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ORIGINAL CONTRIBUTION

Curcumin, a natural colorant as initiator for photopolymerization of styrene: kinetics and mechanism

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Abstract The photopolymerization of styrene in presence of an efficient, eco-friendly, and a cost-effective photoinitiator, curcumin, which is found in turmeric root, has been reported for the first time. The catalytic concentration (10^{-6} M) of curcumin is effective to photoinitiate the polymerization of styrene. The kinetic data, inhibiting effect of benzoquinone and electron spin resonance studies, indicate that the polymerization proceeds via a free radical mechanism. The system follows non-ideal kinetics ($R_p \propto [Cur]^{0.36}\ [Sty]^{1.04}$) due to both primary radical termination and degradative chain transfer reactions. The broad peaks due to methine and methylene protons in ^{1}H-NMR (nuclear magnetic resonance [NMR]) spectrum and a band of resonances at 145–146 ppm in ^{13}C-NMR indicate atactic nature of the polystyrene formed. The maximum conversion at 30±0.2 °C in 17 h has been limited to 23% without gelation. The formation of radicals and mechanism of polymerization are also discussed.

Keywords Curcumin · Photopolymerization · NMR · ESR · Non-ideal kinetics

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Introduction

Photoinitiated polymerization reactions form the basis of several commercially important technologies used in electronics and chemical industries [1–4]. Development of improved and more efficient photoinitiators and photosensitizers, eco-friendly new reactive monomers from renewable resources, is likely to upgrade the existing technologies. A vast number of new initiators have been reported for the polymerization of styrene [5–10].

Colorants make up a large class of molecules extensively used as initiators/sensitizers for UV and visible light photoinitiation. Colorants are mostly organic compounds containing two or more chromophores, which are unsaturated groups, as part of a conjugated system of alternating single and double bond. The conjugation generally extends throughout the entire molecule and gives rise to ionic resonance structure, which significantly lowers the energy of attainable excited states. They belong to well-known structures, xanthene, thiazene, acridine, anthraquinone, cyanine, merocyanine, etc. Synthetic dyes have been extensively used to initiate or sensitize the polymerization of monomers [11–17]. Natural dyes and pigments being cheap, nontoxic, and renewable reservoir to materials for many applications have attracted the attention of the scientific community to use them in dyeing textile fibers [18] and in photosensitized solar cells [19, 20]. However, the use of these natural dyes/pigments as photoinitiators in polymerization reactions is scarcely reported in the scientific literature [21–23].

Turmeric is a common Indian spice and well known for its medicinal properties. In the present communication, we highlight the use of curcumin, 1,7-bis-(4-hydroxy-3-methoxyphenyl)-1, 6-heptadiene-3,5-dione, a yellow-orange dye derived from the rhizome of the plant *Curcuma*

longa, as a novel natural photoinitiator for polymerization of Sty. The results of kinetic investigations and mechanism have been discussed.

Experimental

Materials

The styrene (Merck–Schuchardt) and solvents were purified by the usual methods [24, 25] and distilled under vacuum before use. Curcumin (Aldrich; M=368.39 gm/mol, mp= 182 °C) was used as received. Hydroquinone was recrystallized twice from methanol.

Polymerization procedure

The required amounts of monomer and curcumin dissolved in a drop of dimethyl sulfoxide were charged into a quartz tube. This tube was degassed under vacuum by the conventional freeze and thaw technique and sealed off under vacuum. The tube was illuminated by UV light of 253-nm wavelength through eight Philips UV 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 lx. 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 by using the following equation and were independently confirmed using replicate runs:

$$\%\text{Conversion} = \frac{\text{Weight of polymer}}{\text{Weight of monomer}} \times 100$$

The rates of polymerization (R_p) were calculated by the following equation [26]:

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

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

Characterization

The Fourier transform infrared (FTIR) and nuclear magnetic resonance (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 trimethylsilyl as an internal reference, respectively. UV spectrum was recorded on Perkin–Elmer Lambda 40 spectrophotometer. The ESR spectrum was recorded on an X-band Bruker EMX-EPR Spectrometer (Model 1444) at liquid N_2 temperature.

Results and discussion

Figure 1 shows the UV spectrum of curcumin showing two λ_{max} at 257 and 403 nm. The polymerization could be done

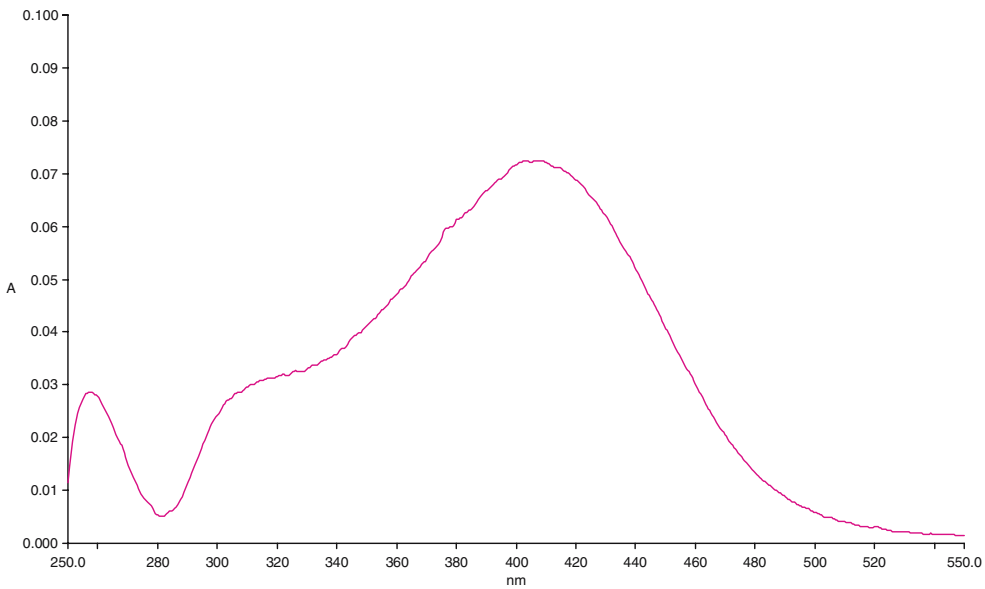


Fig. 1 UV spectrum of curcumin in methanol (2.71×10^{-5} mol/l)

Table 1 Effect of [Sty] and [Cur] on R_p

Sample no.	[Cur]×10^6 (mol/l)	[Sty]×10^3 (mol)	% conversion	R_p×10^5 (mol l^{-1} s^{-1})
1	1.508	8.74	3.36	0.81
2	3.016	8.74	4.33	1.04
3	6.032	8.74	5.55	1.34
4	12.064	8.74	7.05	1.70
5	12.064	4.37	3.44	0.83
6	12.064	13.11	10.6	2.56
7	12.064	17.48	14.75	3.56

Polymerization time=10 h; polymerization temperature=30±0.2 °C

at visible light, but 257 nm was preferred for polymerization reactions.

Polymerization kinetics

The kinetics of photopolymerization has been studied by varying the concentration of the initiator (Cur), styrene (Sty), and reaction time. The maximum conversion has been limited to 23% without gelation, and polymerization runs have induction period of 2 h. Under all similar conditions, neither azobisisobutyronitrile (AIBN) nor benzoyl peroxide (BPO), the commercially available photoinitiators, is effective to bring about the polymerization. At the commonly used concentration of AIBN and BPO (5×10^{-3} mol/l), the % conversions brought about under similar conditions are 6.71 and 3.79%, respectively. The concentration of Cur used in this study was much less in comparison to that of both the commercially used initiators. In fact, the catalytic concentration (10^{-6} M) of Cur was effective to photoinitiate the polymerization of Sty.

The effect of monomer concentration on R_p is studied by varying [Sty] from 4.37×10^{-3} mol to 17.48×10^{-3} mol, keeping [Cur] constant at 1.2064×10^{-5} mol/l. The respective data are shown in Table 1. Because Sty is polymerized to 0.5–0.7% conversion by the light employed in absence of any initiator, the data in Table 1 presents % conversion after having deducted the yield for blank experiments in each set. The monomer exponent value, calculated from the slope of the linear plot of log R_p vs log [Sty] is 1.04 (Fig. 2).

The effect of [Cur] on R_p has been studied by varying [Cur] from 1.508×10^{-6} mol/l to 12.064×10^{-6} mol/l, keeping [Sty] constant at 8.74×10^{-3} mol (Table 1). The R_p increases with increasing concentration of initiator as expected for free radical polymerization. The upward trend of the curve of log R_p vs log [Cur] is greatly reduced at high concentrations of [Cur], which can be ascribed to the

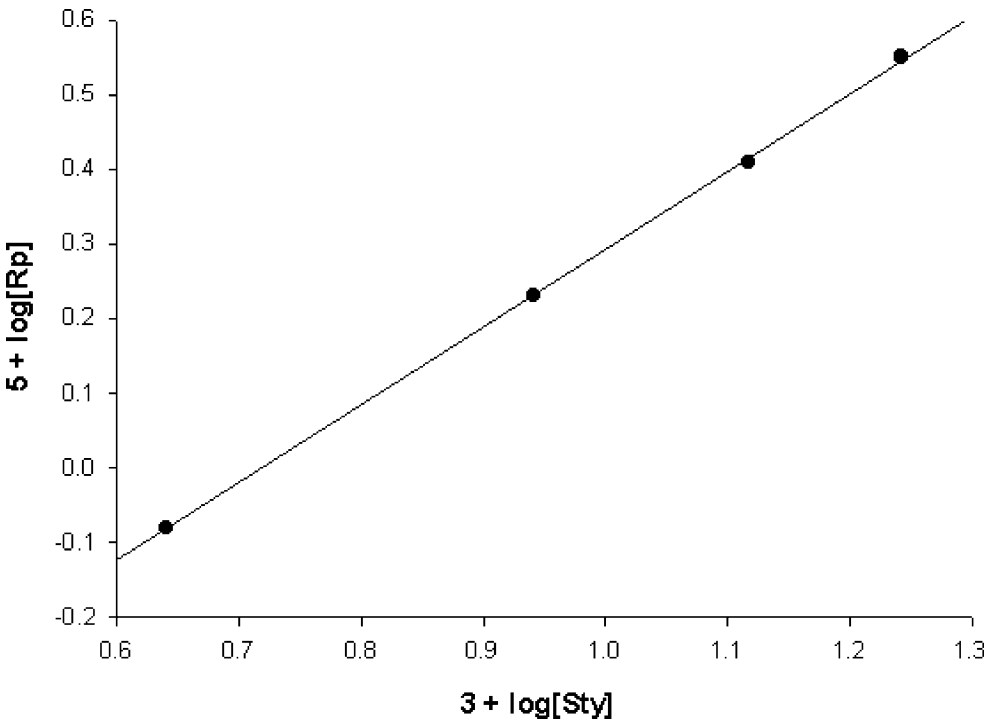


Fig. 2 Effect of [Sty] on R_p. [Cur]=12.064×10^{-6} mol/l; polymerization time=10 h; polymerization temperature=30±0.2 °C

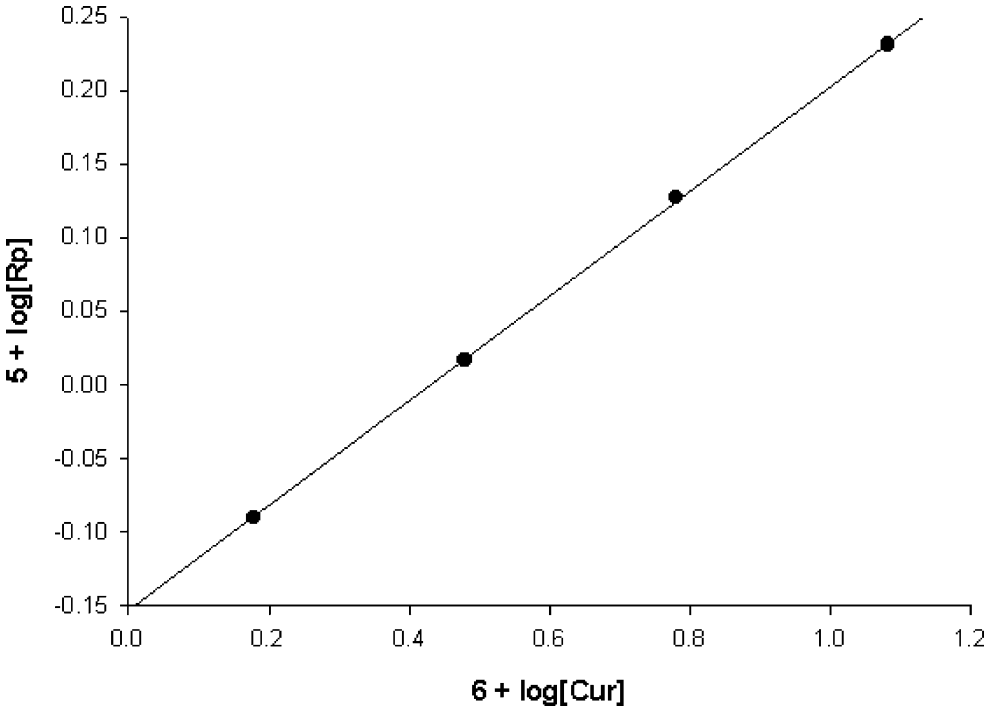


Fig. 3 Effect of [Cur] on R_p. [Styrene]=8.74×10^{-3} mol; polymerization time=10 h; polymerization temperature=30±0.2 °C

consumption of [Cur] in a fast chain transfer reaction. The order of reaction with respect to [Cur], calculated from the slope of the plot of log R_p vs log [Cur] is 0.36 (Fig. 3). The deviation in the exponent value of initiator from 0.5 suggests that the present system follows non-ideal 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 [27, 28] has been used:

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

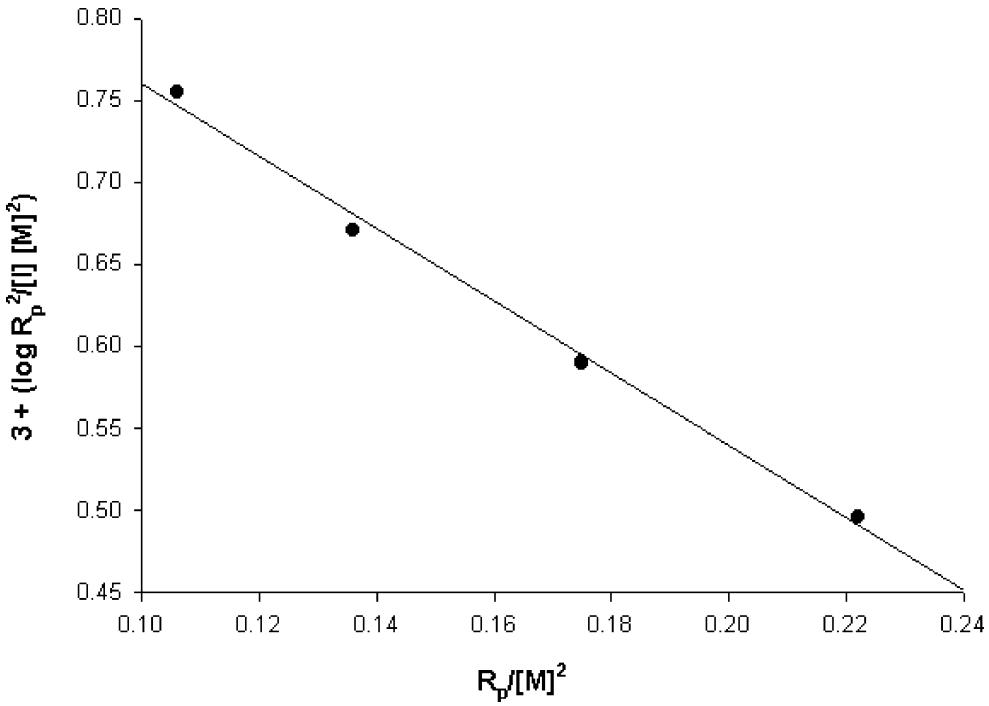


Fig. 4 Plot of log $R_p^2/[I][M]^2$ vs $R_p/[M]^2$. [Sty]=8.74×10^{-3} mol; polymerization time=10 h; polymerization temperature=30±0.2 °C

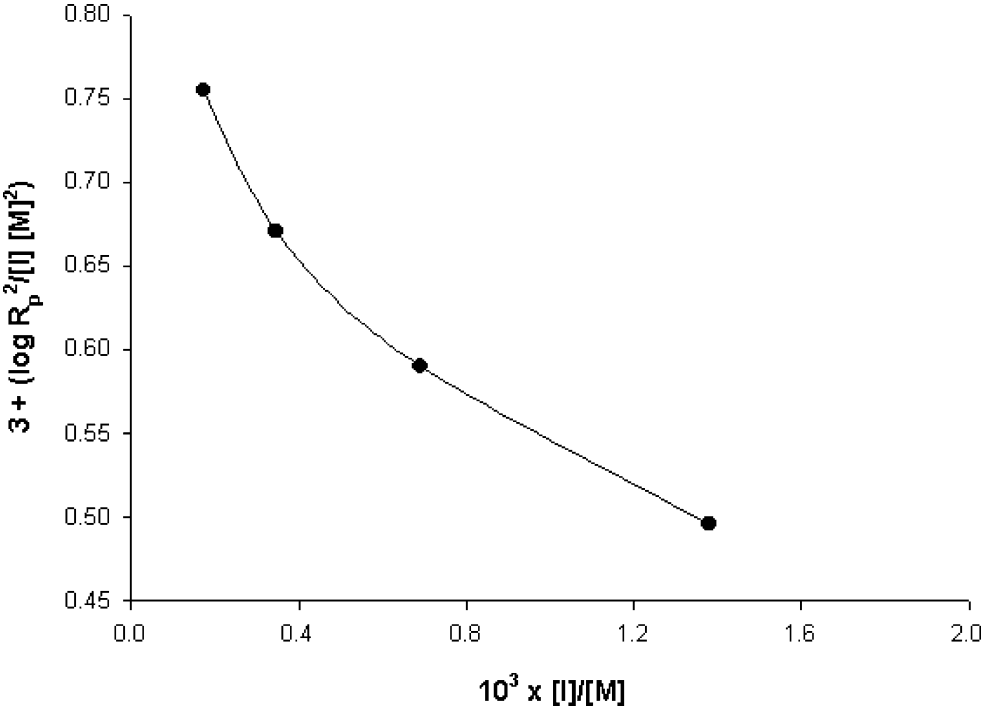


Fig. 5 Plot of $\log R_p^2/[I][M]^2$ vs $[I]/[M]$. [Sty]=8.74×10^{-3} mol; polymerization time=10 h; polymerization temperature=30±0.2 °C

where f_k represents the fraction of free radicals 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 vs $R_p/[M]^2$ gave a linear negative slope (Fig. 4), indicating significant primary radical termination along

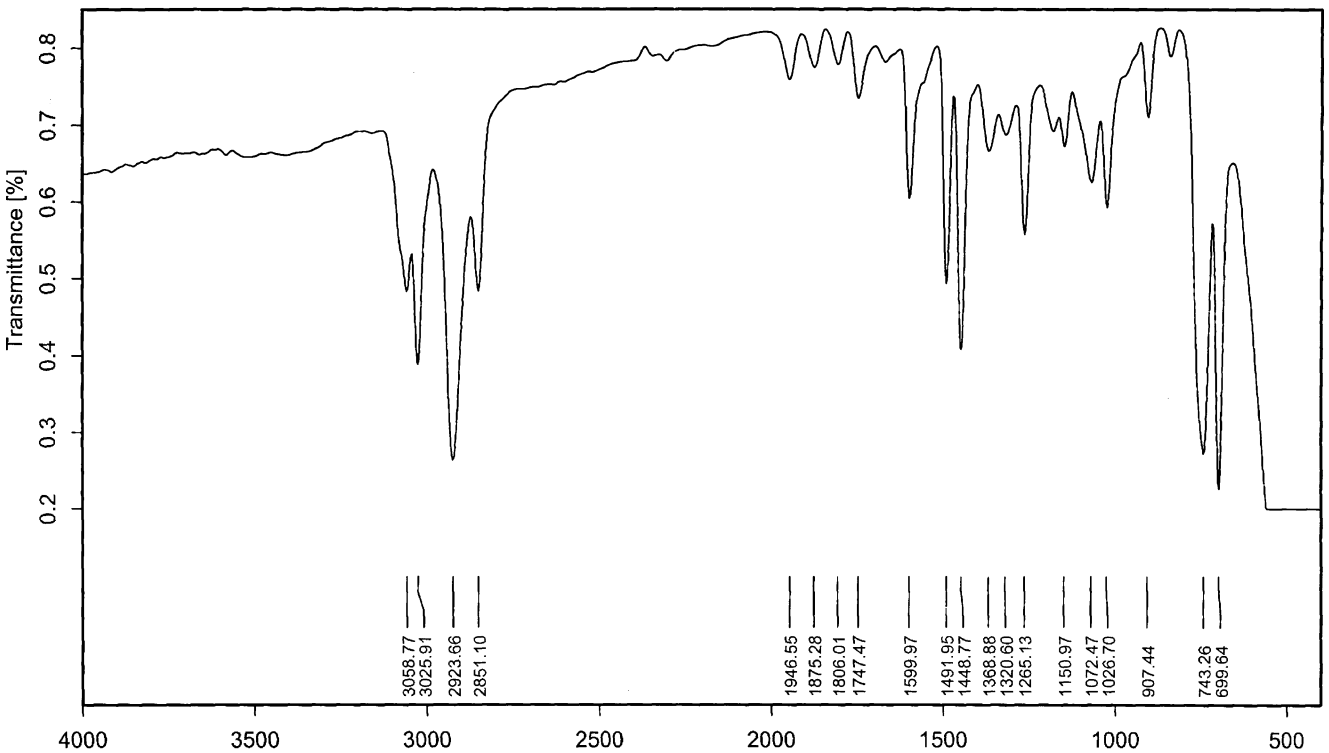
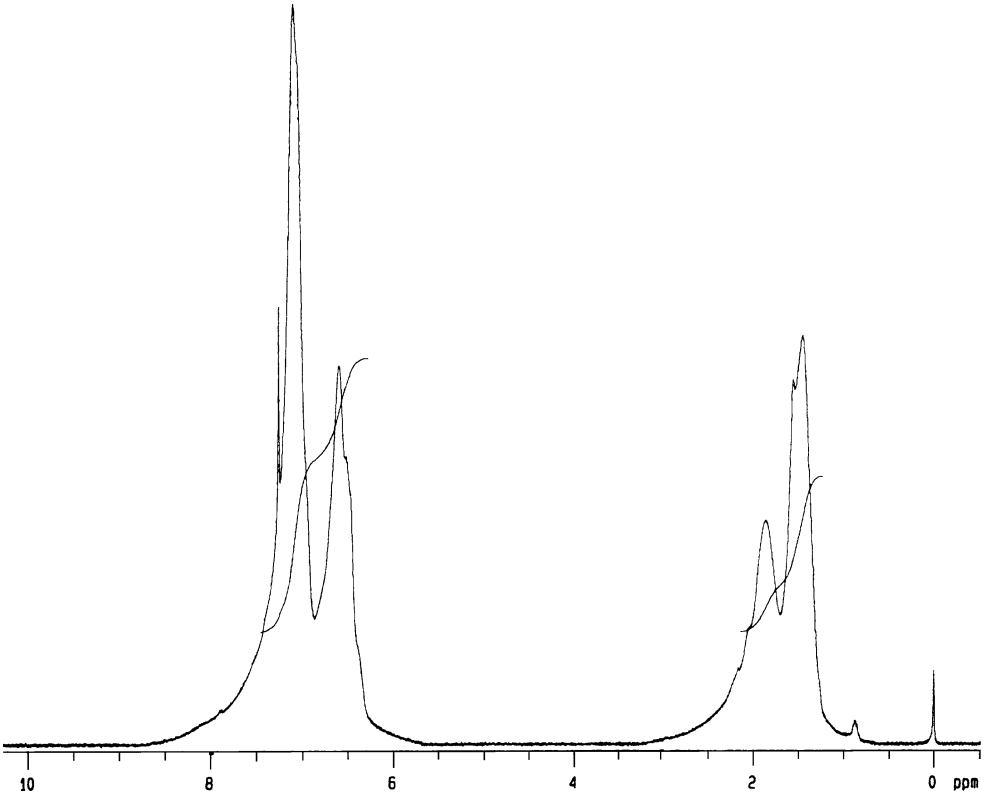


Fig. 6 FTIR spectrum

Fig. 7 ^{1}H-NMR spectrum



with simultaneous bimolecular termination. The following equation has frequently been used to examine degradative chain transfer:

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

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 vs $[I]/[M]$ gave a negative slope (Fig. 5), suggesting measurable degradative initiator transfer [29]. The non-ideality in the present system is attributed to both primary radical termination and degradative initiator transfer.

Characterization of polymer

FTIR spectroscopy

The FTIR spectrum (Fig. 6) of polymer shows the characteristic bands at 3,025 cm^{-1} due to C–H stretching of the phenyl group of styrene, at 2,923 and 2,851 cm^{-1} due to C–H stretching of methylene and methine protons, at 1,600 cm^{-1} due to conjugated C=C stretching, and at 1,448 and 1,491 cm^{-1} due to C–H deformations.

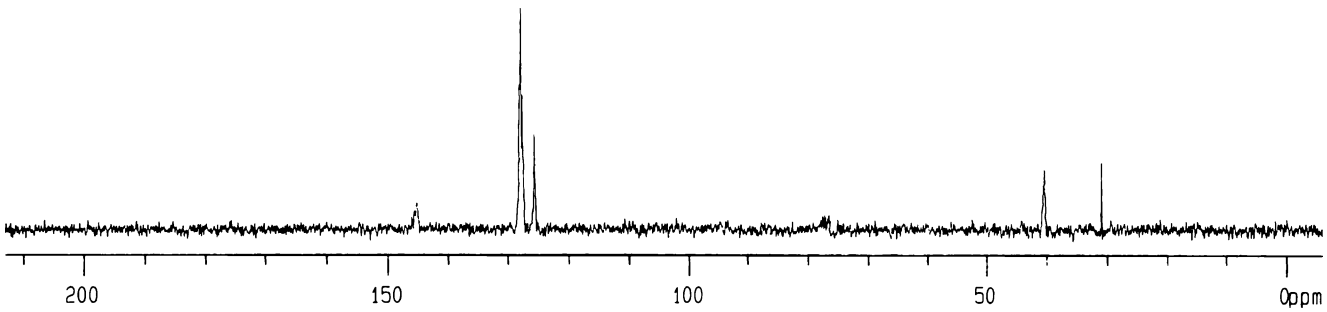


Fig. 8 ^{13}C-NMR spectrum

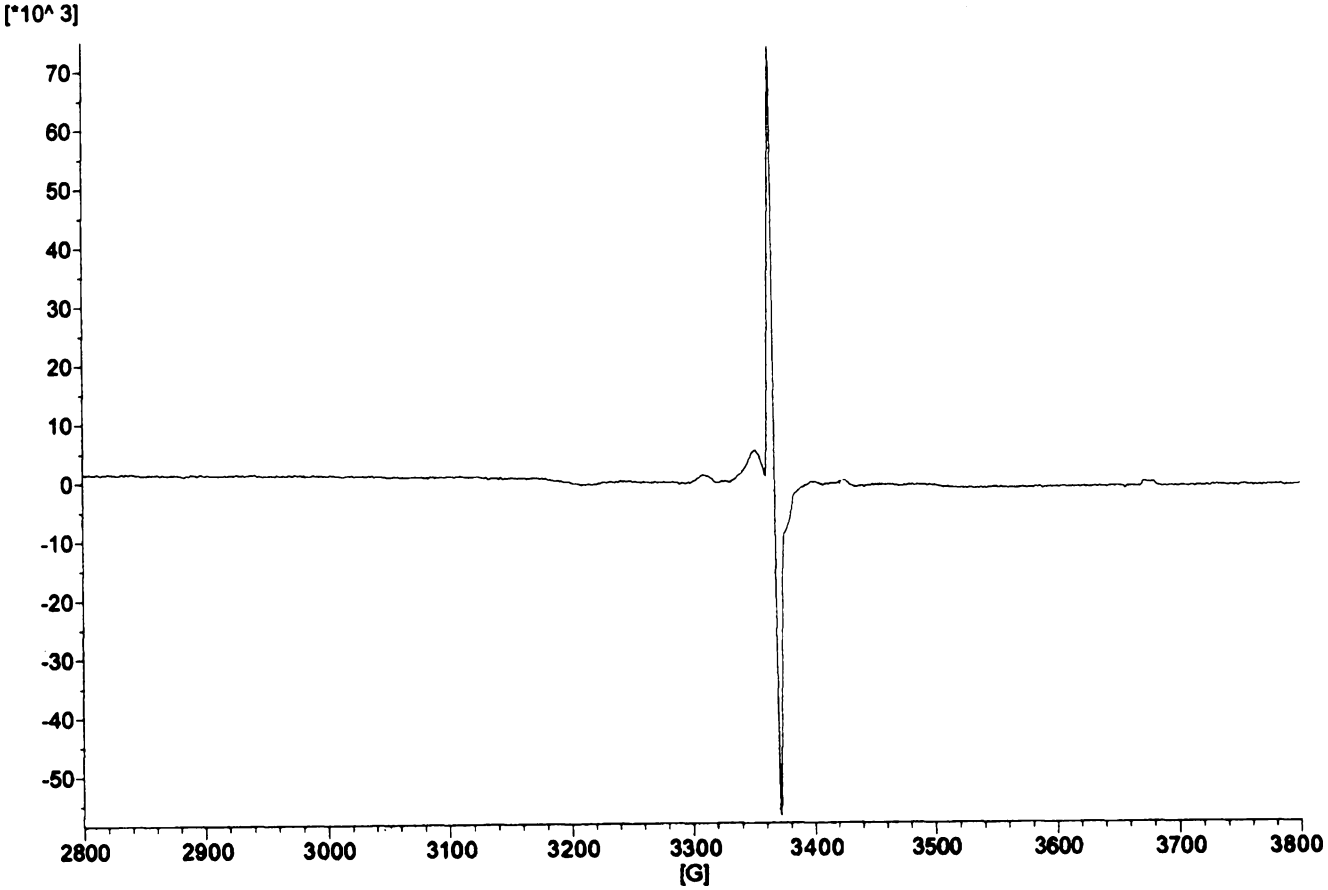


Fig. 9 ESR spectrum

^{1}H-NMR spectroscopy

In the ^{1}H-NMR spectrum (Fig. 7), the peaks due to the phenyl protons appear between 6.5–7.0 δ. Both the methylene and methine protons appear as broad peak at 1.5 and 1.86 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 [30].

^{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 [31]. 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 [30]. 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.

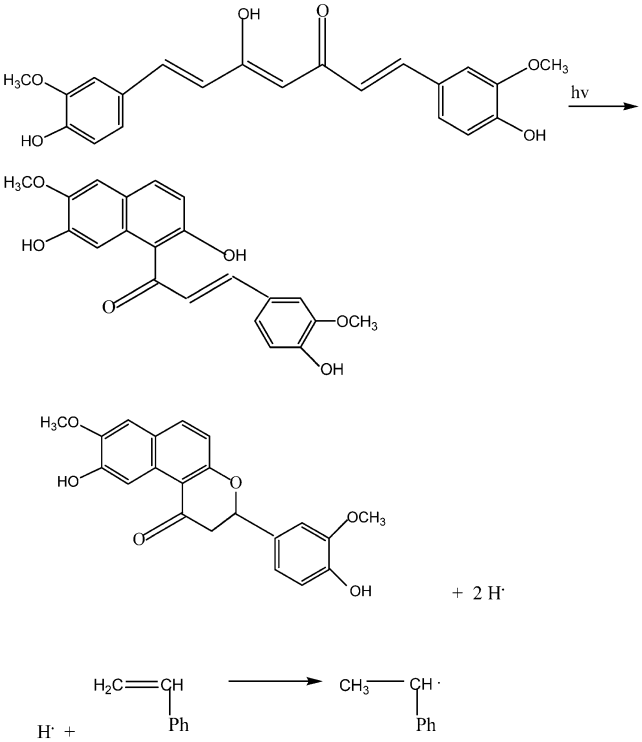
ESR spectroscopy

The spectrum (Fig. 9), taken during polymerization by quenching the propagating radical in liquid nitrogen, shows characteristic free radical absorption at 3,370 G. The presence of a C-centered radical $<g=2.005>$ followed by satellite signals due to ^{13}C ($I=1/2$) was concluded by processing the raw ESR spectrum using Bruker WINEPR system ver.2.11. The appearance of very weak signals may be accounted for the presence of traces of other radicals formed by the photodecomposition of curcumin, which partially consumed with time.

Mechanism

The inhibition to polymerization in the presence of a small quantity of hydroquinone and a single sharp peak in ESR spectrum suggest a free radical mechanism. The photodegradation products of curcumin include benzaldehyde, cinnamaldehyde, 2-hydroxy-5, 6-benzochalcone, flavanone, and some other unidentified compounds. In the formation of flavanone, the release of 2H atoms is involved [32, 33]. Considering the

above facts, the proposed mechanism of polymerization involving initiation by H atom is as follows (Scheme 1):



Scheme 1 Proposed mechanism of polymerization involving initiation by H atom

Conclusions

The photopolymerization of styrene, in presence of curcumin, an unexplored free radical photoinitiator, from reproducible resource has been studied. Curcumin served as an efficient photoinitiator, as its catalytic concentrations (10^{-6} M) initiated the polymerization. Both primary radical termination and degradative chain transfer reactions were thought to be responsible for the kinetic non-idealities. The formation of H radicals from curcumin to initiate polymerization was proposed.

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