Copolymerization of Methylmethacrylate with Styrene Using Triphenylbismuthoniumylide as Radical Initiator

RADHA BAJPAI, A. K. SRIVASTAVA

Department of Chemistry, Harcourt Butler Technological Institute, Kanpur, 208002, India

ABSTRACT: Bismuthoniumylide-initiated radical copolymerization of methylmethacrylate with styrene at $60 \pm 0.2°C$ using dioxane as an inert solvent, follows ideal kinetics ($R_p \propto [\text{ylide}]^{0.5} [\text{MMA}]^{1.0} [\text{sty}]^{1.0}$), and yields alternating copolymer as evident from NMR spectroscopy. The values of reactivity ratios r_1 and r_2, calculated from Finemann–Ross method are 0.48 and 0.45, respectively. The system follows ternary molecular complex mechanism. The radical mode of polymerization has been confirmed by ESR spectroscopy and the effect of hydroquinone. The value of activation energy and k_p^2/k_t are 65.0 KJ mol^{-1} and 2.5×10^{-5} l mole^{-1} s^{-1}, respectively. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 2774–2781, 2001

Key words: methylmethacrylate; triphenyl bismuthoniumylide; radical initiator

INTRODUCTION

Progress in the chemistry of macromolecular compounds results not only from the introduction of increasing numbers of novel monomers but also from new initiators. Among initiator(s), recently reported, are peroxypivalate[1] and ylides (N, P, As).[2–4] However the Bi, ylides, probably because of difficulties associated with their synthesis, have not been examined for their potential applications in the domain of polymer science. Therefore, it is worthwhile to investigate the same and to the best of our knowledge, this is first report that highlights the capacity of Bi ylide to act as radical initiator to yield MMA-alt-sty even in absence of Lewis acids, which are otherwise essential. Moreover, the incorporation of Bi in the copolymer is the interesting feature of the system.

EXPERIMENTAL

Reagent grade monomers and solvents were purified according to the method given by Overberger[5] and Vogel.[6] The triphenylbismuthonium 1,2,3,4-tetraphenyl cyclopentadieneylide was proposed by the method of Lloyd et al.[7]

Synthesis of Diazo Compound

A solution containing 2.19×10^{-4} mol of 1,2,3,4-tetraphenylcyclopentadiene (Aldrich), 7.46×10^{-4} mol of p-toluenesulphonylhydrazide (Fluka), 6.3 mL diethylamine was kept at 0°C for 10 days. It was followed by addition of 3.5 mL water, 5 mL ether, and, finally, dried over silica gel. The compound was

Table I   Effect of [Triphenylbismuthoniumylide] on Rate of Copolymerization of MMA and sty

Serial No.	[Ylide] $\times 10^5$ mol l^{-1}	Conversion (%)	$R_p \times 10^6$ mol l^{-1} S^{-1}	$\bar{P}_n$
1	8.27	1.1	2.45	178
2	10.33	1.6	3.12	165
3	12.39	1.9	3.21	132
4	14.46	2.1	3.58	124
5	16.52	2.2	4.15	116

[sty] = 1.92 mol l^{-1}, [MMA] = 1.49 mol l^{-1}, time = 6 h; temperature = 60 ± 0.2°C.

washed with methyl alcohol to give yellow crystals of diazo compound (yield = 20.5%).

Synthesis of Bismuthonium Ylide

A solution containing 2.64×10^{-4} mol of diazo compound, 7.35×10^{-5} mol of Cu(II)bishexafluoroacetyleacetanato catalyst (Merck) and 4.95×10^{-5} mol of triphenylbismuth (Merck) in benzene were refluxed for 2 h. The evaporation of the solvent in vacuum yielded ylide.
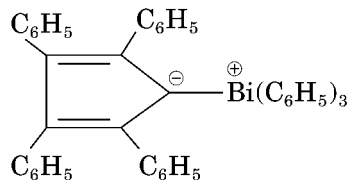
Color   : dark blue purple color
Melting point : 107°C (Lit. value 107°C)
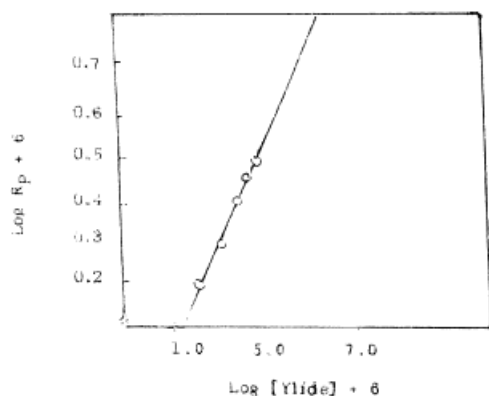**Yield**   : 18% (Lit. value 22%)

Figure 1   Plot between log [ylide] vs. log [R_p], [sty] = 1.91 mol l^{-1}, [MMA] = 1.49 mol l^{-1}, time = 6 h; temp. = 60 ± 0.2°C.
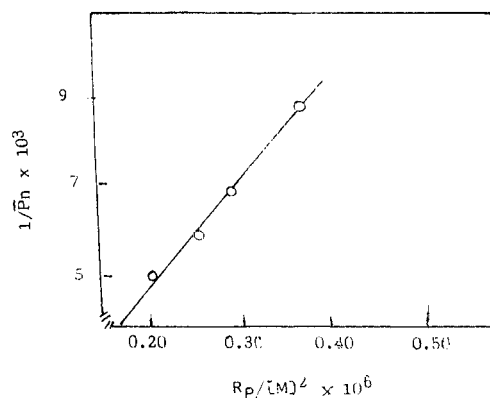

Figure 2   Plot between $1/\bar{P}_n$ vs. $R_p/[M]^2$, [ylide] = 16.52×10^{-5} mol l^{-1}, [sty] = 1.91 mol l^{-1}, [MMA] = 1.49 mol l^{-1}, time = 6 h; temp. = 60 ± 0.2°C.

Dilatometric technique (lower bulb capacity: 6 mL, capillary dia.: 2 mm, capillary length: 15 cm) has been used to carry out the polymerization at 60 ± 0.2°C for 6 h under nitrogen atmosphere using dioxane as inert solvent. The copolymers precipitated with acidified methanol, dried to constant weight, were refluxed with acetonitrile and cyclohexane to remove homopolymers of MMA and sty, respectively. No detectable weight loss was noticed.

The rate of polymerization (R_p) was calculated from the slopes of linear conversion–time plots. The intrinsic viscosity of copolymers was measured in benzene solution at 32°C using an Ubbelohde viscometer. The average degree of polymerization ($\bar{P}_n$) was calculated by using the following equation[8]

$$[\eta]_{int} = 5.76 \times 10^{-3} \bar{P}n^{0.746}$$

The IR and NMR spectra were recorded with a Perkin-Elmer 599B and varion 100 HA spectrometer at room temperature. The EPR spectrum was

Table II   Effect of MMA Concentration on the Rate of Copolymerization of MMA and sty

Serial No.	[MMA] mol l^{-1}	Conversion %	$R_p \times 10^6$ mol l^{-1} S^{-1}
1	0.745	0.55	1.03
2	1.49	1.07	2.45
3	2.08	1.10	2.61
4	2.68	2.01	4.08

[ylide] = 8.27×10^{-5} mol l^{-1}, [sty] = 1.92 mol l^{-1}, time = 6 h; temperature = 60 ± 0.2°C.

Table III   Effect of sty Concentration on the Rate of Copolymerization of MMA and sty

Serial No.	[sty] mol l^{-1}	Conversion %	$R_p \times 10^6$ mol l^{-1} S^{-1}
1	0.96	0.41	0.815
2	1.92	0.59	1.07
3	2.68	1.18	2.45
4	3.45	1.38	2.56

[ylide] = 8.27×10^{-5} mol l^{-1}, [MMA] = 1.49 mol l^{-1}, time = 6 h; temperature = 60 ± 0.2°C.

recorded on a X-band EPR-109E-line century series spectrometer at room temperature (20°C). The scanning electron microscope was a JEOL model JSM-840A. Ultraviolet spectrum was obtained by using on UV-VIS double-beam recording spectrophotometer UV 2500.
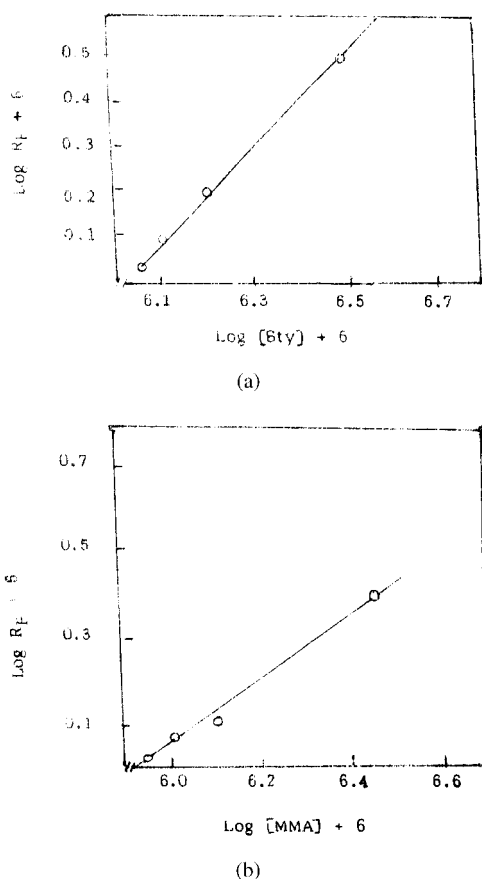

(a)

(b)

Figure 3   Plot between the rate of copolymerization and comonomer. (a) [ylide] = 8.27×10^{-5} mol l^{-1}, with constant [MMA] = 1.49 mol l^{-1}, time = 6 h, temp. 60 ± 0.2°C. (b) [ylide] = 8.27×10^{-5} mol l^{-1}, with constant [sty] = 1.91 mol l^{-1}, time = 6 h, temp. = 60 ± 0.2°C.
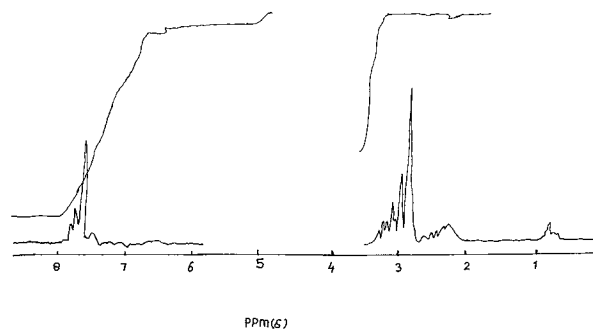

Figure 4   NMR [sty] = 1.91 mol l^{-1}, [MMA] = 1.49 mol l^{-1}, time = 6 h, temp. = 60 ± 0.2°C.

RESULTS AND DISCUSSION

The results have been shown in Tables I–V and Figures 1–11, and it is clear that the polymerization proceeds with an induction period of about 110–120 min.

Effect of [ylide]

The effect of [ylide] on R_p has been studied by varying the concentration from 8.27×10^{-5} mol^{-1} to 16.52×10^{-5} mol^{-1} (Table I). The R_p increases with increasing [ylide] from 8.27
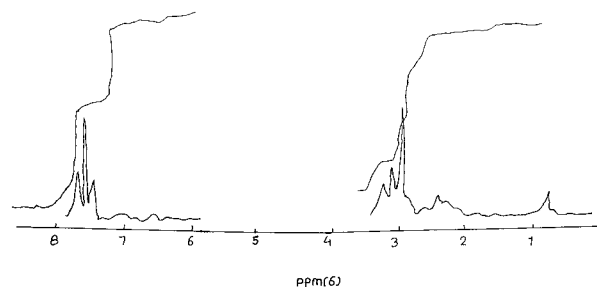
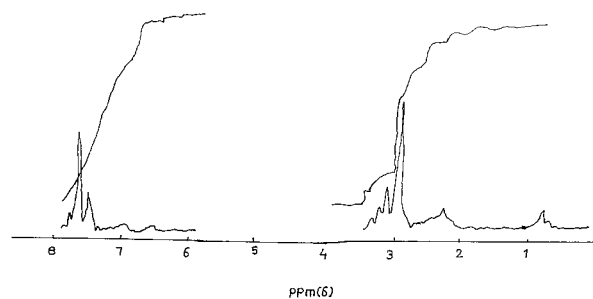**Figure 5**   NMR, [sty] = 0.96 mol l^{-1}, [MMA] = 1.49 mol l^{-1}, time = 6 h; temp. = 60 ± 0.2°C.

Figure 6   NMR [sty] = 0.96 mol l^{-1}, [MMA] = 0.74 mol l^{-1}, time = 6 h; temp. = 60 ± 0.2°C.

Table IV   Copolymer Composition

Serial No.	Molar Ratio in Feed $(F) \times = S/M$	% Conversion	Styrene mol Fraction from Phenyl Proton	MMA mol Fraction from Methoxy Protons
1	0.849	0.55	0.455	0.539
2	0.863	1.6	0.460	0.539
3	0.903	2.2	0.475	0.524
4	0.986	3.3	0.494	0.505

[Ylide] = 8.27×10^{-5} mol l^{-1}, [sty] = 1.92 mol l^{-1} [MMA] = 1.49 mol l^{-1}, time = 6 h; temperature = 60 ± 0.2°C.

$\times 10^{-5}$ mol^{-1} to 16.52×10^{-5} mol^{-1}. The initiator exponent value, calculated from the slope of the plot of log R_p vs. log [ylide] is 0.5 ± 0.01 (Fig. 1). The average degree of polymerization $(\bar{P}_n)$ of copolymers decreases on increasing ylide concentration. The plot of $1/\bar{P}_n$ vs. [ylide]$^{0.5}$ passing through the origin indicates a bimolecular mode of termination. The value of k_p^2/k_t determined from the slope of the linear plot of $1/\bar{P}_n$ vs. $R_p/[M]^2$ is found to be 2.5×10^{-5} l mol^{-1} s^{-1} (Fig. 2).

Effect of [Monomer(s)]

The effect of [monomer(s)] (Tables II and III), namely, MMA and sty on the rate of polymerization, was studied by varying the concentration of monomers [MMA] = 0.74–2.68 mol l^{-1}, [sty] = 0.96–3.45 mol l^{-1}, keeping the [initiator] = 8.27×10^{-5} mol l^{-1} constant, and the results are shown in Tables II and III. It is noteworthy that R_p increases as [monomer] increases in all cases. The exponent values calculated from the slope of the plot of log R_p vs.

log $[M]^2$ [Fig. 3(a) and (b)] are 1 for both monomers.

Effect of Temperature

The R_p is a direct function of temperature, and the apparent activation energy determined from the slope of Arrhenius plot is 65 KJ mol^{-1}. This value is in good argument with some reported values for radical polymerization.[2]

Characterization of Copolymers

Nuclear Magnetic Resonance Spectroscopy

The NMR spectra of the copolymers are shown in Figures 4–6, the phenyl protons appeared at 6.2–7.0 δ as singlet, the methyl proton at 0.4–0.6 δ as singlet, the methoxy proton appeared at 3.2–3.6 δ as triplet and at about 2.7 δ and 2.9 δ due to methylene and methyne protons. On the basis of the above positions of various peaks, it seems that the copolymer was an alternate copolymer. It is so because in case of alternate copolymer,[9] the phenyl proton of styrene unit
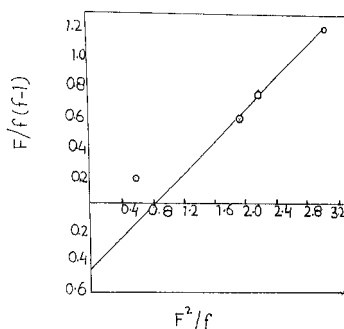

Figure 7 Reactivity ratio curve of F^2 $(f - 1)/f$ vs. F^2/f, [ylide] = 8.27×10^{-5} mol l^{-1}, [sty] = 1.91 mol l^{-1} [MMA] = 1.49 mol l^{-1}, time = 6 h; temp. = 60 $\pm$ 0.2°C.
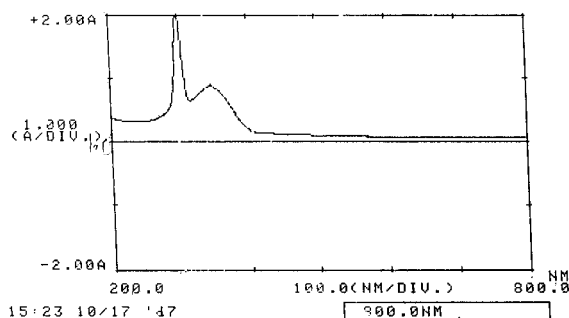
Figure 8 UV Spectroscopy, [sty] = 0.96 mol l^{-1}, [MMA] = 0.74 mol l^{-1}, time = 6 h, temp. = 60 $\pm$ 0.2°C.

Spectrum: 032618   Range:10   keV
                          Total Counts=28250.   Linear   Auto-VS=721
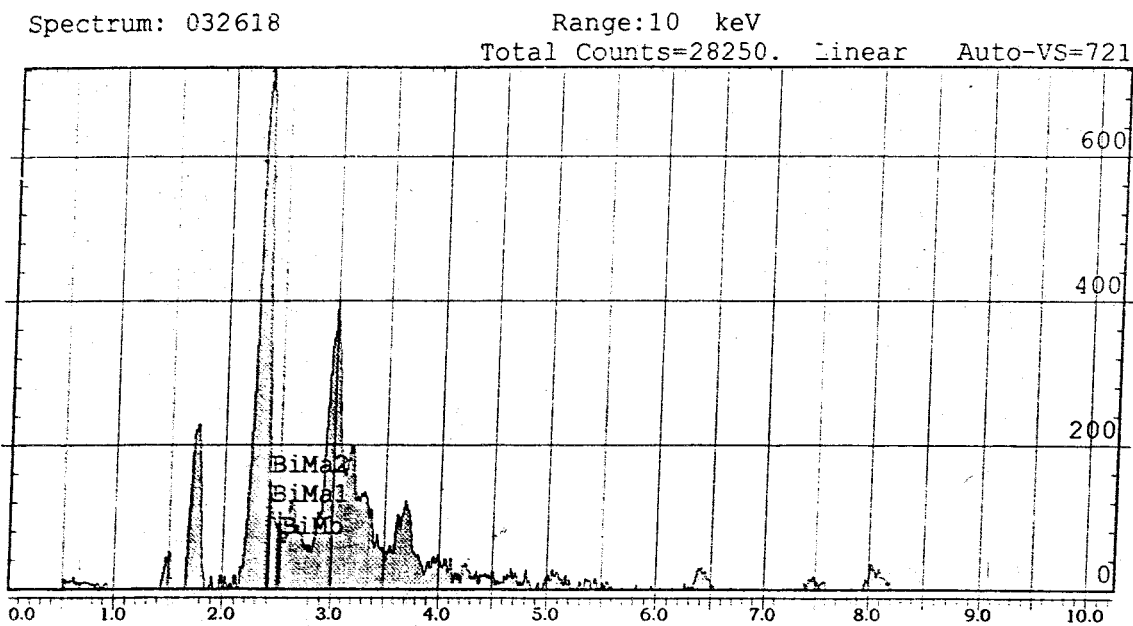
Figure 9   SEM, [sty] = 0.96 mol l^{-1}, [MMA] = 0.74 mol l^{-1}, time = 6 h; temp. = 60 ± 0.2°C.
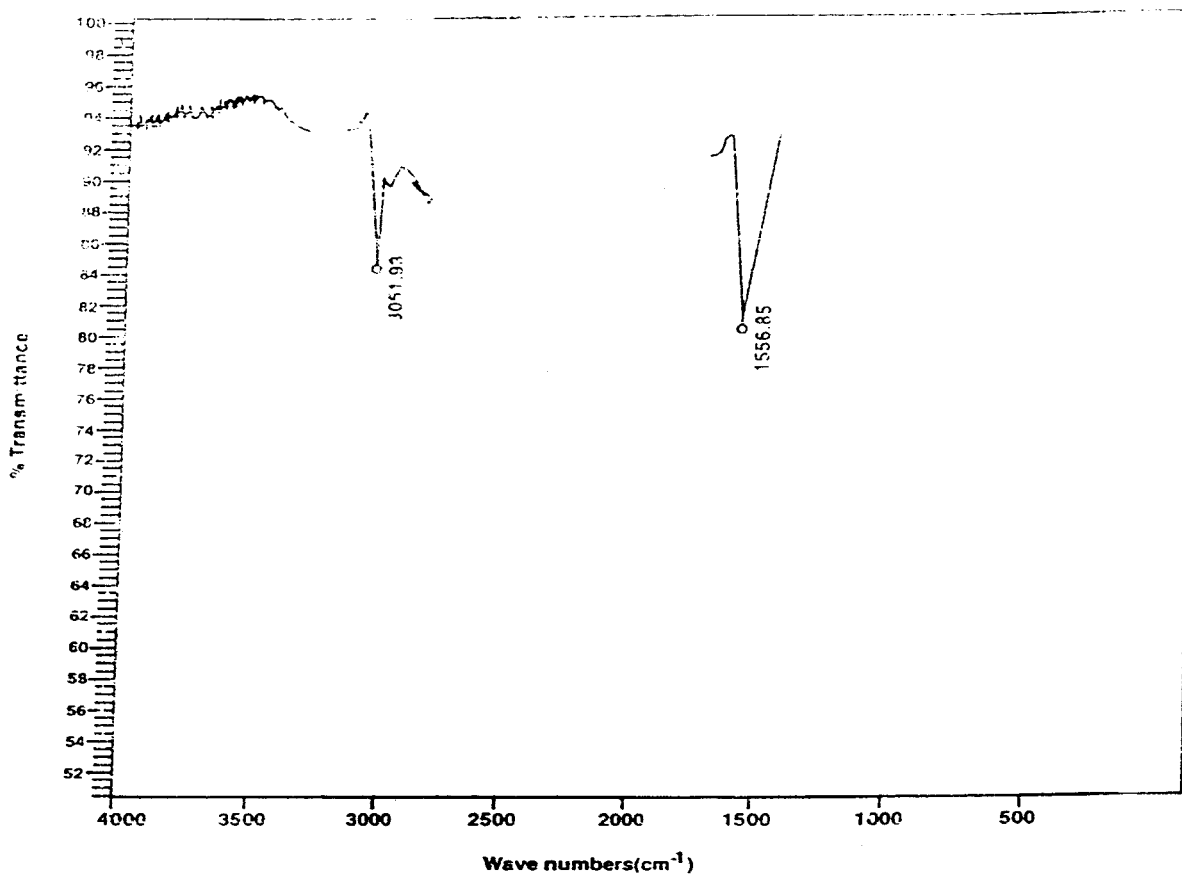
Figure 10   IR, ylide.

Table V   Effect of Additive Concentration on the Rate of Copolymerization of MMA and sty

Serial No.	Additive	[Additive] mol $l^{-1} \times 10^3$	Conversion %	$R_p \times 10^6$ mol l^{-1} S^{-1}
1	—	0.0	2.2	4.15
2	Benzene	1.6	1.1	2.01
3	Hydroquinone	1.4	—	—

[ylide] = 8.27×10^{-5} mol l^{-1}, [sty] = 1.92 mol l^{-1}, [MMA] = 1.49 mol l^{-1} time = 6 h; temperature = 60 ± 0.2°C.

appeared as a singlet at 7–8 δ, and the alpha methyl proton of MMA unit appeared at 0.4–0.6 δ as a sharp singlet.

Copolymer Composition and Determination of Reactivity Ratios

The relationship between the feed composition and the composition of low conversion copolymers (Table IV) was used to calculate the reactivity ratios by applying the Finemann–Ross method[10] as r_1 (sty.) = 0.48 and r_2 (MMA) = 0.45 (Fig. 7).

This further confirms the alternating nature copolymer.

Mechanism

The value of reactivity ratios suggests an alternate mode of copolymerization in the present case. Three mechanisms[11] have been proposed for the alternating copolymerization: (1) the ternary molecular complex mechanism (TMC); (2) the crosspropagation mechanism; and (3) the complex radical mechanism.
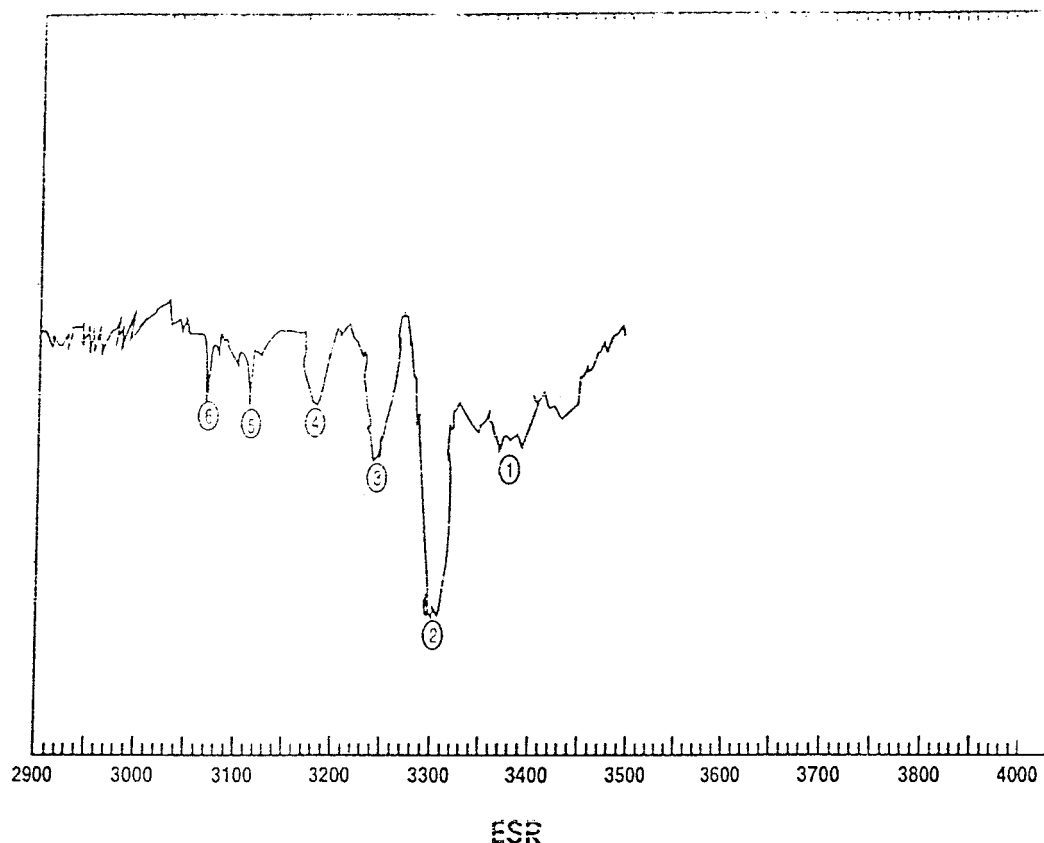

Figure 11   ESR, [sty] = 0.96 mol l^{-1}, [MMA] = 0.74 mol l^{-1}, time = 6 h; temp. = 60 ± 0.2°C.

In the TMC mechanism,[12] a ternary molecular complex between the Lewis acid and the electron donor monomer is formed, which then produces an alternating copolymer. In the present case, the TMC mechanism was confirmed from the UV spectrum (Fig. 8). In the UV spectrum, presence of a new band at 345 nm confirms formation of the ternary molecular complex between the electron acceptor monomer (MMA), ylide, and the electron donor monomer (sty), so the following structure of the ternary molecular complex is:

$$C_6H_5-CH \quad\quad CH_2$$
$$\delta^+ \|\text{\small{||||||||||||||||}}\| \delta^-$$
$$CH_2 \quad\quad C-CH_3$$

T.M.C
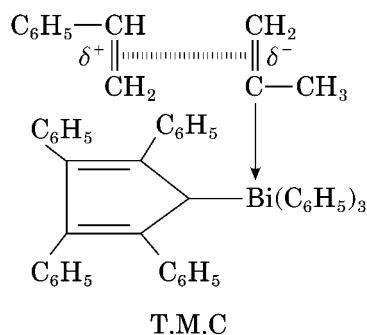
The kinetic data indicate that the system follows ideal kinetics of radical polymerization. The presence of bismuth in the polymer was detected by a qualitative method.[13] Briefly, the scheme is as follows. The polymer was burnt and dissolved in dilute HNO_3, addition of thiourea gave yellow color. The same is further confirmed from SEM photographs (Fig. 9) of the polymer, which show two distinct phases—black and white—which may be attributed to bismuth and polymer matrix, respectively. A comparison of band area due to the C—C bond stretching of aromatic in the polymer as well as ylide (Fig. 10) shows unity. The free radical polymerization has been confirmed from the effect of hydroquinone (Table V) and ESR spectrum (Fig. 11). The ESR spectrum suggests[14] that phenyl radical is responsible for the initiating activity. The spectrum consists of six hyperfine lines and hyperfine constant is 3.73 gausses, which is very close to value given for the phenyl radical (=3.75 gausses). It has been reported in the literature[15] that the phenyl group of triphenylbismuth can be cleaved in the presence of suitable reagents. Therefore, it seems that the ylide dissociates giving phenyl radical (A) and the following radical (B):

INITIATION :

(B)   Resonance stabilized   (A)

Scheme 1

(Resonance stabilized)
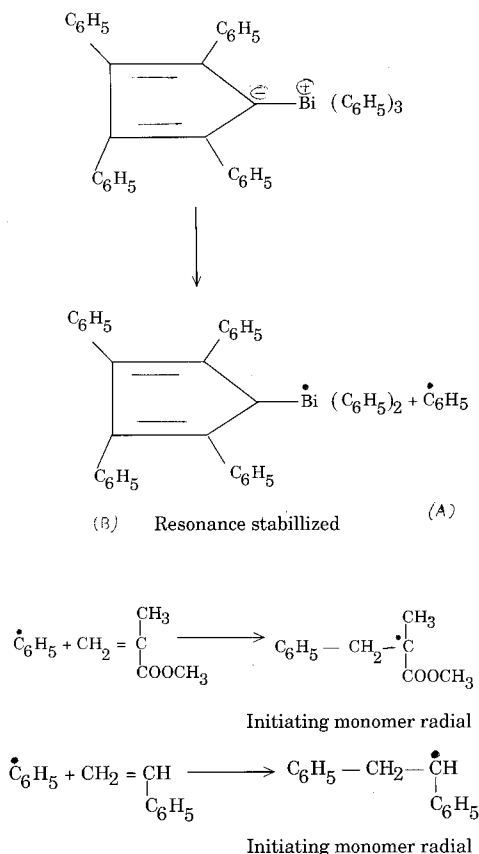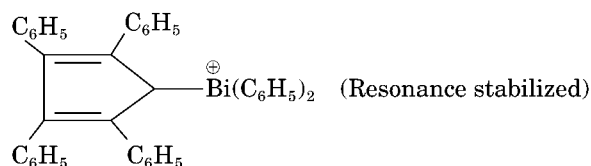
The initiation may be due to the phenyl radical. The presence of little amount of bismuth may be due to simultaneous initiation by the radical (B) to a small extent, or it might have been trapped in the polymer matrix. The steps of the initiation mechanism are given in Scheme 1.

CONCLUSIONS

From these studies, we infer that copolymerization of methylmethacrylate with styrene is initiated by triphenylbismuthonium 1,2,3,4-tetraphenylcyclopentadieneylide in dioxane. The alternating copolymer is formed by the TMC mechanism.

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