

Synthesis and Characterization of Copolymer of Styrene with Methacrylic Acid Initiated by Triphenylbismuthonium 1,2,3,4-Tetraphenylcyclopentadienylide

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ABSTRACT: The radical copolymerization of styrene with methacrylic acid (MAA) initiated by triphenylbismuthonium 1,2,3,4-tetraphenylcyclopentadienylide in dioxan at 80 ± 0.1 °C for 3 h results in the formation of alternating copolymer as evidenced from the values of reactivity ratios as r_1 (styrene) = 0.03 and r_2 (MAA) = 0.025. The kinetic expression is $R_p \propto [I]^{0.5} [\text{Sty}] [\text{MAA}]$ and overall energy of activation is computed to be 23 kJ/mol. The FTIR spectrum of the copolymer shows the presence of bands at 3054 cm^{-1}

assigned to the phenyl group of styrene and at 1724 cm^{-1} assigned to the $-\text{COOH}$ group of MAA. The $^1\text{H-NMR}$ spectrum of the copolymer shows peaks between 7.20 and 7.27 δ assigned to the phenyl protons of styrene and at 12.5 δ assigned to the COOH proton of MAA. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1838–1843, 2005

Key words: activation energy; FTIR; viscosity

INTRODUCTION

Methacrylic acid (MAA) copolymerizes readily with other monomers. Their versatility arises from the combination of their highly reactive double bonds and their miscibility with both water-soluble and oil-soluble monomers. The copolymers of MAA, because of its unique properties like adhesion and water sensitivity, have been widely used in adhesives, mining, textiles and paper manufacture, oil-well drilling, secondary oil recovery, agriculture soil modification, and water classification.

A literature survey shows that the copolymerization of MAA with butyl acrylate,¹ *N,N'*-ethylene dimethacrylamide,² acrylonitrile,³ and vinylidene chloride,⁴ using AIBN/BPO as the radical initiator, has been carried out. However, insufficient literature is available on the copolymerization of MAA with styrene using ylide as the radical initiator.

Ylides are 1,2-dipolar compounds in which a carbanion is attached directly to a heteroatom bearing a positive charge ($> \overset{\ominus}{\text{C}}-\overset{\oplus}{\text{X}}$, where, X = N, P, As, S, Bi, Se, Te). The properties of ylides are very much dependent on the identity of the heteroatoms.⁵ The use of ylides containing N,⁶ P,⁷ S,⁸ As,⁹ and Sb¹⁰ as heteroatom in the domain of polymer science are sufficient and those

containing Bi as heteroatom are rare, e.g., the homopolymerization of methyl methacrylate,¹¹ styrene,¹² methyl acrylate,¹³ and copolymerization of styrene and methyl methacrylate.¹⁴ Therefore, this paper reports the copolymerization of MAA with styrene using triphenylbismuthonium 1,2,3,4-tetraphenylcyclopentadienylide as the radical initiator.

EXPERIMENTAL

Materials

Reagent grade styrene (Merck-Schuchardt) was purified by the standard methods^{15,16} followed by vacuum distillation before polymerization. Methacrylic acid (Merck-Schuchardt) was used as such. Triphenylbismuthonium 1,2,3,4-tetraphenylcyclopentadienylide was synthesized by the method given by Lloyd and Glidewell.¹⁷

Polymerization procedure

Dilatometric technique was used to follow the copolymerization runs under oxygen-free conditions. Copolymerization in dioxan at 80 °C was continued up to 3 h to limit the percentage conversion up to 10%. The polymer, isolated with benzene and dried under vacuum, was treated with cyclohexane and methanol to remove polystyrene and polymethacrylic acid, respectively. Finally, the copolymer was dried to constant weight and the percentage conversion was calculated.

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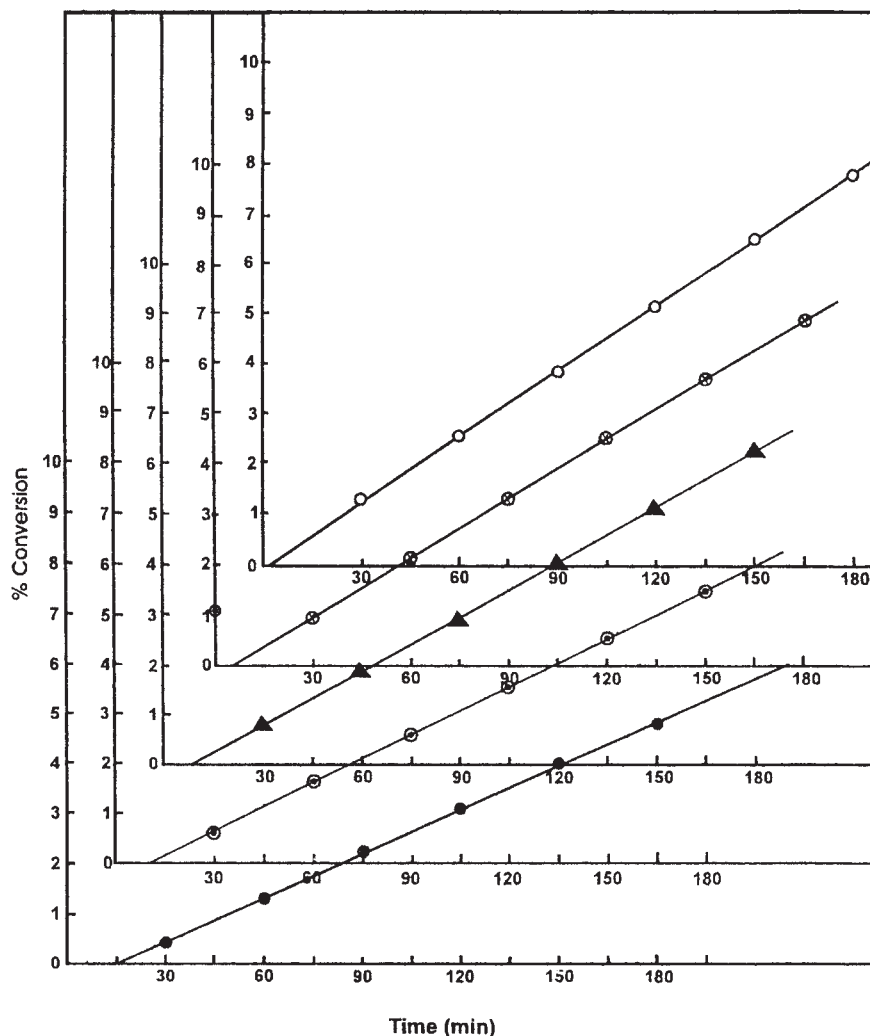


Figure 1 Relationship between percentage conversion and time(min). [Sty] = 2.019 mol L⁻¹; [MAA] = 1.937 mol L⁻¹; [ylide] ● = 4.1 × 10⁻⁶ mol L⁻¹; ○ = 12.50 × 10⁻⁶ mol L⁻¹; ▲ = 20.90 × 10⁻⁶ mol L⁻¹; ⊗ = 29.30 × 10⁻⁶ mol L⁻¹; ○ = 37.60 × 10⁻⁶ mol L⁻¹; copolymerization time = 180 min; copolymerization temperature = 80 ± 0.1 °C.

The rate of polymerization (R_p) was calculated from the slope of the graph between the percentage conversion and time. The intrinsic viscosity $[\eta]$ of the copol-

TABLE I
Effect of Ylide Concentration on the Rate of Copolymerization of Styrene with Methacrylic Acid

Sample	[Ylide] × 10 ⁶ (mol L ⁻¹)	Conversion (%)	R_p × 10 ⁶ (mol L ⁻¹ s ⁻¹)	$[\eta]^a$ (dL/g)
1	4.10	4.8	1.842	0.184
2	12.50	5.5	2.171	0.178
3	20.90	6.2	2.632	0.166
4	29.30	6.8	3.290	0.156
5	37.60	7.7	3.488	0.140

Note. Copolymerization time, 3 h; copolymerization temperature, 80 ± 0.1 °C; [Styrene], 2.019 mol L⁻¹; [MAA], 1.93 mol L⁻¹.

^a Temperature, 30 °C.

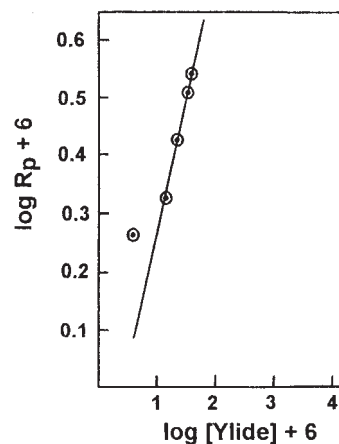


Figure 2 Relationship between the rate of copolymerization and [ylide]. [Sty] = 2.019 mol L⁻¹; [MAA] = 1.937 mol L⁻¹, copolymerization time = 180 min; copolymerization temperature = 80 ± 0.1 °C.

TABLE II
Effect of Concentration of the Comonomer on the Rate of Copolymerization

Sample	[Sty] (mol L ⁻¹)	[MAA] (mol L ⁻¹)	Conversion (%)	$R_p \times 10^6$ (mol L ⁻¹ s ⁻¹)	$[\eta]^a$ (dL/g)
6	0.255	1.937	4.6	1.072	0.114
7	0.865	1.937	5.1	1.304	0.142
8	1.442	1.937	5.7	1.854	0.154
3	2.019	1.937	6.2	2.632	0.166
9	2.596	1.937	7.8	3.313	0.172
10	2.019	0.387	4.9	1.114	0.102
11	2.019	1.162	5.8	1.749	0.120
3	2.019	1.937	6.2	2.632	0.166
12	2.019	2.713	8.0	3.940	0.320
13	2.019	3.455	9.3	5.048	0.326

Note. Copolymerization time, 3 h; copolymerization temperature, 80 ± 0.1 °C; $[\text{Ylide}] = 20.90 \times 10^{-6}$ mol L⁻¹.

^a Temperature, 30 °C.

mer, determined in tetrahydrofuran at 25 °C using an Ubbelohde viscometer, is expressed in deciliters per gram.

The FTIR spectrum was recorded with a Perkin-Elmer 599B (with KBr pellets) spectrophotometer and the ¹H-NMR spectrum was recorded with a Varian 100 HA Joel 400 LA spectrophotometer using CDCl₃ as a solvent and tetramethylsilane as an internal reference. The monomer reactivity ratios were determined using the Kelen-Tüdös method.¹⁸

RESULTS AND DISCUSSION

The kinetics of copolymerization was studied by varying $[\text{ylide}]$ from 4.1×10^{-6} mol L⁻¹ to 37.6×10^{-6} mol L⁻¹, $[\text{styrene}]$ from 0.288 to 2.596 mol L⁻¹, and $[\text{MAA}]$

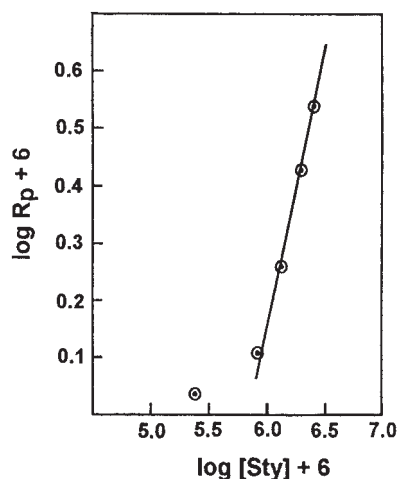


Figure 3 Relationship between the rate of copolymerization and $[\text{Sty}]$. $[\text{Ylide}] = 20.90 \times 10^{-6}$ mol L⁻¹; $[\text{MAA}] = 1.1937$ mol L⁻¹, copolymerization time = 180 min; copolymerization temperature = 80 ± 0.1 °C.

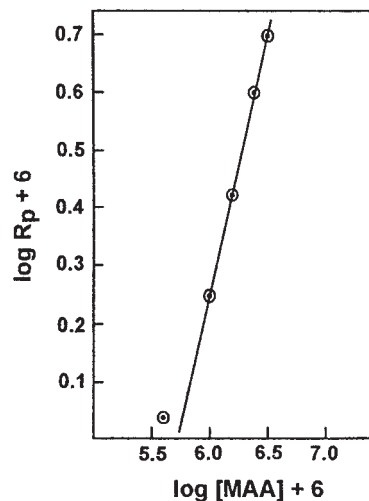


Figure 4 Relationship between the rate of copolymerization and $[\text{MAA}]$. $[\text{Ylide}] = 20.90 \times 10^{-6}$ mol L⁻¹; $[\text{Sty}] = 2.019$ mol L⁻¹, copolymerization time = 180 min; copolymerization temperature = 80 ± 0.1 °C.

from 0.357 to 3.455 mol L⁻¹. The reaction proceeds with a induction period of 3–15 min (Fig. 1).

Effect of initiator concentration

The effect of $[\text{ylide}]$ on R_p was studied by varying the $[\text{ylide}]$ from 4.1×10^{-6} mol L⁻¹ to 37.6×10^{-6} mol L⁻¹, keeping $[\text{styrene}]$ and $[\text{MAA}]$ constant at 2.019 and 1.93 mol L⁻¹, respectively. It is clear that the R_p is a direct function of $[\text{ylide}]$ and the exponent value of initiator, obtained from a linear graph of $\log R_p$ vs. $\log [\text{ylide}]$ is 0.5 (Table I, Fig. 2).

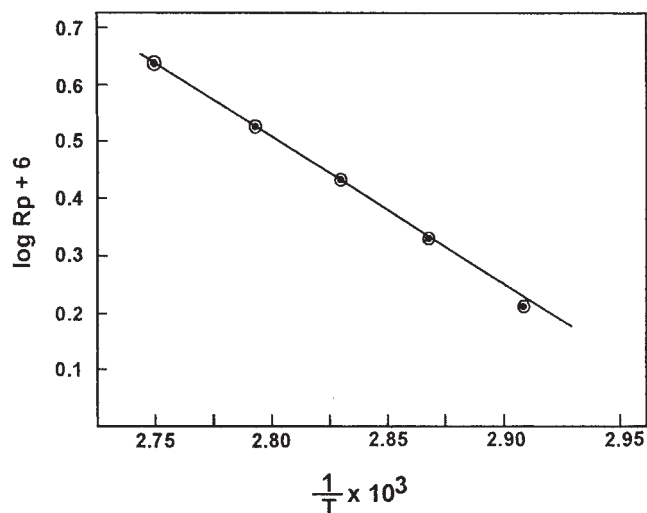


Figure 5 Arrhenius plot of the rate of copolymerization and copolymerization temperature. $[\text{Ylide}] = 20.90 \times 10^{-6}$ mol L⁻¹; $[\text{Sty}] = 2.019$ mol L⁻¹; $[\text{MAA}] = 1.937$ mol L⁻¹, copolymerization time = 180 min.

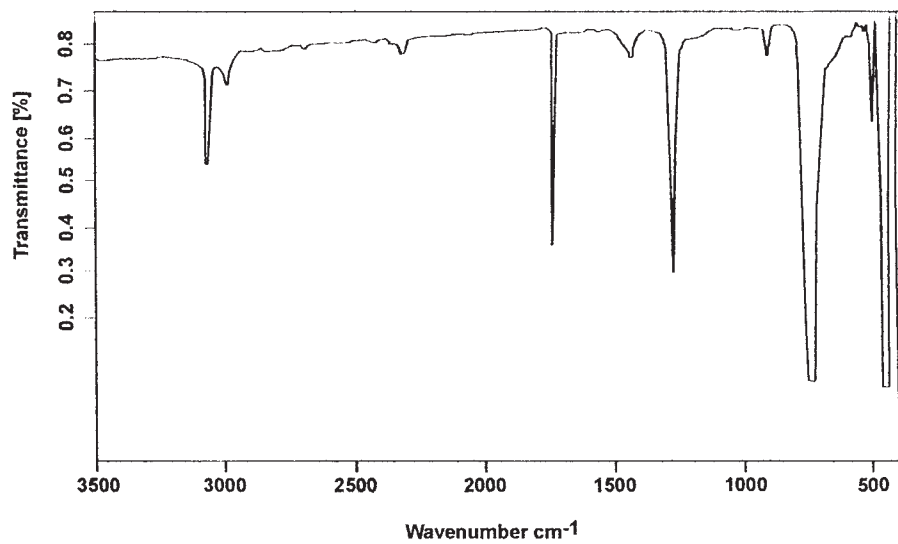


Figure 6 FTIR spectrum of copolymer (sample 3).

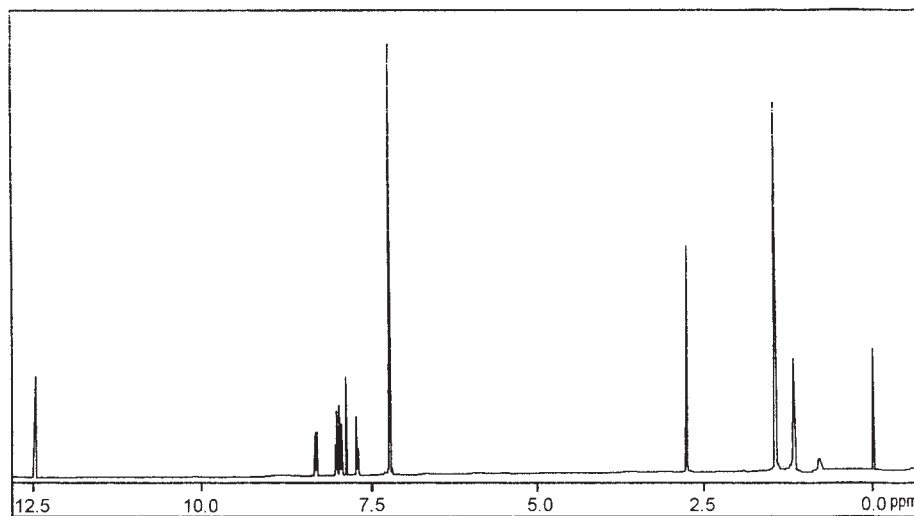


Figure 7 ¹H-NMR spectrum of copolymer (sample 3).

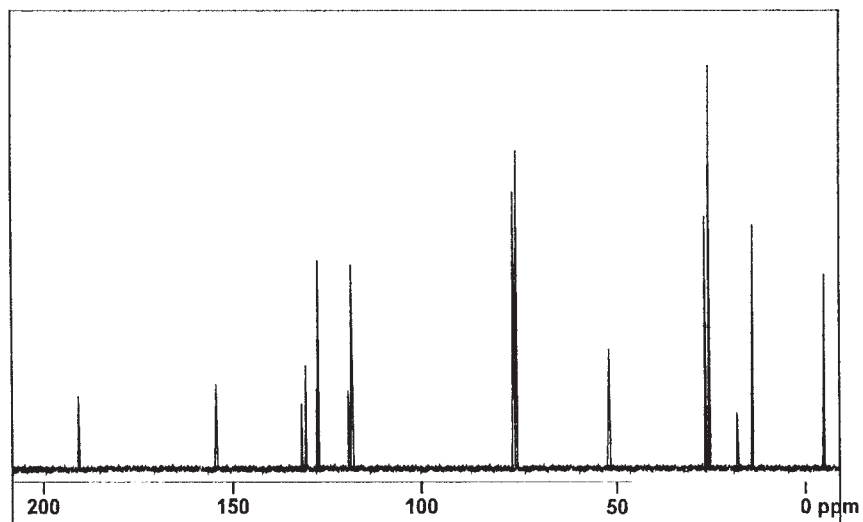


Figure 8 ¹³C-NMR spectrum of the copolymer (sample 3).

TABLE III
Copolymer Composition

Sample	Molar ratio in monomer feed [Sty/MAA] (F)	Conversion (%)	Mole fraction of [Sty] in copolymer	Mole fraction of [MAA] in copolymer	Molar ratio in copolymer [Sty/MAA] (f)
8	0.744	5.7	0.504	0.495	1.02
3	1.042	6.2	0.514	0.485	1.05
9	1.345	7.8	0.509	0.490	1.03
11	1.737	5.8	0.511	0.488	1.04
12	0.744	8.0	0.522	0.477	1.09

Effect of comonomer concentration

The effect of [styrene] on the R_p was studied by varying the [styrene] from 0.288 mol L⁻¹ to 2.596 mol L⁻¹, while [MAA] and [ylide] were kept constant at 1.93 mol L⁻¹ and 20.9×10^{-6} mol L⁻¹, respectively. The R_p is a direct function of [styrene]. A plot of log R_p vs. log [styrene] is linear and the order of reaction with respect to styrene is unity (Table II, Fig. 3).

The effect of [MAA] was studied by varying the [MAA] from 0.357 to 3.455 mol L⁻¹ while [styrene] and [ylide] were kept constant at 2.019 mol L⁻¹ and 20.9×10^{-6} mol L⁻¹, respectively. The R_p is a direct function of [MAA]. A plot of log R_p vs. log [MAA] is linear and the order of reaction with respect to MAA is unity (Fig. 4).

Effect of temperature

Polymerization runs were also carried out at 70, 75, 85, and 90 °C to evaluate the energy of activation because no polymerization occurred below 70 °C. The R_p is a direct function of temperature and the apparent activation energy, determined from the slope of the Arrhenius plot of log R_p vs. $1/T$, is 23 kJ/mol (Fig. 5).

vation energy, determined from the slope of the Arrhenius plot of log R_p vs. $1/T$, is 23 kJ/mol (Fig. 5).

CHARACTERIZATION OF THE COPOLYMER

Fourier transform infrared spectroscopy

The FTIR spectrum of the copolymer (Fig. 6) shows bands of C—H stretching at 3054 cm⁻¹ due to the phenyl group of styrene and at 1724 cm⁻¹ due to the COOH group of MAA.

¹H-nuclear magnetic resonance spectroscopy

The ¹H-NMR spectrum of the copolymer (Fig. 7) showed peaks in the range 7.20 to 7.27 δ due to the phenyl protons of styrene and at 12.5 δ due to the COOH proton of MAA. This confirms the formation of the copolymer.

¹³C-nuclear magnetic resonance spectroscopy

The ¹³C-NMR spectrum of the copolymer (Fig. 8) showed peaks at 155 ppm because of the aromatic carbon resonance of the styrene residue and at 190 ppm because of the carbonyl group of MAA residue.

COPOLYMER COMPOSITION AND THE VALUES OF THE REACTIVITY RATIOS

The composition of the copolymers (Table III) was evaluated from the high-resolution ¹H-NMR spectra. The relative peak area at 7.20–7.27 δ due to the phenyl protons of styrene and the peak area at 1.3 δ due to the methyl protons of MAA have been used to calculate the copolymer composition. The copolymer composition

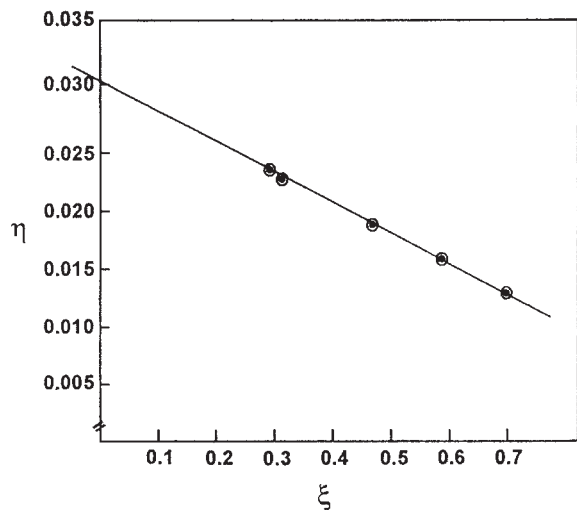


Figure 9 Kelen-Tüdös method for the determination of reactivity ratios.

TABLE IV
Reactivity Ratio

r_1	r_2	$r_1 r_2$
0.025	0.03	0.00075

tion data were used to calculate the monomer reactivity ratios using the Kelen-Tüdös method (least-squares method). The values of r_1 = (styrene) and r_2 = (MAA) were calculated using the least-squares method as 0.03 and 0.025, respectively, (Fig. 9, Table IV). The product of $r_1 r_2 = 0.00,075$, which indicates that the copolymer is alternating in nature.

MECHANISM

The product of $r_1 r_2$ confirms alternating nature of the copolymer. It has been reported in the literature¹¹⁻¹⁴ that the ylide dissociated to form a phenyl radical that brings about the polymerization. This has also been confirmed from the ESR spectrum¹⁹ (Fig. 10), which shows six hyperfine lines with value of hyperfine constant as 3.73 G. The ESR spectrum was recorded on an X-band EPR 109 E-line century series spectrometer at room temperature. The mechanism is shown in Scheme 1.

CONCLUSIONS

The copolymerization of styrene with methacrylic acid, initiated by triphenylbismuthonium 1,2,3,4-tetra-

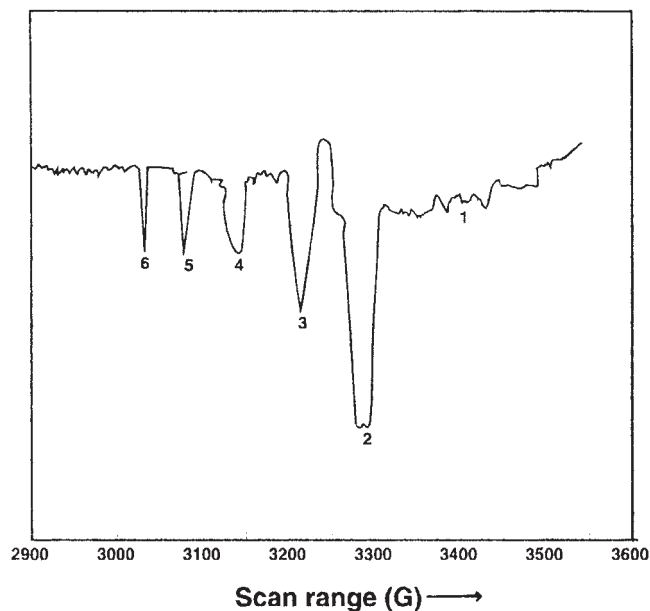
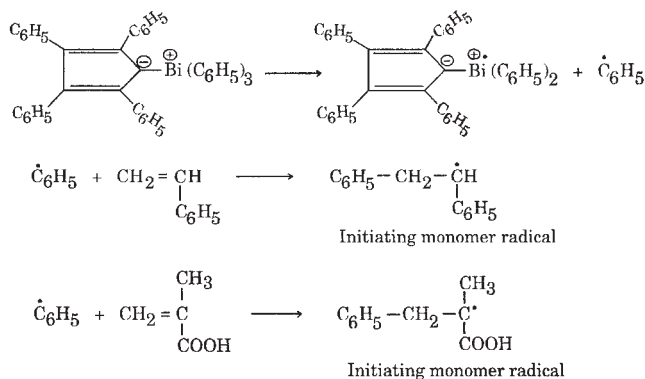


Figure 10 ESR spectrum of the copolymer.



Scheme 1

phenylcyclopentadienylide in dioxan, follows ideal kinetics and results in the formation of an alternating copolymer.

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