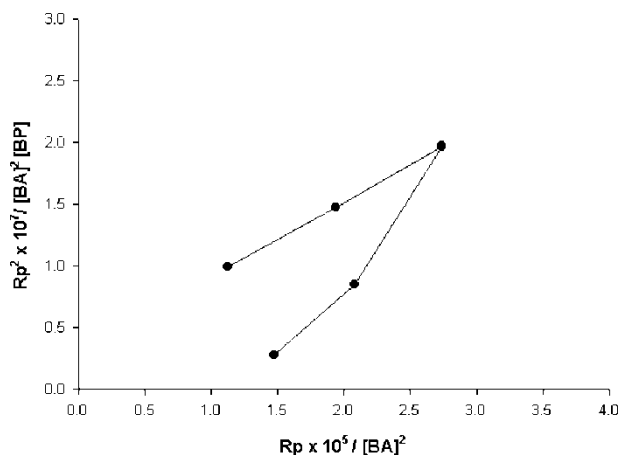


Figure 4. Plot of $R_p^2/[BA]^2 \cdot [BP]$ vs. $R_p/[BA]^2 \cdot [BA] = 1.74 \text{ mol/l}$; $t = 3 \text{ h}$; polymerization temp. = $25 \pm 0.2^\circ\text{C}$.

main termination process instead of degradative initiator transfer or primary radical termination (29).

The viscosity average molecular weight for poly n-butylacrylate obtained by varying [BP] are reported in Table 1. No polymerization was observed in the absence of DMSO. As is evident, M_v decreased more rapidly with an increase in [BP] than expected for an ideal free-radical polymerization. Moreover, the exponent value of 0.8 and the positive slope of Figure 4 ruled out the possibility of chain transfer to initiator (29). Hence, BP would go into a fast transfer reaction with the solvent resulting into a decrease in M_v . Therefore, the unusual kinetic behavior for the BP-BA system can be interpreted in light of degradative transfer and the emergence of occlusion.

The data obtained to see the effect of monomer and initiator concentration on R_p for the APAS-BA system are shown in Table 2. The monomer exponent value, calculated from the slope of the linear plot of $\log R_p$ vs. $\log [BA]$ is 1.07 (Figure 5(a)) while the initiator exponent value, calculated from the slope of the linear plot of $\log R_p$ versus

Table 2
Effect of [APAS] and [BA] on R_p , polymerization
temp. = $25 \pm 0.2^\circ\text{C}$; $t = 6 \text{ h}$

S. no.	[APAS] $\times 10^4$ (mol/l)	[BA] (mol/l)	% Conversion	$R_p \times 10^5$ (mol/l/s)
1	1.19	1.74	4.29	1.388
2	1.58	1.74	4.96	1.603
3	1.98	1.74	5.51	1.778
4	2.38	1.74	6.05	1.954
5	1.19	2.32	5.83	1.883
6	1.19	2.79	7.09	2.291
7	1.19	3.17	8.18	2.642
8	1.19	3.48	9.03	2.917

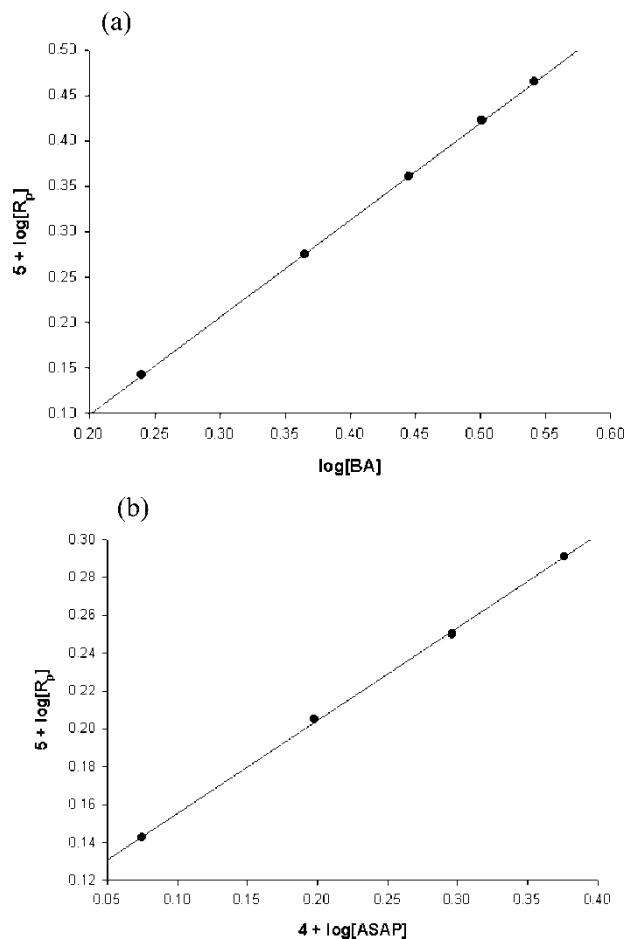


Figure 5. (a) Plot of $\log [BA]$ vs. $\log R_p$, $[APAS] = 1.19 \times 10^{-4}$ mol/l; (b) Plot of $\log [APAS]$ vs. $\log R_p$, $[BA] = 1.74$ mol/l, polymerization temp. = $25 \pm 0.2^\circ\text{C}$; $t = 3$ h.

$\log [APAS]$ is 0.49 (Figure 5(b)) suggesting that the system follows ideal kinetics with respect to both monomer and initiator concentration.

Statistical Analysis

The exponent values reported for initiators and monomer has been obtained by linear regression/curve fittings on the data points using Sigma Plot. All the exponent values reported are well within the 95% confidence limits (30).

Characterization of Polymer

FTIR Spectroscopy. The FTIR spectrum (Figure 6) of polymer consists of the following group of bands—C–H str vibrations of methyl and methylene groups in the region $2980\text{--}2910\text{ cm}^{-1}$; $>\text{C}=\text{O}$ str vibrations of ester carbonyl at 1735 cm^{-1} ; C–O str bands in the region of $1180\text{--}1260\text{ cm}^{-1}$.

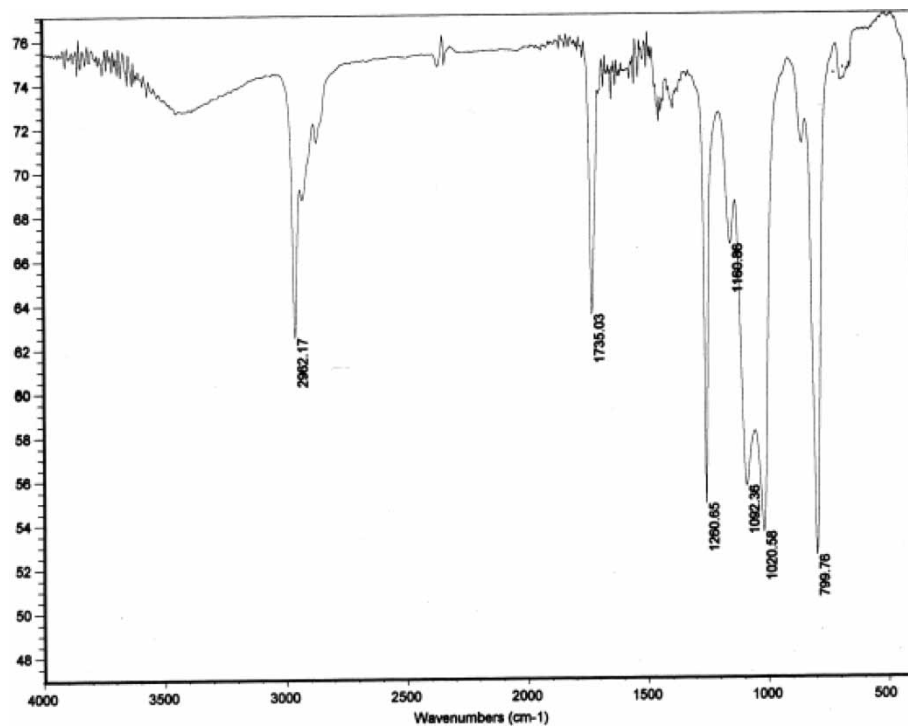


Figure 6. IR spectrum of polymer.

¹H-NMR Spectroscopy. In the ¹H-NMR spectrum (Figure 7), a singlet due to -OCH₂ protons, appears at 3.96 δ. Methyl protons appear at 0.9, methylene protons between 1.18–1.33 and methine protons at 2.2 δ. Peak positions were almost the same for poly(n-butylacrylate) formed by both initiators.

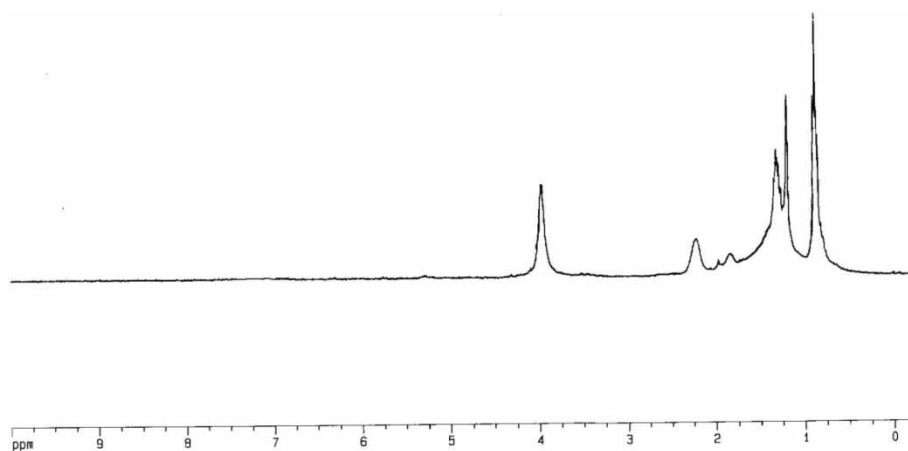


Figure 7. ¹H-NMR Spectrum of Polymer.

E.S.R. Spectroscopy

The spectrum (Figure 8) shows characteristic free radical absorption at 3370 G for both BP-Sty and APAS-Sty systems. Figure 8(a) shows a sharp peak with a 'g' value 2.00 which may be conveniently assigned to the $\text{Py-CO-CH}_2(\text{I})$ radical formed by the homolytic cleavage of BP. The remaining peaks may be assigned to the Br radical formed at the same time. Figure 8(b) shows a number of peaks in addition to a sharp peak again at 2.00 'g', which may quite probably be due to triphenyl arsonium cation radical. Hence, it is concluded that both the photoinitiators serve free-radically.

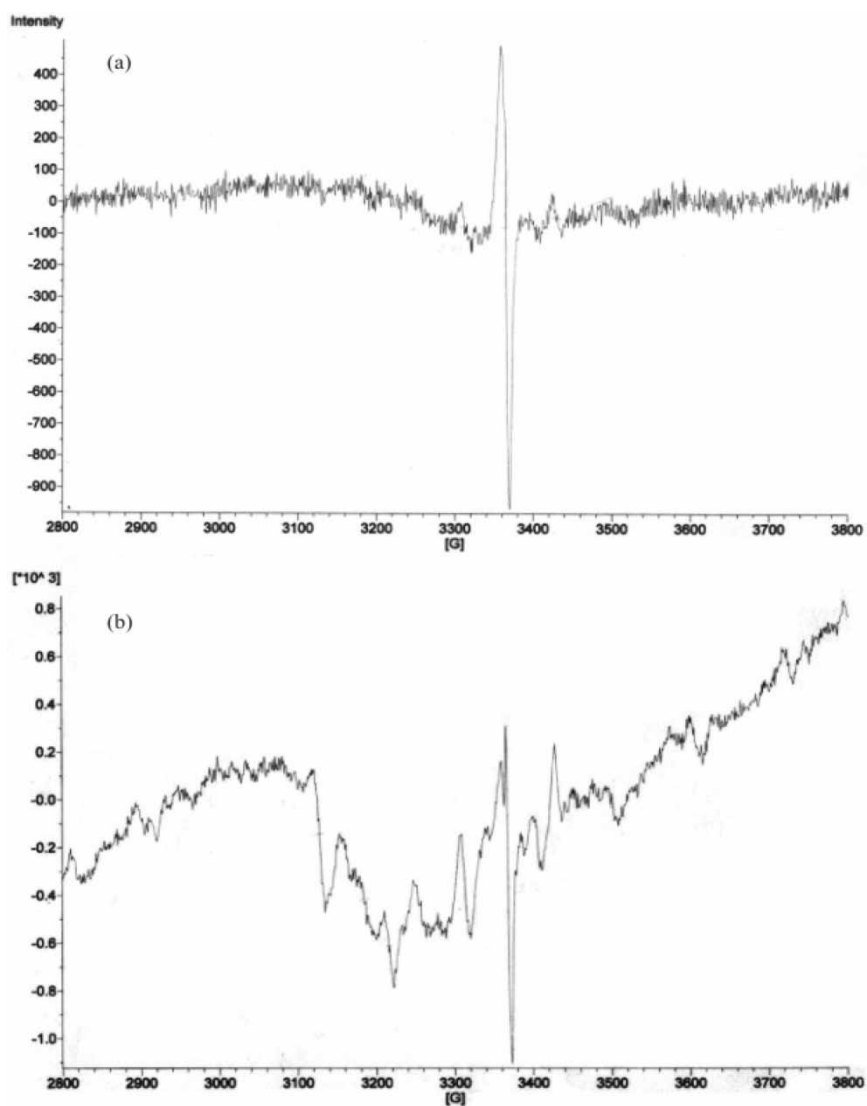
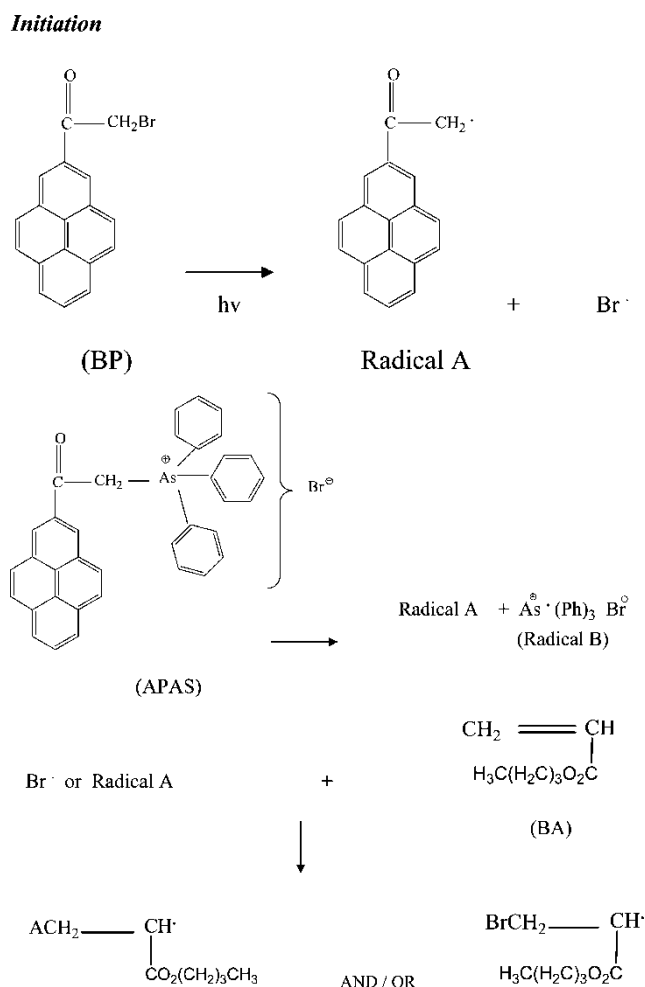


Figure 8. ESR spectra, a) BP: b) APAS.

Mechanism

Inhibition to polymerization in the presence of a small quantity of hydroquinone, ESR studies and the kinetics suggest a radical mechanism for both BP-BA and APAS-BA systems. The possible radicals generated by the initiator, BP, are radical A and bromine and from APAS are radical A and B (Scheme 1) as is evident by the ESR studies. This is also supported by recent studies on flash photolysis of dialkylphenacyl sulphonium salts (31), wherein the authors report the formation of phenacyl radicals formed as a result of cleavage of C–S bond. Based on the structural similarity of these salts with APAS and ESR studies, arsonium salt (APAS) may be satisfactorily cleaved into the above-mentioned radicals.

The greater polymerization efficiency of BP than that of APAS, as suggested from the kinetic data may now be explained by the propagation of BA by both bromine and radical A formed from BP. In addition, cation radical (B) formed in APAS is too reactive to participate in polymerization. Hence, it was concluded that only radical A



Scheme 1.

must be involved in polymerization for the APAS-Sty system. A proposed mechanism is as given in Scheme 1.

Conclusions

Modification of pyrene by introducing chromophoric group such as $-\text{COCH}_3$ and heavy atom such as bromine to make it more efficient photoinitiator for polymerization of butyl acrylate has been successfully done. The bromoacetyl derivative, 1-(Bromoacetyl)pyrene (BP) and its arsonium salt, 1-Acetylpyrene triphenyl arsonium bromide (APAS) proved to be effective photoinitiators. The APAS-BA system followed ideal kinetics whereas the BP-BA system followed non-ideal kinetics. A plausible mechanism for free radical polymerization was suggested on the basis of the data obtained by kinetic investigation and ESR studies.

Acknowledgements

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