Copolymerization of *n*-Butylacrylate with Styrene by a Novel Photoinitiator, 1-(Bromoacetyl)pyrene

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ABSTRACT: A comparative study on photoinitiated solution copolymerization of *n*-butylacrylate (BA) with styrene (Sty) using pyrene (Py), 1-acetylpyrene (AP), and 1-(bromoacetyl)pyrene (BP) as initiators showed that the introduction of a chromophoric moiety, bromoacetyl ($-COCH_2Br$), significantly increased the photoinitiating ability of pyrene. The kinetics and mechanism of copolymerization of BA with Sty using BP as photoinitiator have been studied in detail. The system follows nonideal kinetics ($R_p \propto [BP]^{0.34} [BA]^{1.07} [Sty]^{0.97}$). The nonideality was attributed to both primary radical termination and degradative initiator transfer. The monomer reactivity ratios of Sty and BA have been estimated by the Finemann–Ross and Kelen–Tudos methods, by analyzing copolymer compositions determined by ^{1}H NMR spectra. The values of r_1 (Sty) and r_2 (BA) were found to be 0.78 and 0.25, respectively, which suggested the high concentration of alternating sequences in the random copolymers obtained. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 3233–3239, 2006

Key words: photoinitiator; degradative transfer; BA-*co*-Sty; nonideal kinetics

INTRODUCTION

Photopolymerization has found wide applications in imaging and radiation curing technology e.g., photoresist, photolithography, photocurable coatings and inks, etc.[1–4] Progress in the chemistry of photopolymerizable compounds results from the development of new and novel monomers/initiators. Development of improved and more efficient photoinitiators/photosensitizers is likely to upgrade the existing technologies. Dyes have been extensively used as photosensitizers/photoinitiators for the polymerization of commercially important monomers.[5–9] In the development of dye photoinitiators, several factors are important—the location of dye absorption in the area required by application, increased rate of polymerization, solubility in monomers and a dark stability.[6] Dyes can be made fast photoinitiators by introducing such groups that produce free radicals either by intramolecular cleavage, or intermolecular H abstraction.[3–7]

Copolymerization is one of the important techniques adopted in affecting systematic changes in the properties of the commercially important polymers. Multicomponent polymers based on styrene/acrylate formulations are a basis for many important applications such as paints, adhesives, and coatings. This has stimulated the considerable body of study on copolymerizations of styrene with various acrylate monomers. There is sufficient literature on the copolymerization of Sty and BA using various types of techniques[10–15] and many commercially available and new initiators have been reported by several workers.[16–18] However, there is hardly any reference available for the photoinitiated copolymerization of Sty and BA.

Pyrene, an aromatic hydrocarbon dye, has been reported as photosensitizer/photoinitiator.[9,19] Introduction of chromophoric group ($-COCH_3$) in pyrene is expected to enhance its efficiency. Moreover, heavy atoms like Br and Cl are also known to cause a significant rise in the photoinitiation ability of the dyes.[6] In this communication, 1-(bromoacetyl)pyrene, is reported as photoinitiator for the first time for copolymerization of BA with Sty. A detailed polymerization kinetics and mechanism are also discussed.

EXPERIMENTAL

Materials

Reagent grade MMA (98%; Merck, Germany) and *n*-BA (98%; Merck, Germany) were dried over CaH_2, vacuum distilled, and kept below 5°C before use. Other solvents were purified by the usual methods.[20] Pyrene [[M] = 202.26 g/mol, m.p. = 149–151°C], 1-acetylpyr-
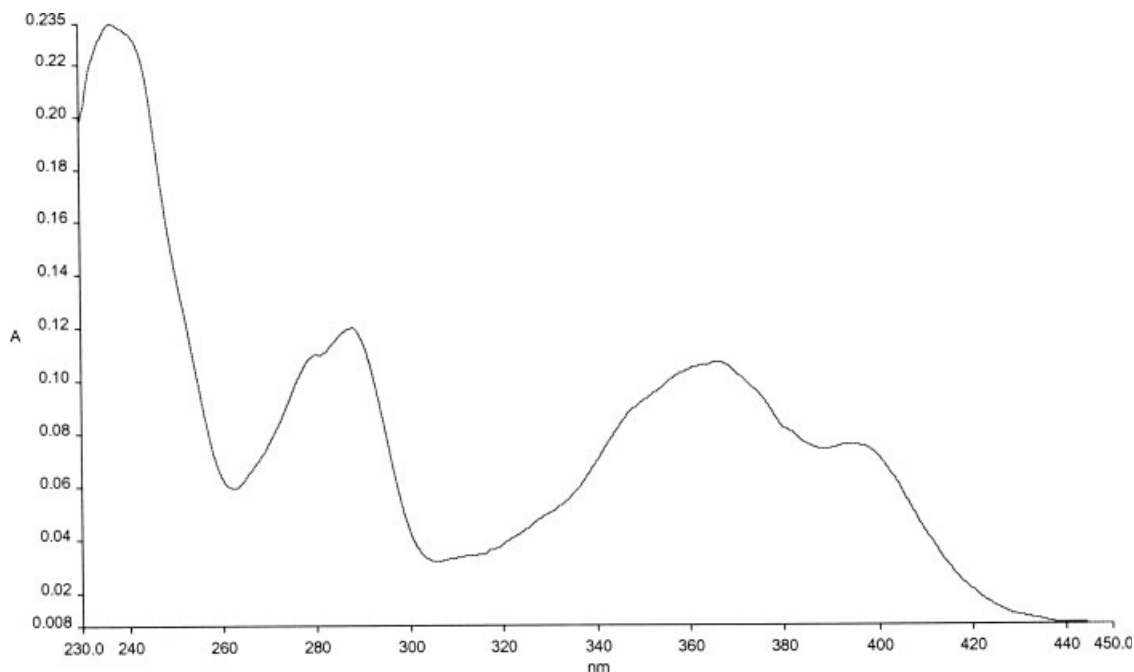
Figure 1 UV Spectrum of BP.

ene [[M] = 244.3 g/mol, m.p. = 86–89°C], and 1-(bromoacetyl)pyrene [[M] = 323.2 g/mol, m.p. = 129–131°C] (Aldrich) were used as received. Hydroquinone was recrystallized twice from methanol.

Photopolymerization procedure

Appropriate solutions of monomers in DMSO containing BP in quartz tube were degassed with nitrogen before irradiation. The tube was illuminated by U.V. light of 253 nm wavelength through 8 Philips U.V. tubes (8 W each, path length = 10 cm) arranged in a circular fashion in the photoreactor. The incident light intensity as measured by Lutron Lux Meter Model No. LX-101 was found to be 3.68×10^3 Lux. At the end of irradiation, the solutions were poured into methanol and the precipitated polymer was washed with acidified methanol. These polymers were dissolved in chloroform, reprecipitated in methanol, and dried in vacuum oven at 70°C. Conversions were determined

gravimetrically and were independently confirmed using replicate runs. The rates of copolymerization (R_p) were calculated by the following equation:

$$R_p(\text{mol L}^{-1} \text{ s}^{-1}) = \frac{6.476 \times C \times 10^{-4}}{t}$$

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

Characterization

UV spectrum was recorded on Perkin–Elmer Lambda 40 spectrophotometer. Low absorbencies of initiators (<0.4) were used to avoid the generation of an inhomo-
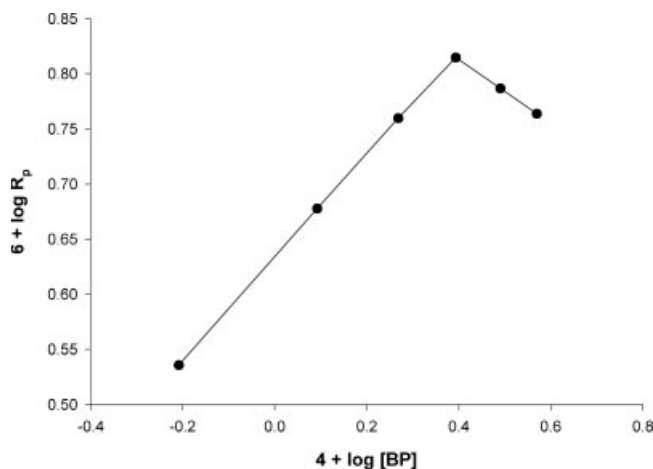
TABLE I
Effect of [BP] on R_p

Serial no.	[BP] (10^4 mol/L)	% Conversion	R_p (10^6 mol/L/s)
1.	0.618	1.91	3.439
2.	1.237	2.65	4.764
3.	1.856	3.20	5.753
4.	2.475	3.63	6.526
5.	3.094	3.41	6.137
6.	3.712	3.23	5.807

[BA] = 1.39 mol/L; [Sty] = 1.748 mol/L; polymerization time = 6 h; polymerization temperature = (30 ± 0.2)°C.

Figure 2 Plot of log [BP] versus log R_p. [BA] = 1.39 mol/L; [Sty] = 1.748 mol/L; polymerization time = 6 h; polymerization temperature = (30 ± 0.2)°C.
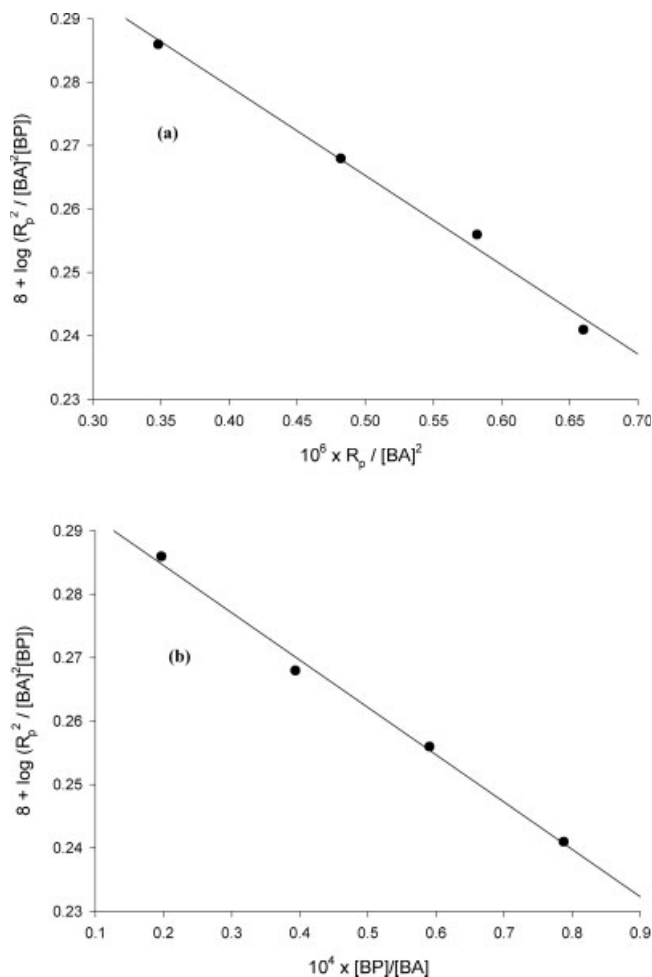
Figure 3 Plot of $R_p^2/[BA]^2[BP]$ versus (a) $R_p/[BA]^2$ and (b) $[BP]/[BA]$. $[BA] = 1.39$ mol/L; $[Sty] = 1.748$ mol/L; polymerization time = 6 h; polymerization temperature = $(30 \pm 0.2)°$C.

geneous free radical distribution.[21] The IR and NMR spectra were recorded on a Perkin–Elmer Model 599 B (KBr pellets) and Jeol JNM LA 400 FT NMR spectrophotometer, using CDCl₃ as a solvent and TMS as an internal reference, respectively. The ESR spectrum was recorded on an X-band Bruker EMX-EPR Spectrometer

TABLE II
Effect of [Sty] and [BA] on R_p

Serial no.	[Sty] (mol/L)	[BA] (mol/L)	% Conversion	R_p (10^6 mol/L/s)
1.	1.748	0.488	0.69	1.240
2	1.748	0.697	0.98	1.762
3.	1.748	1.046	1.44	2.589
4.	1.748	1.395	1.91	3.439
5.	0.611	1.395	0.62	1.114
6.	0.874	1.395	0.92	1.654
7.	1.311	1.395	1.42	2.553

$[BP] = 6.18 \times 10^{-5}$ mol/L; polymerization time = 6 h; polymerization temperature = $(30 \pm 0.2)°$C.

(Model 1444) at liquid N₂ temperature (Center Field: 3300 G, sweep width: 1000 G, Mod. Amplitude: 10 G, sweep time: 167.77 s, Microwave power 0.201 mW).

RESULTS AND DISCUSSION

UV spectrum of BP [3.093×10^{-5} mol/L] in dichloromethane shows λ_{max} at 288 and 366 nm (Fig. 1). The longer wavelength band allows assignment of a $\pi \rightarrow \pi^*$ orbital transition to the band and the shorter wavelength band allows the assignment of a $n \rightarrow \pi^*$ orbital transition to the band.

Polymerization kinetics

Effect of initiator concentration

The concentration of Py was varied from 5×10^{-4} to 50×10^{-4} mol/L but no polymer formation was observed up to 10 h, whereas in AP-(BA-*co*-Sty) system, less than 1% conversion was achieved using 50×10^{-4} mol/L

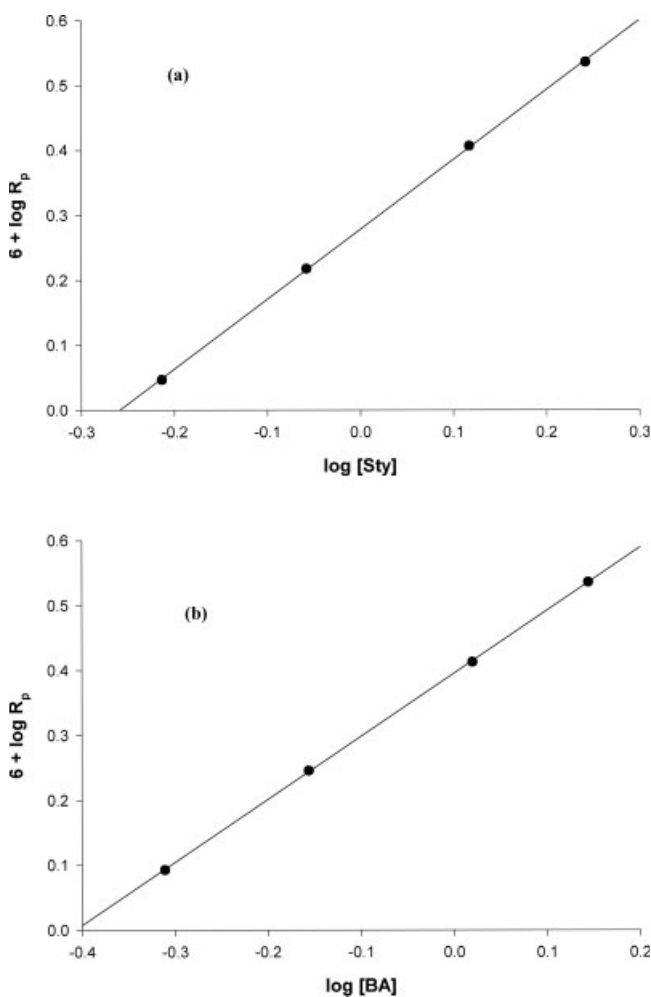**Figure 4** Plot of log [Sty] versus log R_p; $[BA] = 1.39$ mol/L. (b) Plot of log [BA] versus log R_p; $[Sty] = 1.748$ mol/L. $[BP] = 6.18 \times 10^{-5}$ mol/L; polymerization time = 6 h; polymerization temperature = $(30 \pm 0.2)°$C.

[AP]. However, the introduction of bromine in the acetyl moiety (BP-(BA-*co*-MMA) system) significantly enhanced the percent conversion.

The effect of [BP] on R_p was studied by varying its concentration from 0.618×10^{-4} to 3.712×10^{-4} mol/L for a fixed monomer feed ratio (Table I). No polymerization was observed, in absence of initiator, by the light employed. All conversions were limited to < 10% to obtain kinetic data. Dependence of R_p on [BP], keeping [BA] and [MMA] constant, displayed a maximum at [BP] = 2.475×10^{-4} mol/L (Table I). The upward trend of the curve of log R_p versus log [BP] is greatly reduced at high concentrations of [BP], which can be ascribed to the consumption of [BP] in a fast chain transfer reaction. The initiator exponent calculated from the slope of the plot of log R_p versus log [BP] is 0.34 (Fig. 2). The deviation in the exponent value of initiator from 0.5 suggests that the present system follows nonideal kinetics, which can be explained on the basis of primary radical termination and degradative chain transfer.

To analyze the effect of primary radical termination, the following expression given by Deb and Meyerhoff[22,23] has been used

$$\log R_p^2/[I][M]^2 = \log 2f_k k_d k_p^2/k_t - 0.8684 k_{prt} R_p/k_t k_p[M]^2$$

where, f_k represents the fraction of free radical to initiate chain growth; k_d is the initiator decomposition rate constant; k_p is the propagation rate constant; k_{prt} is the primary radical termination constant; and [I] and [M] are initiator and monomer concentrations, respectively. In the present study, a plot on the left hand side

of the above equation versus $R_p/[M]^2$ gave a linear negative slope [Fig. 3(a)], indicating significant primary radical termination along with simultaneous bimolecular termination. The following equation has frequently been used to examine degradative chain transfer as

$$\log R_p^2/[I][M]^2 = \log 2f_k k_d k_p/k_t$$
$$- 0.434 k_p^2 k_{itI} C_l[I]/k_t k_{iI} k_p[M]$$

where, C_I is the initiator transfer constant; k_{itI} is the rate constant for degradative chain transfer to initiator; and k_{iI} is the initiator rate constant. A plot on the left hand side of the above equation versus [I]/[M] gave a linear negative slope [Fig. 3(b)], suggesting measurable degradative initiator transfer.[24] The nonideality in the present system is attributed to both primary radical termination and degradative initiator transfer.

Effect of comonomer concentration

The effect of BA concentration on R_p was studied by varying [BA] from 0.48 to 1.39 mol/L, keeping [BP] and [Sty] constant. Similarly, the effect of [Sty] on R_p was studied by varying its concentration from 0.61 to 1.74 mol/L, keeping [BP] and [BA] constant (Table II). It was observed that R_p increased with increase in monomer concentration in both the cases. The exponent values calculated from the slope of the linear plot of log R_p versus log [Sty] [Fig. 4(a)] and log R_p versus log [BA] [Fig. 4(b)] are 0.97 and 1.07, respectively.
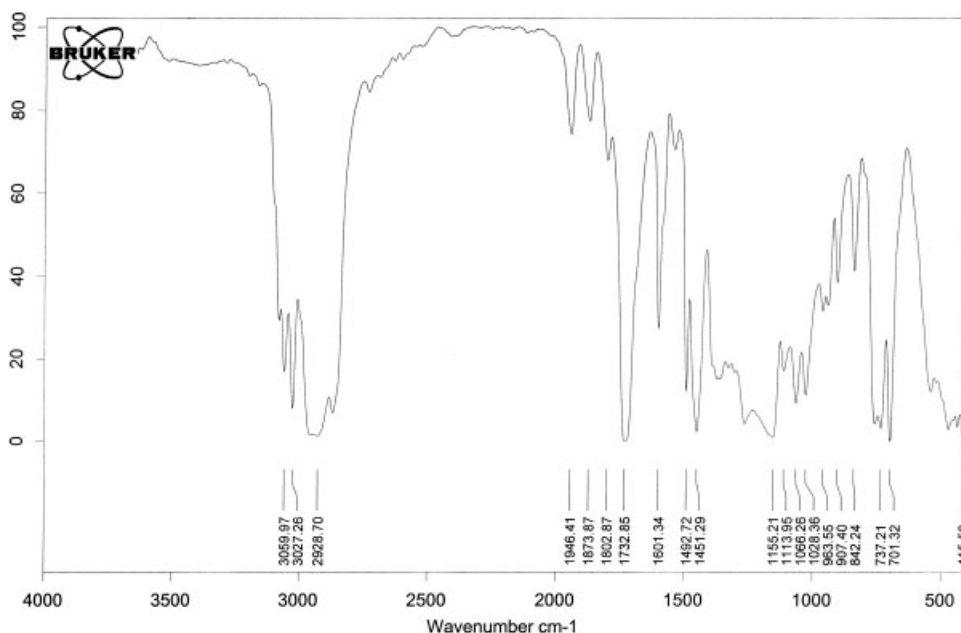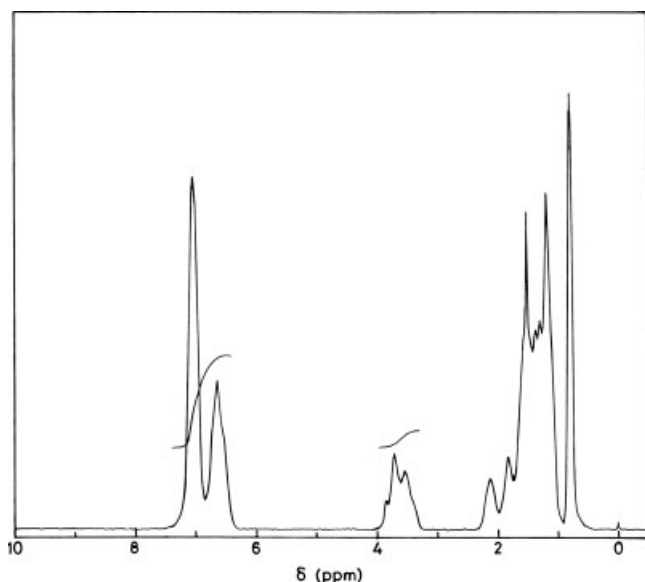

Figure 5   IR spectrum of copolymer.

Figure 6 NMR Spectrum of copolymer. [BA] = 1.39 mol/L; [Sty] = 1.748 mol/L; [BP] = 6.18 × 10^{-5} mol/L; polymerization time = 6 h; polymerization temperature = (30 ± 0.2)°C.

Characterization of copolymers

Spectral analysis

Infrared spectroscopy. The IR spectrum (Fig. 5) of copolymer shows band at 3059–2928 cm^{-1} due to C—H str vibrations of methyl, methylene, and methine groups, 1732 cm^{-1} due to $\rangle$C=O str vibrations of ester carbonyl, 1492–1451 cm^{-1} due to C—H deformation bands, and 1155–1028 cm^{-1} due to C—O—C str vibrations.

NMR spectroscopy. In the NMR spectrum of copolymer (Fig. 6), the signals at 3.5–3.8 δ are assigned to —OCH$_2$ protons of BA unit, the signals at 6.6–7.1 δ to aromatic protons of Sty, 0.9 δ to methyl protons of BA unit, 1–2.1 δ to methine and methylene protons of both units. It is believed that the range of chemical shifts, observed for the —OCH$_2$ signal, stems from different triad and tacticities possible for the copolymer.

Copolymer composition and monomer reactivity ratios

For calculating the copolymer compositions (F_M), the relative areas of the proton resonances of —C$_6$H$_5$ of
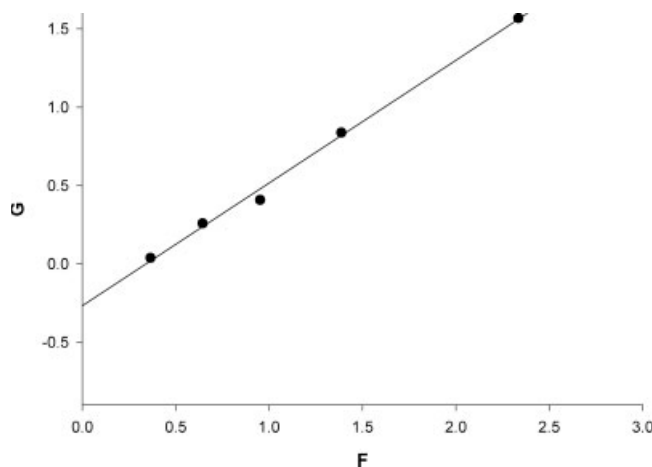

Figure 7 Finemann–Ross plot.

the Sty unit and —OCH$_2$ of the BA unit in the ^{1}H NMR spectrum were used (Table III). Various methods have been used to obtain MRRs from the copolymer composition data.[25] The Finemann–Ross[26] equation is one of the earliest attempts to linearize the copolymer composition equation:

$$G = r_1 F - r_2 \tag{1}$$

where,

$$G = X(Y - 1)/Y \quad \text{and} \quad F = X^2/Y$$

$$X = [M_1]/[M_2] \quad \text{and} \quad Y = d[M_1]/d[M_2]$$

In the Kelen–Tudos method,[27] the linear form is refined by introducing an arbitrary constant α, to spread the data more evenly so as to give equal weighting to all data points. Their results are expressed in the form of
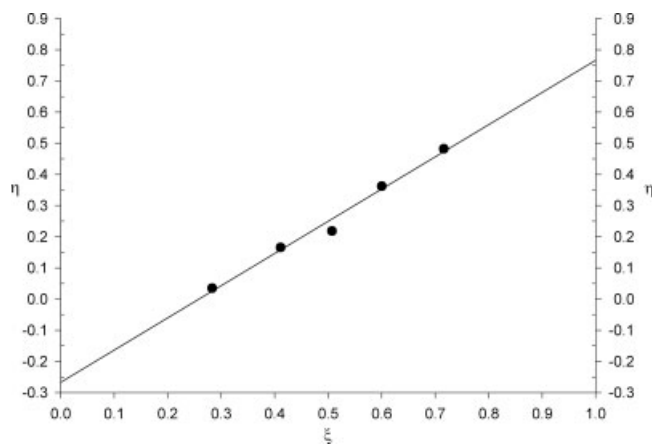
$$\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha \tag{2}$$

TABLE III
Copolymer Composition

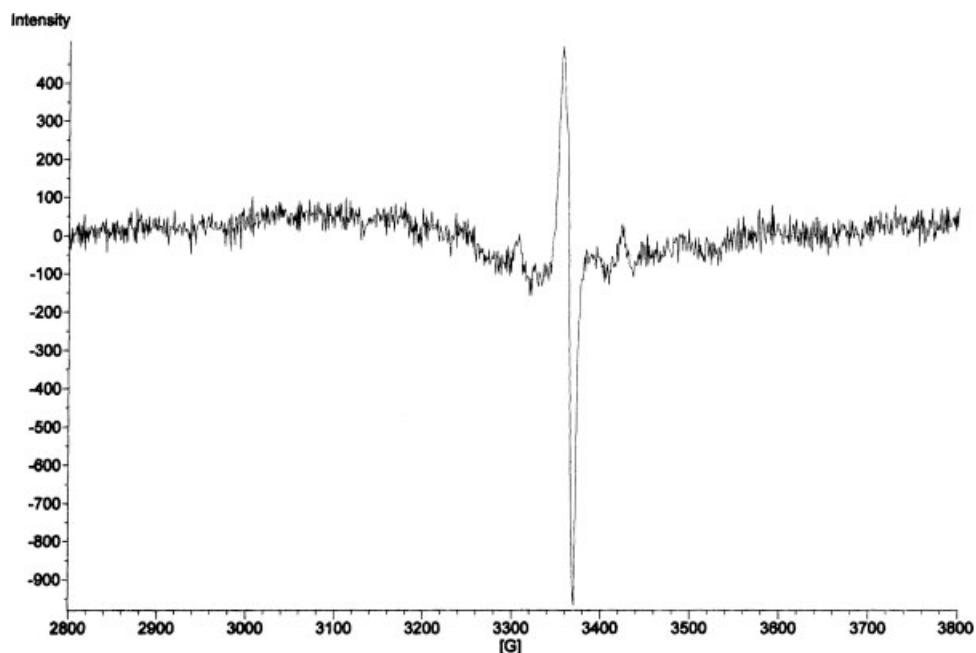| Serial no.	Molar ratio in monomer feed [Sty]/[BA] (X)	Molar ratio in copolymer [Sty]/[BA] (Y)
1.	0.628	1.079
2	0.943	1.381
3.	1.257	1.659
4.	1.671	2.012
5.	2.506	2.690

Figure 8 Kelen–Tudos plot.

Figure 9 ESR Spectrum of BP in DMSO.

where,

$$\eta = G(\alpha + F), \quad \xi = F(\alpha + F) \quad \text{and} \quad \alpha = (F_{min} \times F_{max})^{1/2}$$

The intercepts at $\xi = 0$ and $\xi = 1$ of the η versus ξ plot gives $-r_2/\alpha$ and r_1, respectively.

The Finemann–Ross (FR) and Kelen–Tudos (KT) plots are given in Figures 7 and 8, respectively. The reactivity ratios as calculated by FR and KT methods are r_1 (Sty) = 0.78 and r_2 (BA) = 0.25. The MRR of Sty is much higher than that of BA showing more reactivity than that of BA. The random copolymers so obtained contain

a high concentration of alternating sequences, as anticipated by the three times higher value of r_1 than r_2.[28]

ESR spectroscopy

The spectrum (Fig. 9) shows characteristic free radical absorption at 3370 G. Spectrum shows a sharp peak with a "g" value 2.00, which may be conveniently assigned to the Py—CO—CH$_2$ radical (A) formed by the homolytic cleavage of BP. Remaining peaks may be assigned to the Br radical formed at the same time assuming that a few peaks have been overlapped by
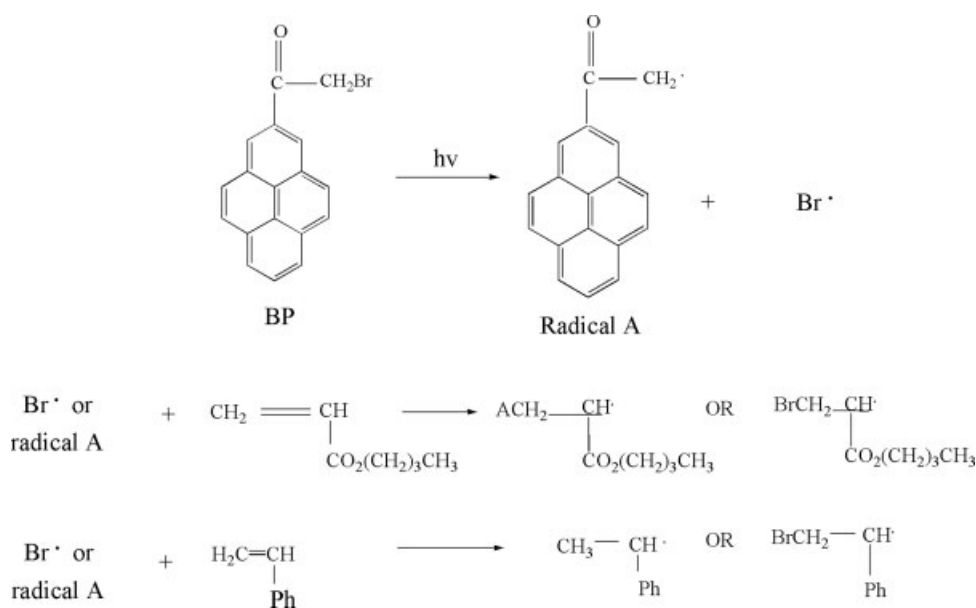
Scheme 1

the peak due to radical (A). This strongly suggests a free radical mechanism for the polymerization.

Mechanism

The inhibition to polymerization in the presence of a small quantity of hydroquinone, ESR studies, and the kinetics suggest a radical mechanism for BP-(BA-*co*-Sty) system. As evidenced by ESR, the possible radicals generated by the initiator, BP, are radical A and bromine. Considering the above facts, a proposed mechanism is given in Scheme 1.

CONCLUSIONS

The incorporation of a chromophoric moiety, bromoacetyl ($—COCH_2Br$), significantly increased the photoinitiating ability of pyrene. The values of r_1 (Sty) and r_2 (BA) were found to be 0.78 and 0.25, respectively, which suggested the high concentration of alternating sequences in the random copolymers obtained. The system followed nonideal kinetics with respect to initiator. Degradative chain transfer and primary radical termination reasonably explained the kinetic nonidealities.

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