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Curcumin, A Novel Natural Photoinitiator for the Copolymerization of Styrene and Methylmethacrylate

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Curcumin (Cur), a natural colorant found in the roots of the Turmeric plant, has been reported for the first time as photoinitiator for the copolymerization of styrene (Sty) and methylmethacrylate (MMA). The kinetic data, inhibiting effect of benzoquinone and ESR studies indicate that the polymerization proceeds via a free radical mechanism. The system follows ideal kinetics ($R_p\ \alpha[Cur]^{0.5}[Sty]^{0.97}[MMA]^{1}$). The reactivity ratios calculated by using the Finemann–Ross and Kelen-Tudos models were $r_1(MMA) = 0.46$ and $r_2(Sty) = 0.52$. IR and NMR analysis confirmed the structure of the copolymer. NMR spectrum showing methoxy protons as three distinct groups of resonance between 2.2–3.75 δ and phenyl protons of styrene at 6.8–7.1 δ confirmed the random nature of the copolymer. The mechanism for formation of radicals and random copolymer of styrene and MMA [Sty-co-MMA] is also discussed.

Keywords photopolymerization, curcumin, Sty-co-MMA, NMR, ESR

Introduction

Photopolymerization, the utilization of electromagnetic radiation as the energy source for polymerization of functional monomers, oligomers, and polymers, is the basis of important commercial processes with broad applicability (1–4). The traditional way to initiate polymerization has been by direct photolysis of a precursor that provides free radicals by direct bond scission. Photoinduced intermolecular electron transfer represents an alternative (5). Progress in the chemistry of photopolymerizable compounds results not only from the development of new and novel monomers but also from new initiators. Development of improved and more efficient photoinitiators and photosensitizers is likely to upgrade the existing technologies.

Initiators, such as 3-methoxy carbonyl–3-methyl-2, 2,5,5-tetraphenylhexanedinitrile (6), trialkyl boron organometallic peroxide (7), 4-[diphenyl (trimethyl silyl) methyl] benzophenone (8), peroxypivalate (9), several ylides (10, 11), zinc chloride (12) are among those recently reported for copolymerization of MMA with Sty. Colorants make up a large class of molecules extensively used to start or sensitize the polymerization of

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monomers (13). The studies related to dyeing with natural colorants have attracted the attention of the textile experts, but the use of these natural dyes/pigments in photopolymerization reactions is rarely reported in the scientific literature (14–16).

In the present communication, we highlight the use of Curcumin, bis(4-hydroxy-3-methoxyphenyl)-1,6-diene-3,5-dione, a yellow-orange dye derived from the rhizome of the plant Curcuma longa, as a novel natural photoinitiator for copolymerizing Sty with MMA. The results of kinetic investigations and mechanism have been discussed.

Experimental

Materials

Reagent grade MMA (Merck-Schuchardt), Sty (Merck-Schuchardt) and other solvents were purified by the usual methods (17, 18) and distilled under vacuum before use. Curcumin (Aldrich) [M = 368.39 gm/mole, m.p. = 182°C] was used as received. Hydroquinone was recrystallized twice from methanol.

Photopolymerization Procedure

The required amounts of monomers and curcumin dissolved in a drop of DMSO were charged into a quartz tube. This tube was degassed under vacuum by the conventional freeze and thaw technique and sealed off under vacuum. This reaction mixture was irradiated in a photochemical reactor containing eight 253 nm U.V. tubes (8 W each, path length = 10 cm), arranged in a circular fashion, for known periods of time at 30°C. The incident light intensity as measured by Lutron Lux Meter Model No. LX-101 was found to be 3.68×10^3 Lux. After irradiation, the contents were poured into excess methanol and the precipitated polymer was washed with acidified methanol. After two reprecipitations from methanol, the polymers were dried in vacuum oven at 60°C for 24 h. In order to check the possible formation of homopolymers, copolymer samples were extracted in a Soxhlet extraction apparatus with cyclohexane, which is a solvent for polystyrene and then with acetonitrile, which is a solvent for polymethylmethacrylate (19). The copolymers were finally dried to constant weight. No measurable weight loss was observed. The rates of copolymerization (R_p) were calculated by the following equation (20):

$$R_p(\mathrm{mol\,L^{-1}\,s^{-1}}) = \frac{0.7515 \times C \times 10^{-3}}{t}$$

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

Characterization

The IR and NMR 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 E.S.R. spectrum was recorded on an X-band Bruker EMX-EPR Spectrometer (Model 1444) at liquid N_2 temperature (Center Field: 3300 G, sweep width: 1000 G, Mod. Amplitude: 10 G, sweep time: 671.089 s, Microwave power: 0.201 mW). The intrinsic viscosity $[\eta]$ of the copolymers was measured in benzene at 30°C using an Ubbelohde viscometer, and is expressed in deciliters per gram. The average degree of polymerization $\overline{P}_n$ was calculated by the following equation (21):

$$[\eta] = 5.76 \times 10^{-3}\overline{P}_n 0.746$$

Results and Discussion

Polymerization of styrene was observed up to 0.4–0.6% conversion by the light employed even in the absence of initiator, the data in Tables 1 and 2 present % conversion after having deducted the yield for blank experiments.

Effect of Initiator Concentration

Table 1 reveals the relationship between percent conversion and curcumin concentration for a fixed monomer feed ratio. The R_p increases with increasing curcumin concentration from 4.07×10^{-4} mol/L to 1.085×10^{-3} mol/L, keeping [Sty] and [MMA] constant. The initiator exponent calculated from the slope of the plot of log R_p vs. log [Cur] is 0.5 (Figure 1). The average degree of polymerization ($\overline{P}_n$) of copolymers decreases on increasing [Cur]. The value of the initiator exponent and the observation that the plot of reciprocal average degree of polymerization ($\overline{P}_n$) against the square root of the initiator concentration gives a straight line passing through the origin (Figure 2), suggest radical polymerization with bimolecular termination.

Effect of Comonomer Concentration

The effect of MMA concentration on R_p is studied by varying [MMA] from 2.35 mol/L to 4.7 mol/L, keeping [Cur] and [Sty] constant. Similarly, the effect of [Sty] on R_p was studied by varying its concentration from 2.33 mol/L to 4.37 mol/L, keeping [Cur] and [MMA] constant (Table 2). It is noteworthy that R_p increases as the monomer increases in both cases. The exponent value, calculated from the slope of the linear plot of log R_p vs. log [MMA] (Figure 3) and log R_p vs. log [Sty] (Figure 4) are 1 and 0.97, respectively.

Table 1

Effect of [Cur] on $R_{p.}$ [MMA] = 4.7 mol/L; [Sty] = 4.37 mol/L; polymerization time = 7 h; polymerization temp. = 30 ± 0.2°C

Serial no.	[Cur] × 10^4 (mol/L)	% conversion	$R_p \times 10^6$ (mol/L/s)	$\overline{P}_n$
1	4.07	2.04	3.64	425
2	5.43	2.31	4.14	363
3	6.78	2.61	4.67	327
4	8.14	2.88	5.15	294
5	9.5	3.1	5.55	277
6	10.58	3.3	5.9	263

Table 2
Effect of [MMA] and [Sty] on R_p. [Cur] = 6.78×10^{-4} mol/L; polymerization time = 7 h; polymerization temp. = 30 ± 0.2°C

Serial no.	[MMA] (mol/L)	[Sty] (mol/L)	% conversion	$R_p \times 10^6$ (mol/L/s)
1	2.35	4.37	1.31	2.355
2	2.73	4.37	1.51	2.704
3	3.58	4.37	2.0	3.59
4	4.7	4.37	2.61	4.677
5	4.7	2.33	1.42	2.541
6	4.7	2.93	1.74	3.126
7	4.7	3.19	1.9	3.404

Characterization of Copolymers

Spectral Analysis

Infrared spectroscopy. The IR spectrum (Figure 5) of copolymer shows band at 3020–3060 cm^{-1} due to aromatic C–H str vibrations, 2926 and 2852 cm^{-1} due to C–H str vibrations of methyl, methylene, and methine groups, 1731 cm^{-1} due to >C=O str vibrations of ester carbonyl, 1600–1630 cm^{-1} due to aromatic C=C str vibrations, 1450–1380 cm^{-1} due to C–H deformation bands, 1140–1190 cm^{-1} due to C–O–C str vibrations.

NMR spectroscopy. In the NMR spectrum of copolymer (Figure 6), phenyl protons appear at 6.8–7.1 δ, methyl protons at 0.5–0.6 δ and the region of ester methyl protons (2.2–3.75 δ) is split into three distinct groups of resonances assigned to the different configurational sequences on the basis of phenyl ring current shielding of the methoxy protons by the adjacent styrene units. The resonances appear to be broad, but this is mainly

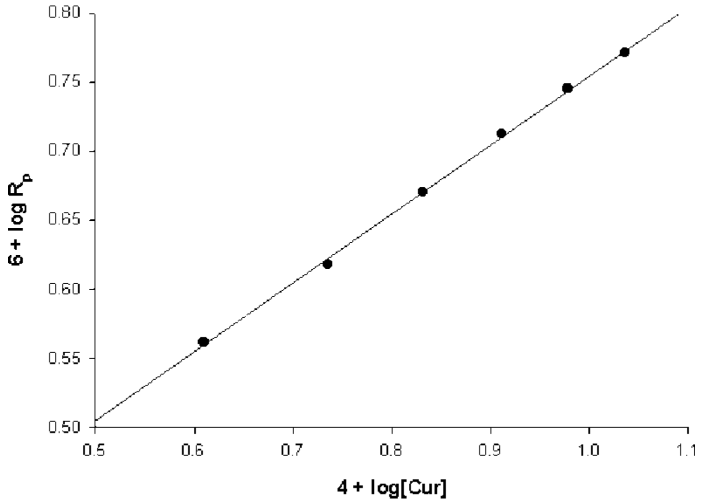


Figure 1. Plot of log [Cur] on log R_p. [MMA] = 4.7 mol/L; [Sty] = 4.37 mol/L; polymerization time = 7 h; polymerization temp. = 30 ± 0.2°C.

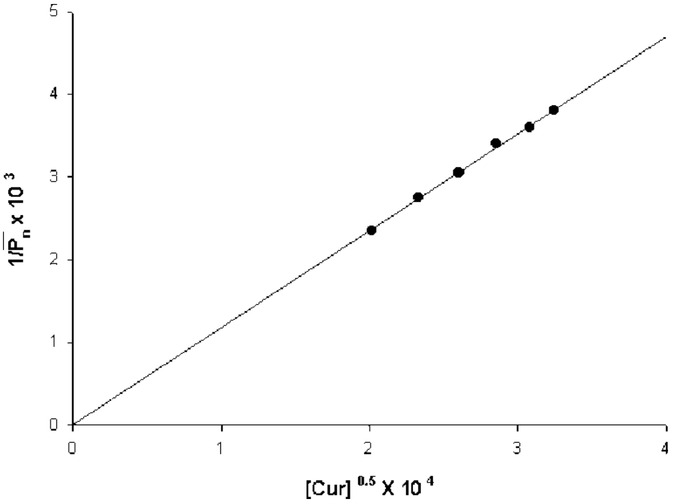


Figure 2. Plot of $1/\overline{P}_n$ vs. $[Cur]^{0.5}$. [MMA] = 4.7 mol/L; [Sty] = 4.37 mol/L; polymerization time = 7 h; polymerization temp. = 30 ± 0.2°C.

because of a multitude of chemical shifts corresponding to the many possible sequences present in the random copolymer (22).

NMR spectra for both alternating and random copolymers of Sty and MMA show the split peaks for methoxy protons. The difference in peaks of methoxy protons of alternating and random copolymers is that the split peaks are quite sharp in the case of alternating copolymers as compared to that of random copolymers (22). In Figure 6, the methoxy protons peaks suggest the random nature of copolymer. Moreover, the presence of the ^{1}H-NMR signals for the MMA---MMA---syn---Sty triad (δ 3.5 ppm) and the MMA---MMA---MMA triad (δ 3.6 ppm) further confirm the random nature of copolymer (23). The term syn denotes the cosyndiotactic dyad.

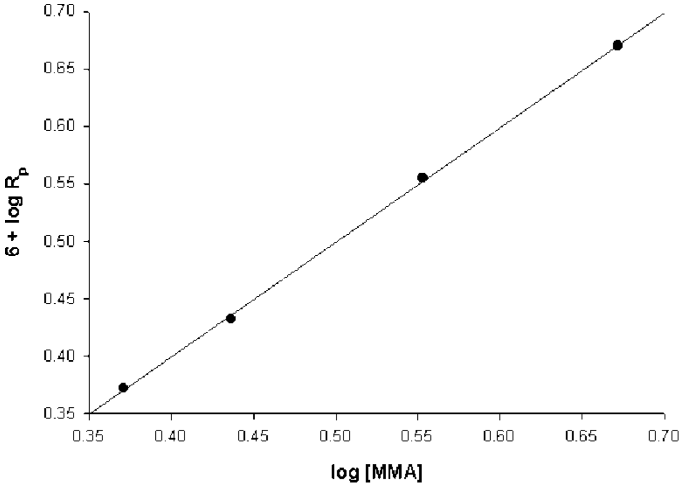


Figure 3. Plot of log [MMA] vs. log R_p. [Cur] = 6.78×10^{-4} mol/L; [Sty] = 4.37 mol/L; polymerization time = 7 h; polymerization temp. = 30 ± 0.2°C.

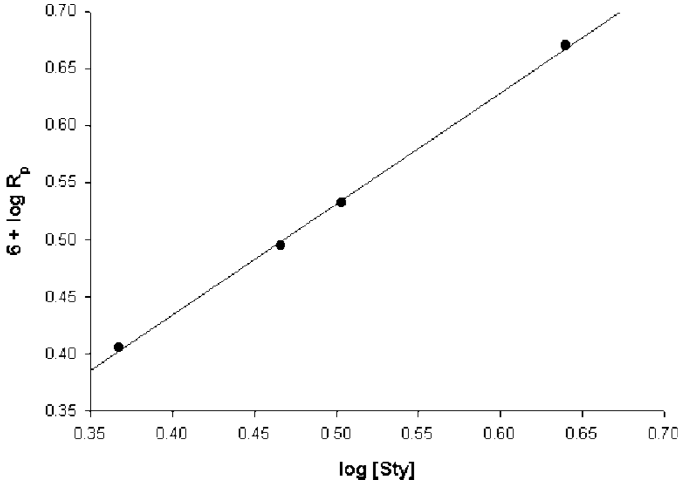


Figure 4. Plot of log [Sty] vs. log R_p. [Cur] = 6.78×10^{-4} mol/L; [MMA] = 4.7 mol/L; polymerization time = 7 h; polymerization temp. = 30 ± 0.2°C.

Copolymer Composition and Monomer Reactivity Ratio

The relative peak areas due to phenyl and α-methyl protons (Table 3) have been used to calculate copolymer composition (24). The Finemann–Ross (25) equation is one of the earliest attempts to linearize the copolymer composition equation:

$$G = r_1F - r_2 \tag{1}$$

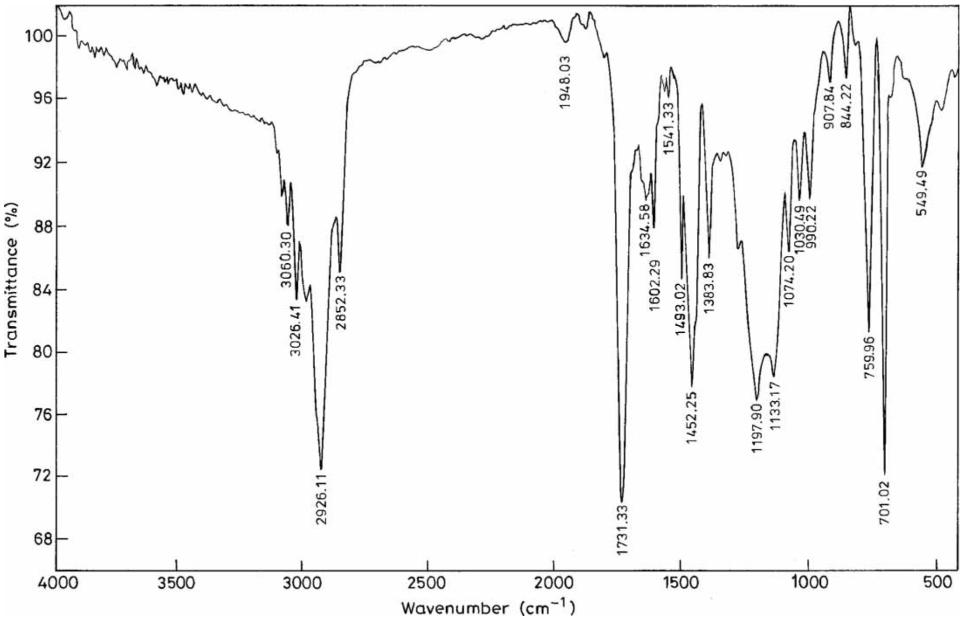


Figure 5. IR spectrum.

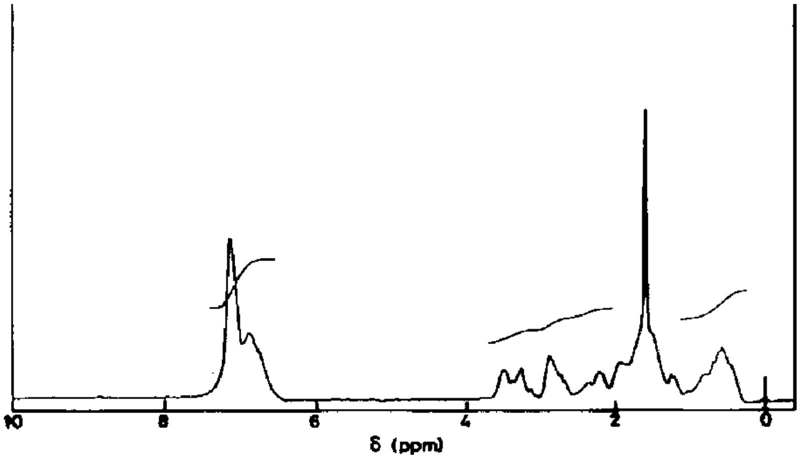


Figure 6. NMR spectrum. [MMA] = 4.7 mol/L; [Sty] = 4.37 mol/L; [Cur] = 6.78 × 10^{-4} mol/L; polymerization time = 7 h; polymerization temp. = 30 ± 0.2°C.

where,

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

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

Kelen-Tudos (26) introduced new parameters into the linearized copolymerization equation, such as η, ξ and α:

$$\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha \tag{2}$$

where,

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

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 Figures 7 and 8, respectively. The reactivity ratios as calculated by FR and KT methods are r_1 [MMA] = 0.46 and r_2 [Sty] = 0.52. Since r_1 and r_2 are both <1 and r_1 nearly equal to

Table 3
Copolymer composition

Serial no.	Molar ratio in monomer feed [MMA]/[Sty](X)	Conversion %	Molar ratio in copolymer [MMA]/[Sty](Y)
1	0.626	1.51	0.709
2	1.079	2.61	1.01
3	1.475	1.9	1.247
4	1.604	1.74	1.313
5	2.01	1.42	1.54

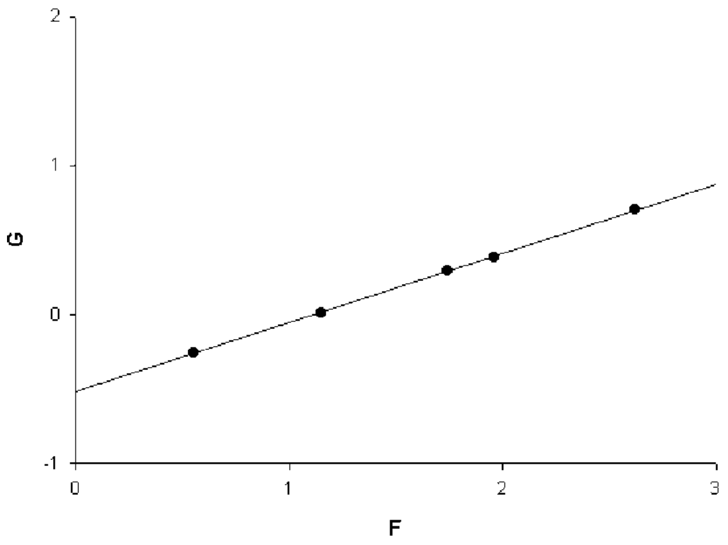


Figure 7. Finemann–Ross plot.

r_2, at equimolar feed ratio, the copolymer is expected to have equal number of Sty and MMA units, but arranged in a random sequence (27).

E.S.R Spectroscopy

The spectrum (Figure 9) taken during polymerization by quenching the propagating radical in liquid nitrogen shows characteristic free radical absorption at 3370 G. The propagating radical with MMA at the end suggests there is just one signal in the spectrum. The humps seen in the spectrum cannot be considered as splitting or hyper-fine lines. The

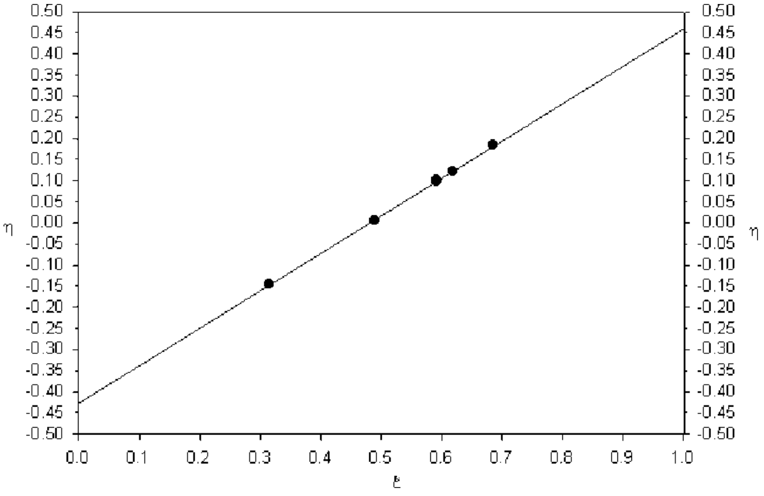


Figure 8. Kelen-Tudos plot.

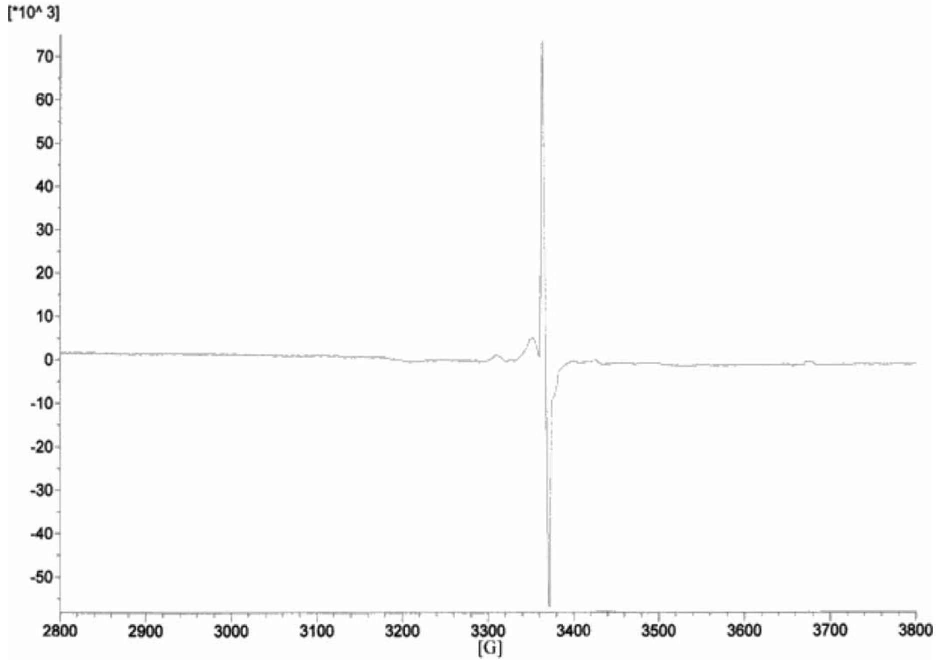


Figure 9. ESR spectrum.

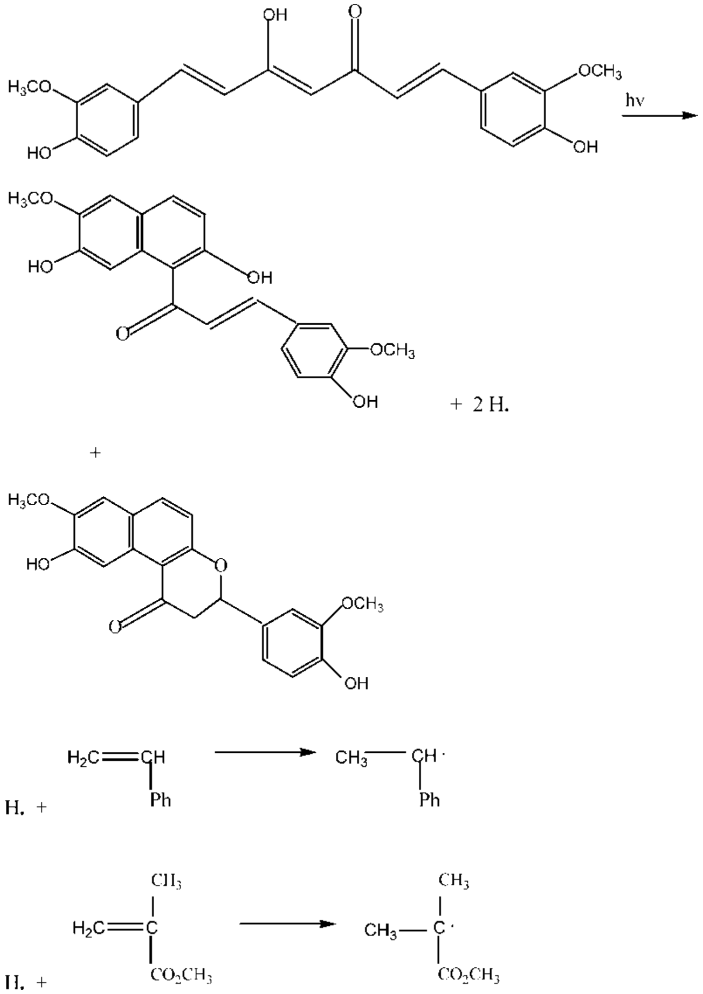
presence of a C centered radical ⟨g = 2.003⟩ followed by satellite signals due to ^{13}C (I = 1/2) was concluded by processing the raw ESR spectrum using a Bruker WINEPR system ver.2.11. The appearance of very weak signals may account for the presence of other trace radicals formed by the photodecomposition of curcumin, which are partially consumed with time.

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 (28, 29). We propose a mechanism of copolymerization involving initiation by H atom depicted as follows (Scheme 1).

Conclusions

Curcumin, an unexplored free radical photoinitiator, from reproducible resource proved efficient for copolymerization of Sty with MMA. NMR studies suggested the random nature of the copolymer. The kinetic data and ESR studies indicate that the copolymerization proceeds via a free radical mechanism. The plausible mechanism of copolymerization suggested the formation of H radical, which initiated the reaction.



Scheme 1.

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