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ORIGINAL CONTRIBUTION

1-(Bromoacetyl)pyrene, a novel photoinitiator for the copolymerization of styrene and acrylonitrile

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Abstract A comparative study on photoinitiated solution copolymerization of Styrene (Sty), with acrylonitrile (AN) using pyrene, 1-acetylpyrene, and 1-(bromoacetyl)pyrene (BrPy) 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 Sty with AN (Sty–co–AN) using BrPy as photoinitiator has been studied in detail. The kinetic data, inhibiting effect of benzoquinone, and electron spin resonance (ESR) studies suggest that the polymerization proceeds via a free radical mechanism. The system followed non-ideal kinetics ($R_p\alpha[BrPy]^{0.7}[Sty]^{1.09}[AN]^{1.01}$) and degradative solvent transfer reasonably explained these kinetic non-idealities. The co-monomer reactivity ratios calculated by using the Finemann–Ross and Kelen–Tudos models were r_1 (Sty)=0.39 and r_2 (AN)=0.05. The reactivity ratios strongly indicate that the two monomers enter in almost alternating arrangement along the copolymer chain.

Keywords Pyrene · Photopolymerization · Degradative transfer · Sty–co–AN · Non-ideal kinetics · ESR

Introduction

Light-induced polymerization is considered one of the most efficient techniques for rapidly producing polymeric materials with well-defined characteristics. Applications in which photopolymerization is used include films and coatings, inks, adhesives, fiber optics, and dentistry [1–4]. The vast majority of photopolymerizations used in the industry involve a free radical mechanism [1–6]. 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 [7, 8].

Copolymerization is the most general and powerful method of effective systematic changes in polymer properties and is widely used in the production of commercial polymers and in fundamental investigation of structure property relations. Sty–AN copolymer is a system of practical interest and has been studied extensively and described in many publications [9–13].

Dyes have been extensively used as photosensitizers/photoinitiators for the polymerization of commercially important monomers [14–17]. Pyrene, an aromatic hydrocarbon dye, was reported as photosensitizer /photoinitiator [18, 19]. Introduction of the 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 [17]. Detailed polymerization kinetics and mechanism with BrPy as initiator for copolymerization of Sty and AN are discussed.

Experimental

Materials

Reagent grade AN (Ranbaxy), Sty (Merck–Schuchardt), and other solvents were purified by the usual methods [20] and distilled under vacuum before use. Pyrene (M=202.26 g/mol, m.p.=149–151 °C), 1-acetylpyrene (M=244.3 g/mol,

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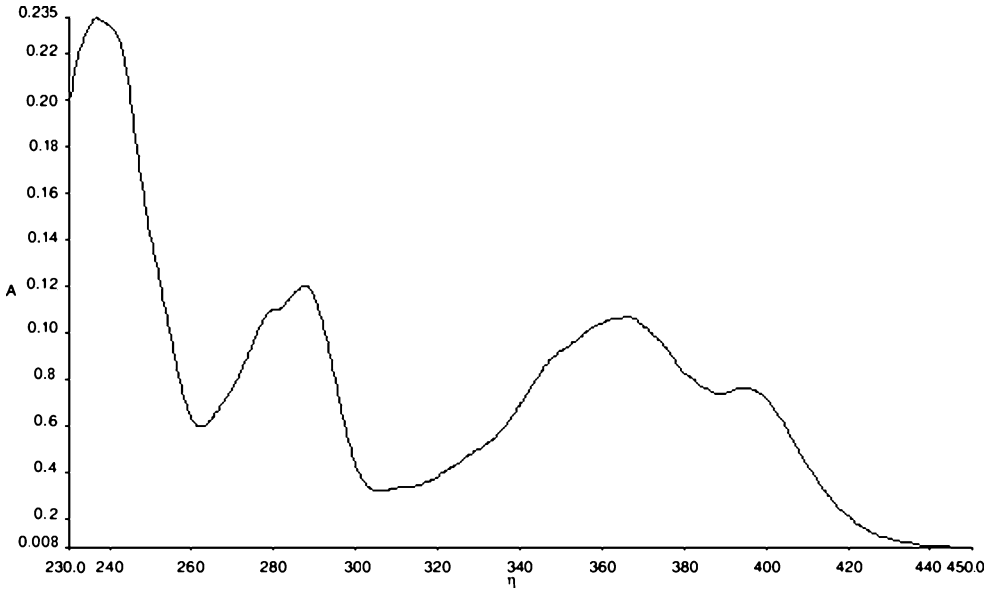


Fig. 1 UV Spectrum of BrPy

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 monomer in dimethyl sulfoxide (DMSO) containing BrPy 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 (8 W each, path length=10 cm) and emitting light nominally at 253 nm at room temperature, the solutions were poured into methanol and the precipitated polymer was washed with acidified methanol. The copolymer was refluxed with cyclohexane to remove homopolymer and then dried to constant weight, but no detectable weight loss was observed. These polymers were then redissolved in methyl ethyl ketone, filtered, reprecipitated in methanol and dried in vacuum oven at 55 °C. The incident light intensity as measured by Lutron Lux Meter Model No. LX-101 was found to be 3.68×10^3 lx. Conversions were determined gravimetrically and were independently confirmed using replicate runs. The rates of copolymerization (R_p) were calculated by the following equation:

$$R_p\left(\text{mol}\,l^{-1}\,s^{-1}\right) = \frac{0.9094 \times C \times 10^{-3}}{t}$$

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 inhomogeneous free radical distribution [21]. The IR and NMR spectra were recorded on a Perkin-Elmer Model 599 B (dry DCM) and Jeol JNM LA 400 Lambda NMR spectrophotometer, using $CDCl_3$ as a solvent and TMS as an internal reference, respectively. The C, H, and N analysis were done on a Perkin-Elmer 240 C Elemental Analyser. The ESR spectrum was recorded on an X-band Bruker EMX-EPR Spectrometer (Model 1444) at liquid N_2 temperature (centerfield 3,300 G; sweep width 1,000 G; mod. amplitude 10 G; sweep time 167.77 s, microwave power 0.201 mW). The software Sigma Plot 5.0 was used to perform statistical analysis of the kinetic data obtained by applying linear regression/curve fitting method.

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

Table 1 Effect of [BrPy] on R_p

S. no.	[BrPy]×10^4 (mol/l)	% Conversion	$R_p\times10^6$ (mol l^{-1} s^{-1})
1	0.618	2.342	5.070
2	1.236	3.841	8.315
3	1.854	5.062	10.959
4	2.472	6.230	13.488
5	3.090	7.422	16.068

[Sty]=1.748 mol/l, [AN]=3.034 mol/l, polymerization time=7 h, polymerization temp.=30±0.2 °C

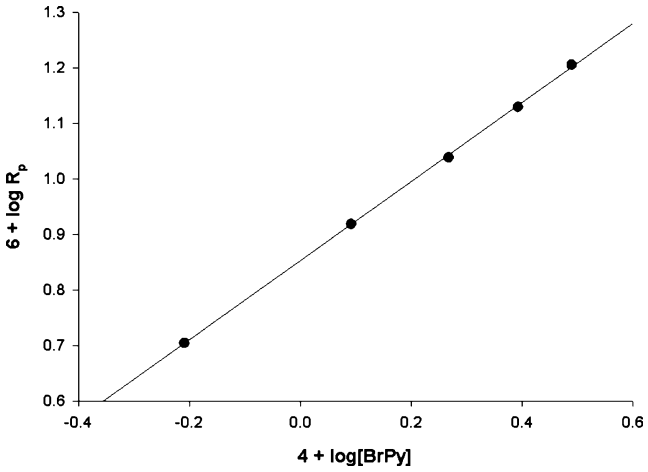


Fig. 2 Plot of log [BrPy] vs log R_p · [Sty] = 1.748 mol/l?; [AN]= 3.034 mol/l; polymerization time=7 h; polymerization temp.=30±0.2 °C

allows the assignment of a $n \rightarrow \pi^*$ orbital transition to the band.

Polymerization kinetics

Effect of initiator concentration

The concentration of pyrene was varied from 5 to 50×10^{-4} mol/l, but no polymer formation was observed up to 10 h, whereas with 1-acetylpyrene (5×10^{-4} mol/l), percent conversion was less than 1% only. However, the introduction of bromine in the acetyl moiety of pyrene significantly enhanced the percent conversion.

The effect of [BrPy] on R_p was studied by varying its concentration from 0.618×10^{-4} to 3.09×10^{-4} mol/l for a fixed monomer feed ratio (Table 1). No polymerization was observed, in absence of initiator, by the light employed.

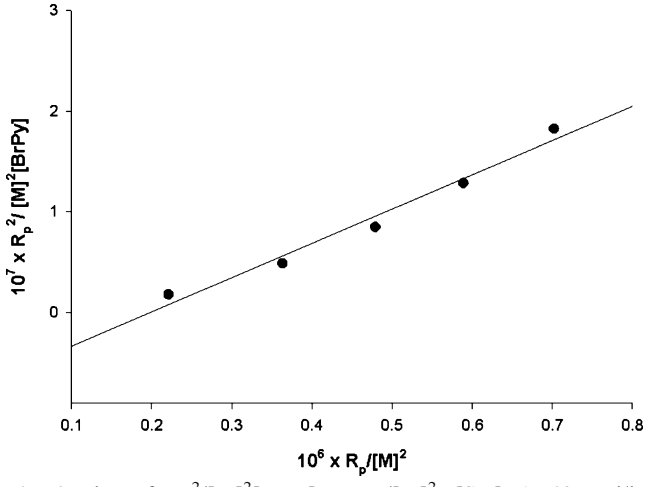


Fig. 3 Plot of $R_p^2/[M]^2[BrPy]$ vs $R_p/[M]^2$. [Sty]=1.748 mol/l; [AN]=3.034 mol/l; polymerization time=7 h; polymerization temp.=30±0.2 °C

Table 2 Effect of [Sty] and [AN] on R_p

S. no.	[Sty] (mol/l)	[AN] (mol/l)	% Conversion	$R_p \times 10^6$ (mol l^{-1} s^{-1})
1	0.611	3.034	0.75	1.623
2	0.874	3.034	1.09	2.359
3	1.311	3.034	1.72	3.724
4	1.748	3.034	6.83	14.789
5	1.748	1.062	2.34	5.070
6	1.748	1.517	3.23	6.999
7	1.748	2.275	4.83	10.469

[BrPy]=6.18×10^{-5} mol/l; polymerization time=7 h; polymerization temp.=30±0.2 °C

The reaction time was selected to give conversions of less than 10% to satisfy the differential copolymerization equation. The R_p increased with increasing [BrPy], keeping [Sty] and [AN] constant. The initiator exponent calculated from the slope of the plot of log R_p vs. log [BrPy] was 0.71 (Fig. 2). The deviation in the exponent value from 0.5 suggested that the system followed non-ideal kinetics. To explain this unusual behavior and to ascertain the nature of

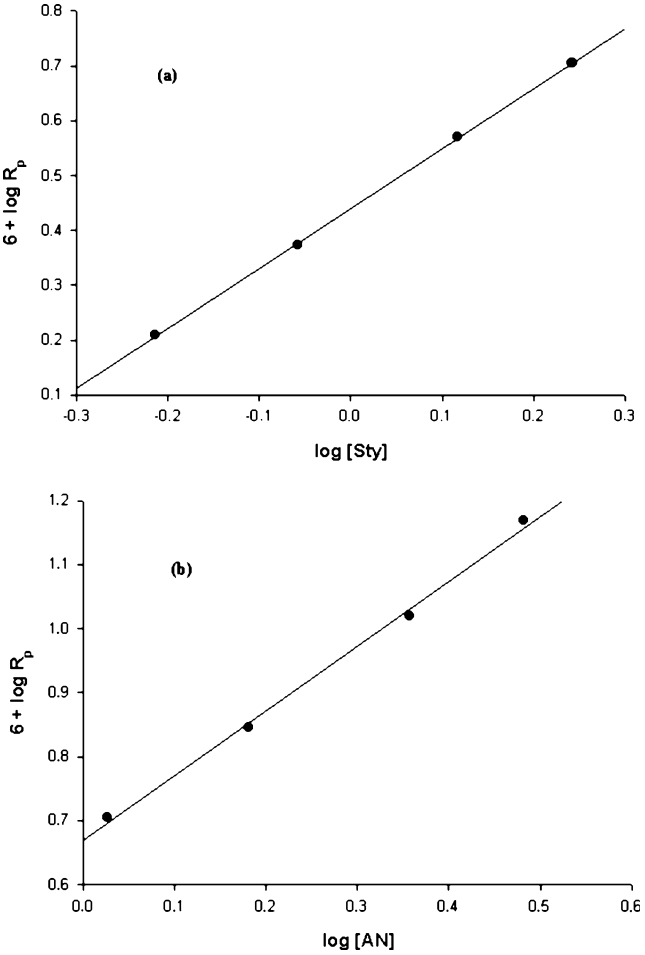


Fig. 4 **a** Plot of log [Sty] vs log R_p. [AN]=3.034 mol/l. **b** Plot of log [AN] vs log R_p. [Sty]=1.748 mol/l. [BrPy] = 6.18×10^{-5} mol/l; polymerization time=7 h; polymerization temp.=30±0.2 °C

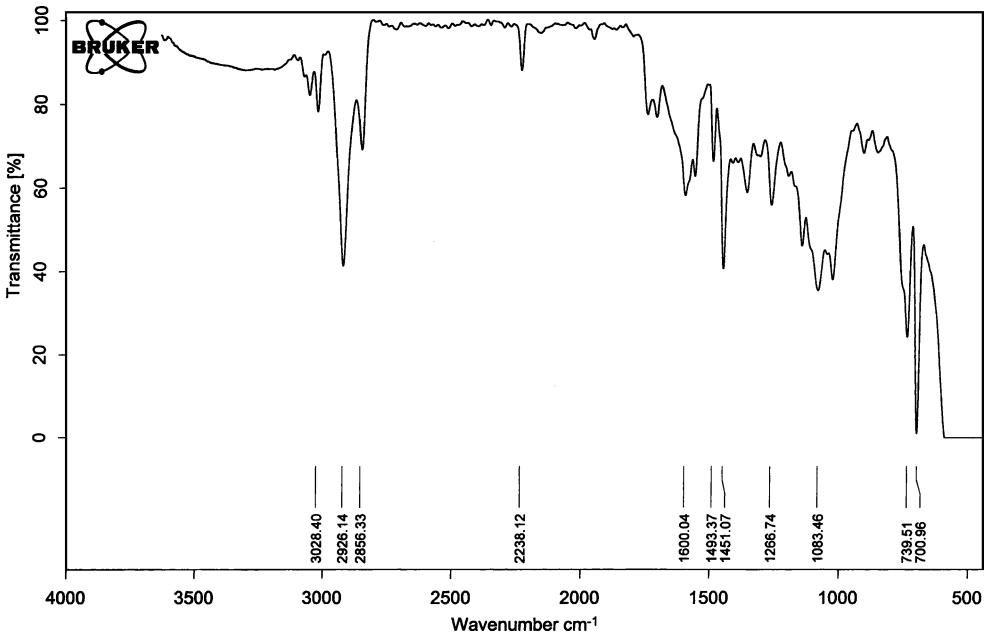


Fig. 5 IR Spectrum of Sty–co–AN

the transfer reactions involved, plots of $R_p^2/([BrPy][M]^2)$ vs $R_p/[M]^2$ (Fig. 3), following the equation of Deb [22] were plotted. The positive slope obtained suggested that degradative solvent transfer was mostly operative in the main termination process instead of degradative initiator transfer or primary radical termination [23].

Effect of comonomer composition

The effect of Sty concentration on R_p was studied by varying [Sty] from 0.61 to 1.74 mol/l, keeping [BrPy] and [AN] constant. Similarly, the effect of [AN] on R_p was studied by varying its concentration from 1.06 to 3.03 mol/l, keeping [BrPy] and [Sty] constant (Table 2). It was found that R_p increased as the concentration of monomer increases in both cases. The exponent values, calculated from the slope of the linear plot of $\log R_p$ vs $\log$ [Sty] (Fig. 4a) and $\log R_p$ vs $\log$ [AN] (Fig. 4b) were 1.09 and 1.01, respectively.

Characterization of copolymers

Spectral analysis

Infrared spectroscopy The IR spectrum (Fig. 5) of copolymer shows bands at 3,028 cm^{-1} due to aromatic C–H str

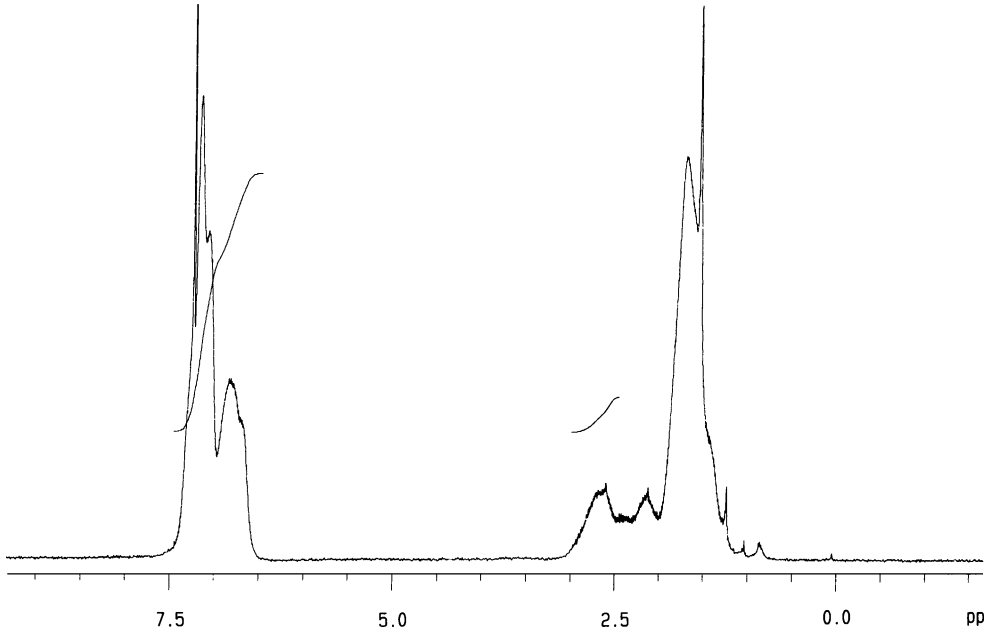


Fig. 6 NMR Spectrum of Sty–co–AN [Sty]=1.748 mol/l; [AN]=3.034 mol/l; [BrPy]=6.18×10^{-5} mol/l; polymerization time=7 h; polymerization temp.=30±0.2 °C

Table 3 Copolymer composition

S. no.	Mol fraction of AN in feed (M_2)	N (%)	Mol fraction of AN in copolymer (m_2)	Molar ratio in monomer feed [Sty]/[AN](X)	Molar ratio in copolymer [Sty]/[AN](Y)
1	0.465	7.11	0.419	1.150	1.386
2	0.566	7.82	0.451	0.766	1.217
3	0.635	8.25	0.471	0.574	1.123
4	0.699	8.68	0.489	0.4306	1.045
5	0.777	9.26	0.514	0.287	0.945

vibrations; 2,926 and 2,856 cm^{-1} due to C–H str vibrations of methylene and methine groups; 2,238 cm^{-1} due to C≡N str vibrations; 1,600 cm^{-1} due to aromatic C=C str vibrations; 1,450–1,390 cm^{-1} due to C–H deformation bands and C–N str vibrations. The characteristic nitrile peaks provide sufficient evidence for the formation of the copolymer.

NMR spectroscopy The ^{1}H NMR spectrum of Sty–co–AN (Fig. 6) shows broad peaks at 6.5–7.5δ (phenyl ring protons), 2.7–2.9δ (–CHCN–), and 1.4–2.6δ (–CH_2–CH–). The main evidence of the polymer formation is certainly the vanishing of two singlets at 6.3 and 5.8δ of the vinyl protons and the appearance of the broad signal at 2.5–1.7δ, which is assigned to an aliphatic –CH_2– group [24].

Copolymer composition and monomer reactivity ratio

^{1}H NMR spectra were not used for the determination of the monomer content in the copolymers since signals from different monomeric units overlap with each other. Elemental analysis was considered to be an accurate method for the determination of copolymer composition. Hence, the copolymer composition was calculated from the percentage of nitrogen in the copolymers (Table 3). The Finemann–Ross [25] equation is one of the earliest attempts to linearize the copolymer composition equation:

$$G = r_1 F - r_2 \quad (1)$$

where

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

$$X = M_1/M_2 \text{ and } Y = m_1/m_2$$

M_1 and M_2 are the monomer molar compositions in the feed.

The variables m_1, m_2 are the copolymer molar compositions.

Kelen–Tudos [26] introduced new parameters into the linearized copolymerization equation, such as η, ξ, and α:

$$\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha \quad (2)$$

where

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

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

The Finemann–Ross (FR) and Kelen–Tudos (KT) plots are given in Figs. 7 and 8, respectively. The reactivity ratios, as calculated by the FR method, are r_1 (Sty)=0.39 and r_2 (AN)=0.05; the reactivity ratios, as calculated by the KT method, are r_1 (Sty)=0.38 and r_2 (AN)=0.05 [27]. Since the product of r_1 and r_2 is approximately 0, the two monomers enter in almost alternating arrangement along the copolymer chain [28].

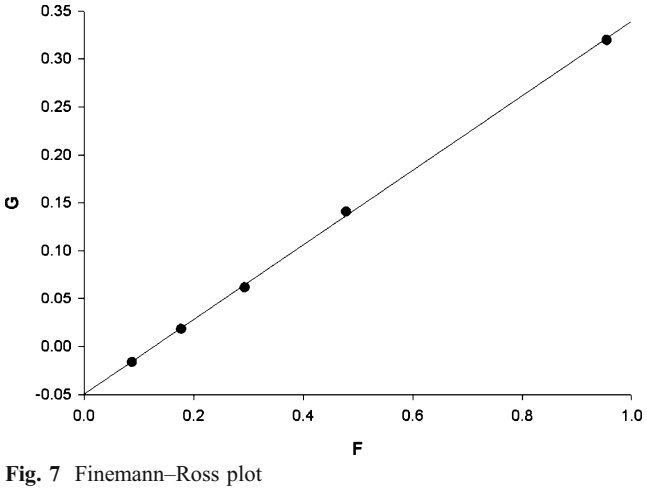


Fig. 7 Finemann–Ross plot

ESR spectroscopy The spectrum (Fig. 9) of BrPy in DMSO (in absence of monomers), by quenching the radicals in liquid nitrogen, showed characteristic free radical absorption at 3,370 G. The spectrum showed a sharp peak with a g value of 2.00, which may be conveniently assigned to the Py–CO–CH_2. (A) radical formed by the homolytic cleavage of BrPy. The radical A, as given in the Scheme 1, would result into a triplet due to two protons; however, already simple quantum chemical calculation shows that the spin is delocalized over the whole molecule, which is inline with

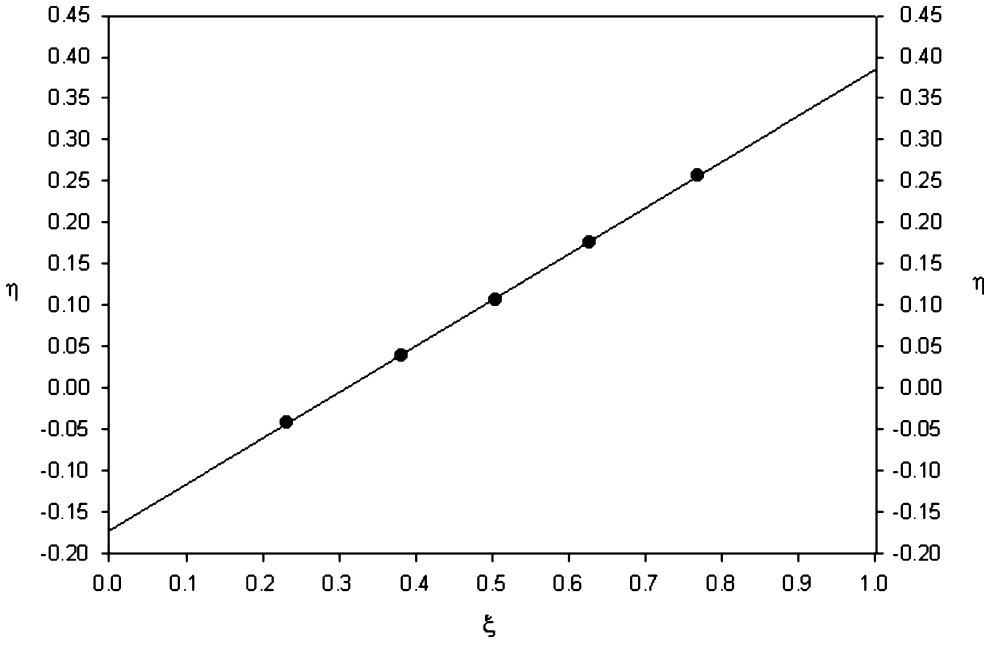


Fig. 8 Kelen–Tudos plot

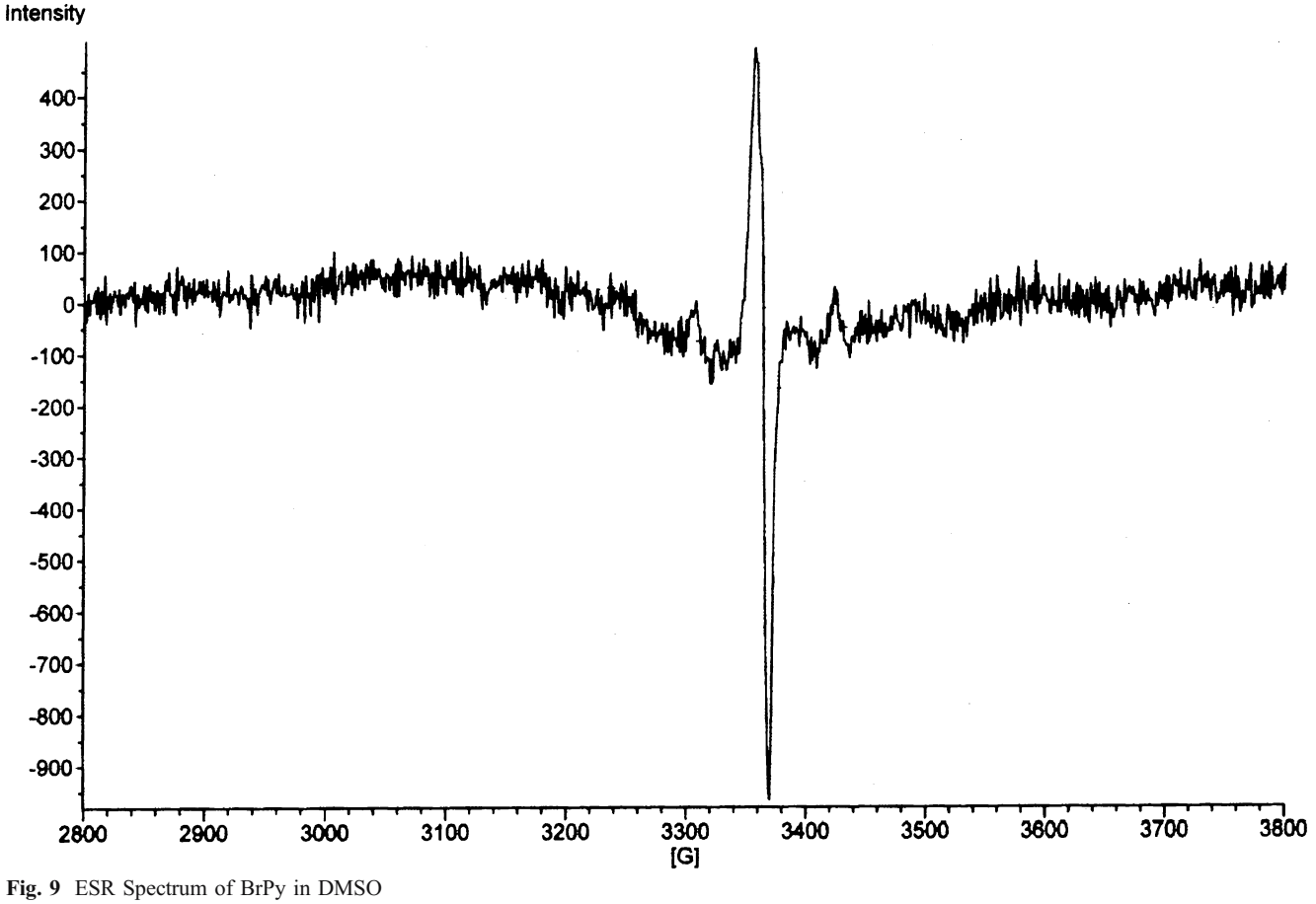
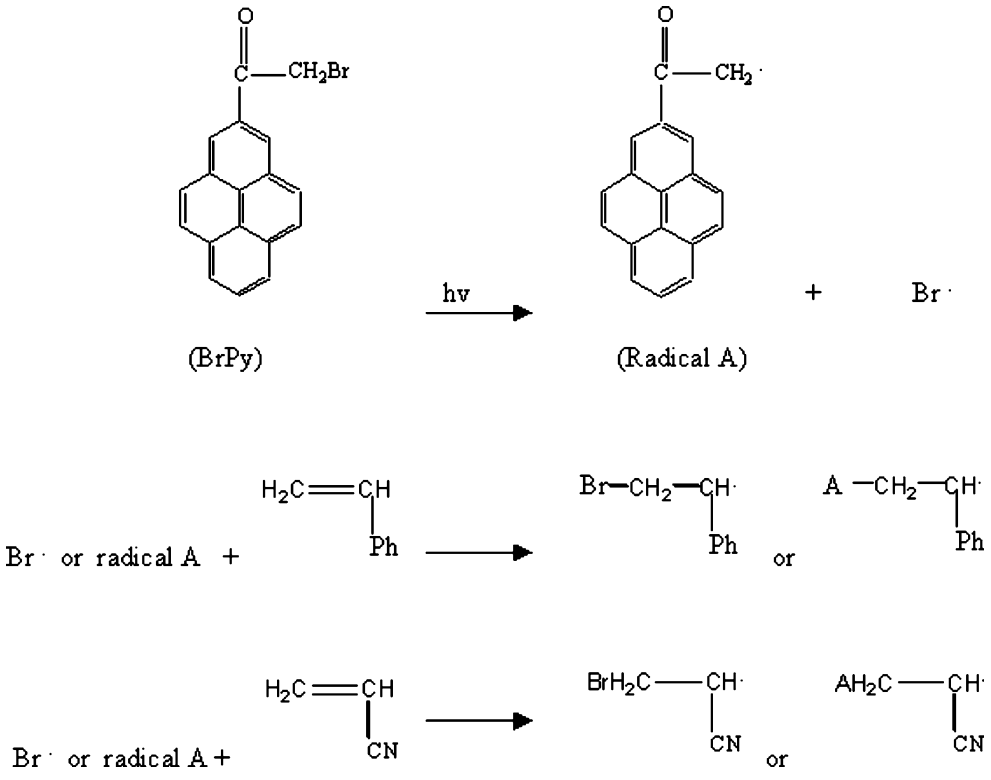


Fig. 9 ESR Spectrum of BrPy in DMSO

Scheme 1 Proposed mechanism for radicals A and Br formation



the observed singlet. Remaining peaks may be assigned to the Br radical formed at the same time, assuming that a few peaks have been overlapped by the peak due to radical (A). The appearance of these peaks 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 Sty–co–AN system. As evidenced by ESR, the possible radicals generated by the initiator, BrPy, are radical A and bromine. Both Br and radical A have the probability of initiating the polymerization reaction. When the facts mentioned above are considered, we come up with a proposed mechanism, which is given in Scheme 1.

Conclusions

A comparative study on photoinitiated solution copolymerization of styrene and AN using pyrene, 1-acetylpyrene, and 1-(Bromoacetyl)pyrene as initiators proved that incorporation of a chromophoric ($-COCH_3$) moiety introduces photoinitiating activity into pyrene, and Br markedly accelerated the rate of polymerization. The copolymerization of Sty with AN, using BrPy as initiator, followed non-ideal kinetics with respect to initiator concentration. Degradative chain transfer was suggested for this unusual behavior. Free radical mechanism was confirmed by ESR spectroscopy.

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