p-ACETYLBENZYLIDENE TRIPHENYLARSONIUM YLIDE (p-ABTAY) INITIATED RADICAL COPOLYMERIZATION OF METHYLMETHACRYLATE WITH STYRENE

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NOTE

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ABSTRACT

p-Acetylbenzylidene triphenylarsonium ylide (p-ABTAY) initiated radical copolymerization of methylmethacrylate (MMA) with styrene in dioxane, at 60 ± 0.1°C, under the inert atmosphere of nitrogen yields alternating copolymer, as evidenced by ^{1}H NMR spectroscopy. The kinetic equation for the present system is Rp µ[p-ABTAY]$^{0.46}$ [MMA] [Sty]. The rate of copolymerization (Rp) is proportional to the square root of [p-ABTAY] indicating bimolecular termination. The values of kp^2/kt and energy of activation have been computed as 6.3×10^{-3} l mol^{-1}s^{-1} and 63 KJ mol l^{-1}, respectively. The reactivity ratios have been calculated as r_1 (MMA)= .60, r_2 (Sty) = .35, by using the Kelen-Tudös method. The copolymerization reaction is initiated by the phenyl free radical. The formation of phenyl radicals may be attributed to the pp-dp overlap between the hybridized sp^2 orbital and the larger and more diffuse 4d orbital of arsenic.

INTRODUCTION

Extensive studies have been carried out on the copolymerization of MMA with styrene using different initiators such as 3-methoxy carbonyl-3-methyl-2,2,5,5-tetraphenyl hexanedinitrile [1], trialkyl boron organometallic peroxide [2],

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4-[diphenyl trimethyl silyl) methyl] benzophenone [3]. Recently different ylides [ylides are 1,2 dipolar compound in which a heteroatom (N, S, P, As, Sb, Bi) is covalently bonded to the carbanion] such as β-picolinium-p-chlorophenacylide [4] pyridinium dicyanomethylide [5], imidazolium-p-chlorophenacrylide [6], and metal-ylide complexes [7] have been applied as radical initiators for the copolymerization of MMA with styrene. The use of arsonium ylide (p-ABTAY) for the copolymerization of MMA with styrene is still in darth [8]. Therefore, it is thought to explore the use of p-ABTAY as radical initiator for the copolymerization of MMA with styrene. The present work communicates the kinetics and mechanism of copolymerization of MMA with styrene.

EXPERIMENTAL

Methylmethacrylate (Merck) and styrene (Merck) were purified by the standard methods [8] and were stored at below 5°C. Dioxane and triphenyl arsine (Merck: Art-808658) were used without further purification. The ylide (p-ABTAY) with the following structure (I) was synthesized by the method reported in the literature [9].

(I)
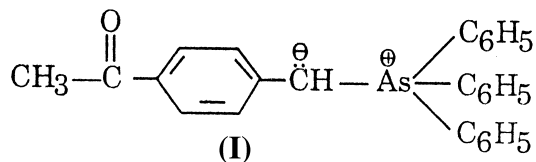
Briefly the scheme is as follows:
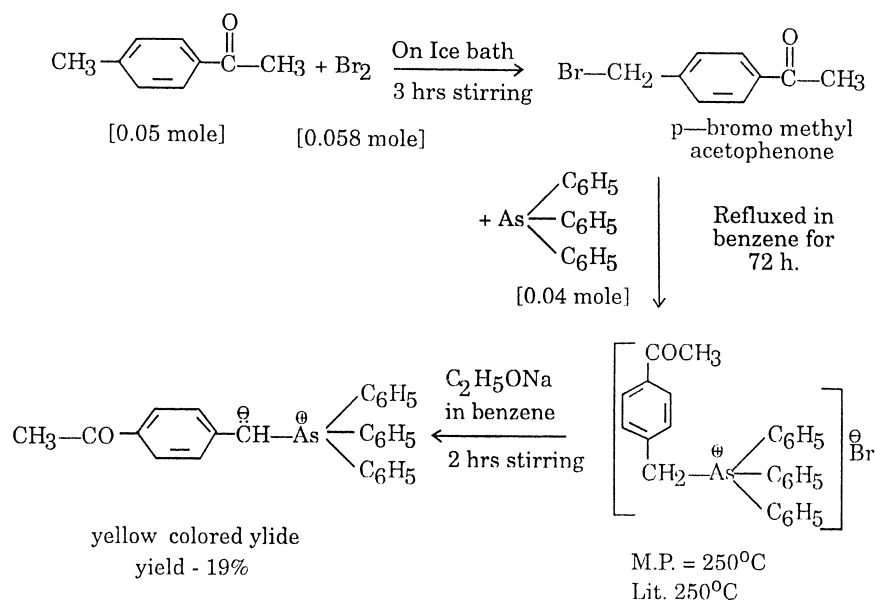
The series of MMA/styrene copolymer(s) containing different mole percents of MMA and styrene in the feed were prepared by solution polymerization under nitrogen at $65 \pm 0.1°C$ for about 10 hours. The copolymer(s) were precipitated with acidified methanol and were refluxed with acetonitrile and cyclohexane to remove homopolymers. There was negligible weight loss in acetonitrile as well as in cyclohexane. The copolymer(s) were then dissolved in benzene and reprecipitated with acidified methanol. The rates of copolymerization (Rp) were calculated from the slopes of the linear zone of percent conversion vs. time plots (Figure 1).

The intrinsic viscosity (h_{int}) of various copolymer samples were determined in benzene at $32 \pm 0.1°C$ with the help of a Ubbelohde viscometer. The Mark-Hownik-Sakurada Equation (1) was used to calculate the viscosity average molecular weight ($\overline{M}_v$).

$$h_{int} = k[\overline{M}_v]^\alpha \tag{1}$$

The values of k and a are $13.2 \times 10\text{-}5$ and 0.71, respectively [10].

RESULTS AND DISCUSSION

The copolymerization reactions have been carried out in dioxane at $60 \pm 0.1°C$ by varying the [p-ABTAY], [MMA], and [Styrene]. The copolymerization runs were associated with an induction period of 2-3 hours. The high induction period could be produced by p-ABTAY molecules being inhibitors as well as slowly dissociating to form initiating radicals [8]. The results are compiled in Tables 1-2 and Figures 1-5.


Effect of [p-ABTAY]

No polymer was obtained below 1.42×10^{-4} mol l^{-1} [p-ABTAY] and Rp decreased as [p-ABTAY] increased beyond 21.40×10^{-4} mol l^{-1} therefore, [p-ABTAY] is varied from 1.42×10^{-4} to 8.56×10^{-4} mol l^{-1} while [MMA] and [Sty] were kept constant at 2.35 and 2.18 mol l^{-1}, respectively (Table 1).

The initiator exponent value, calculated from the slope of log Rp against log [p-ABTAY] is, 0.46 which is slightly less than expected for ideal radical kinetics (Figure 2). The viscosity average molecular weight ($\overline{M}_v$) of copolymer(s) decreases with an increase in [p-ABTAY]. The value of k_p^2/k_t, determined from the slope of the plot of $1/\overline{M}_v$ vs. $R_p/[M]^2$, (Figure 3) is 6.3×10^{-3} l mol l^{-1}s^{-1}. The plot of $1/[\overline{M}_v]$ vs. $[I]^{-5}$ (Figure 4) passes through an origin indicating the bimolecular termination.

Effect of [MMA] and [Sty]

The effect of [MMA] on Rp was studied by varying [MMA] from 2.35 to 2.7 mol l^{-1} while [Styrene] and [p-ABTAY] were kept constant at 2.18 mol l^{-1} and
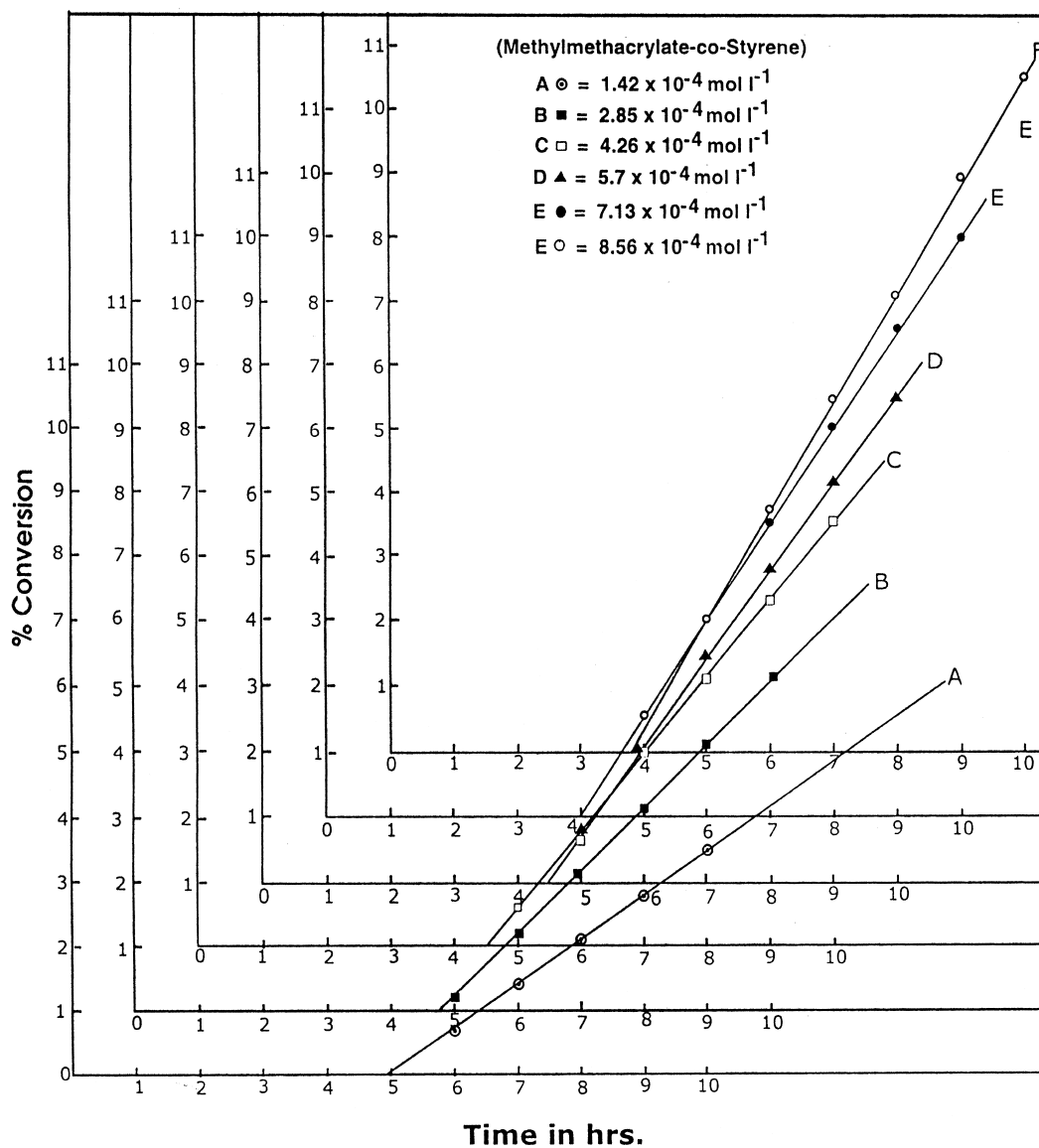
Figure 1. Conversion vs. time plots of radical copolymerization of methylmethacrylate with styrene using p-acetyl benzylidene triphenylarsonium ylide as radical initiator, [MMA] = 2.35 mol l⁻¹, [Sty] - 2.18 mol l⁻¹, Polymerization time = 10 hours, Polymerization temperature = 60 ± 0.1°C.

8.56×10^{-4} mol l⁻¹, respectively. Similarly, the effect of [styrene] was studied by varying its concentration from 1.53 to 2.18 mol l⁻¹ keeping [MMA] and [p-ABTAY] constant at 2.35 mol l⁻¹ and 8.56×10-4 mol l⁻¹, respectively. In both cases, exponent values were computed as unity. The results are compiled in Table 2.

Table 1. Effect of [MMA] and [Sty] on Copolymerization of MMA with Styrene Initiated by p-Acetyl Benzylidene Triphenyl Arsonium Ylide

Run No.	[p-ABTAY] $\times 10^4$ (mol l^{-1})	Percent Conversion	Rp x 10^6 (mol l^{-1}s^{-1})	$\overline{M}_v$* at 30°C
1.	1.42	3.5	8.5	39012
2.	2.85	5.1	12.08	30178
3.	4.26	6.4	14.84	23999
4.	5.7	7.6	17.36	20118
5.	7.13	9.1	19.00	18259
6.	8.56	10.5	21.39	16447

[MMA] = 2.35 mol l^{-1}, [Sty] = 2.18 mol l^{-1}, Polymerization temperature = 60 ± 0.1°C, Polymerization time = 10 hours.
*Solvent benzene.

Effect of Temperature

The influence of temperature on the rate of copolymerization has been studied by carrying out the polymerization at three different temperatures i.e., 60°C, 65°C, and 70°C. The overall energy of activation ΔE) of calculated from
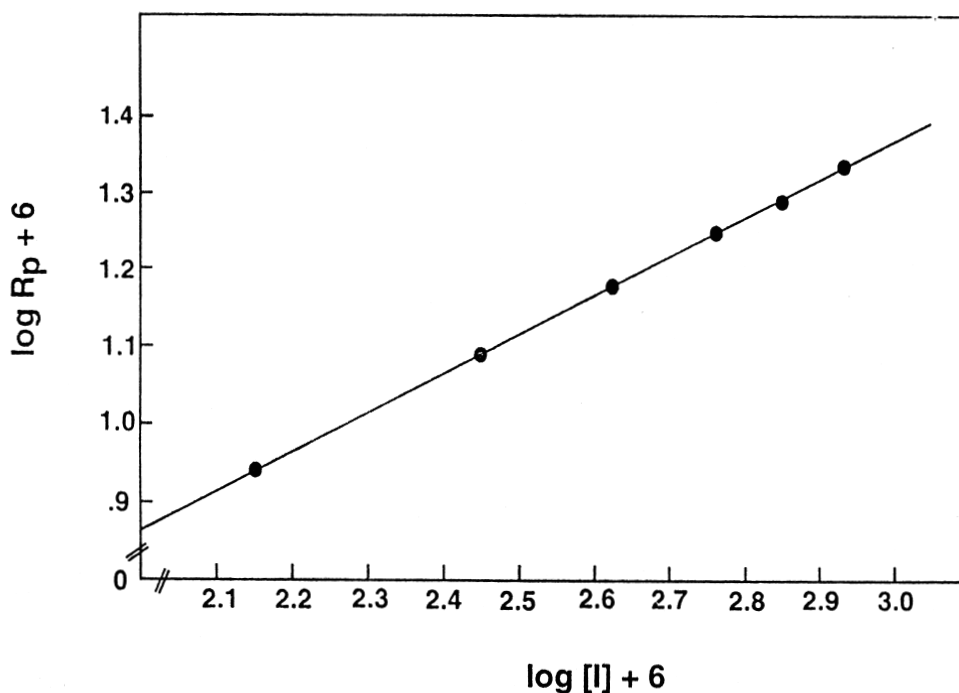
Figure 2. A plot of log (rate of copolymerization) vs. log [p-ABTAY] [MMA] = 2.35 mol l^{-1}, [Sty] = 2.18 mol l^{-1}, Polymerization time = 10 hours, Polymerization temperature = 60 ± 0.1°C.
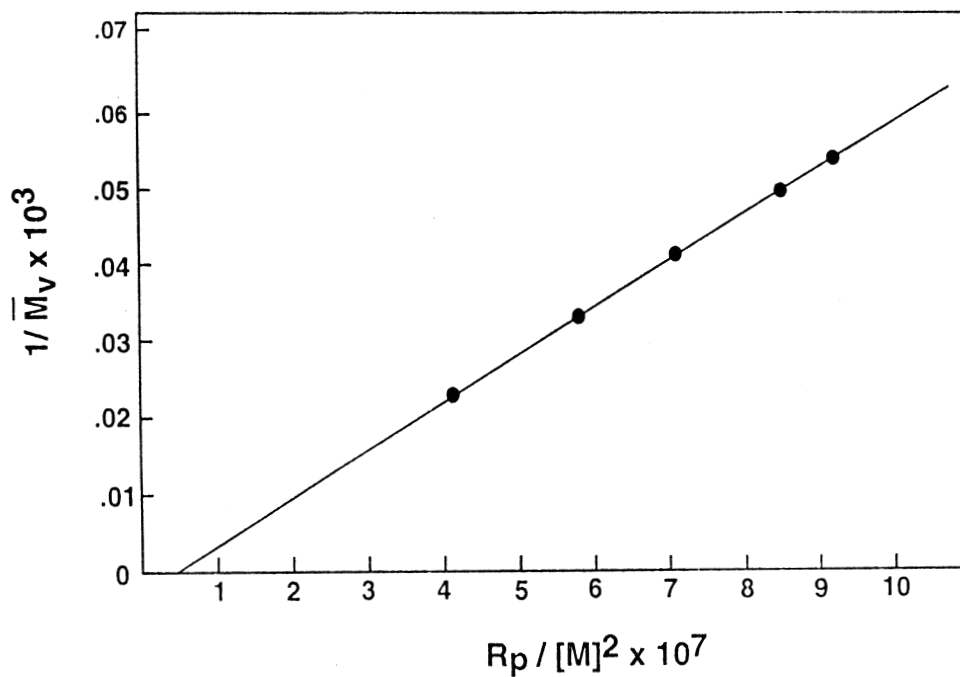
Figure 3. Plot of 1/ vs. $R_p/[M]^2$, [MMA] = 2.35 mol l^{-1}, [Sty] = 2.18 mol l^{-1}. Polymerization time = 10 hours, Polymerization temperature = 60 ± 1°C.
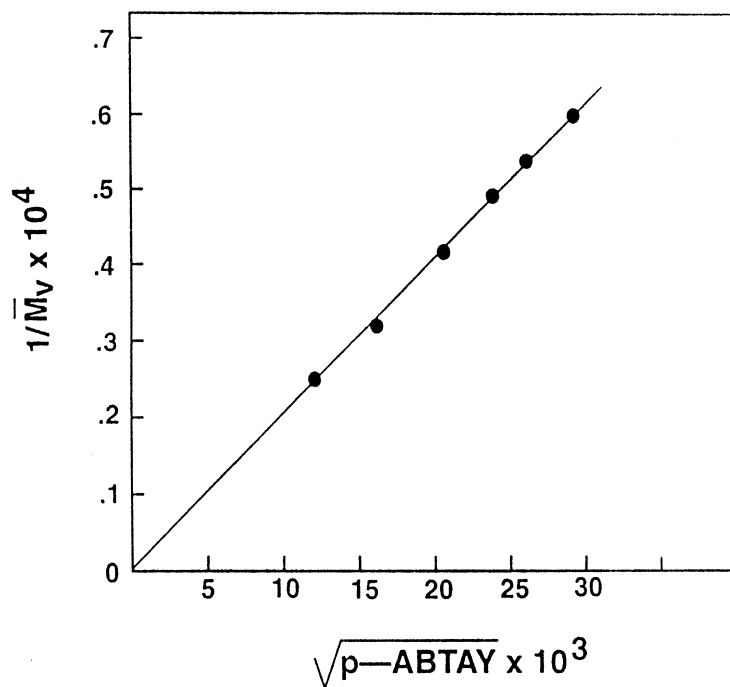
Figure 4. Plot of 1/ Vs [p-ABTAY] 0.5, [MMA]= 2.35 mol l^{-1} [Sty] = 2.18 mol l^{-1}, Polymerization temperature = 60 ± 1°C, Polymerization time = 10 hours.

Table 2. Effect of [MMA] and [Styrene] on Copolymerization of Methylmethacrylate with Styrene Initiated by (p-ABTAY)

Run No.	[MMA] (mol l^{-1})	[Styrene] (mol l^{-1})	Percentage Conversion	Rp × 10^6 (mol l^{-1}s^{-1})
1.	2.35	1.75	9.5	17.42
2.	2.35	1.96	10.1	19.51
3.	2.35	2.18	10.5	21.39
4.	2.46	2.18	11.0	22.81
5.	2.7	2.18	12	25.76

[p-ABTAY] = 8.26 × 10-4 mol l^{-1}, Polymerization temperature = 60 ± 0.1°C, Time = 10 hours.
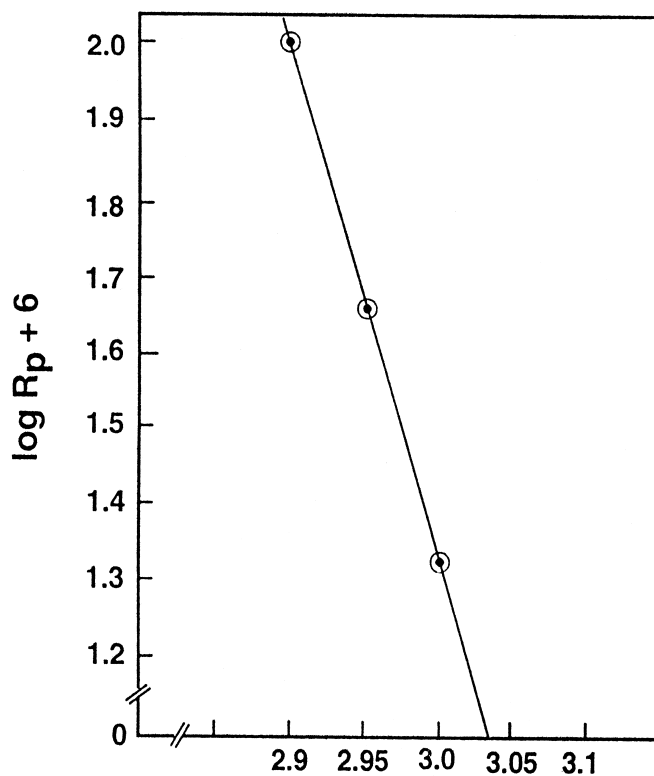
Figure 5. Plot of log (rate of copolymerization) vs. log 1/T, [p-ABTAY] = 8.56 × 10-4 mol l^{-1}, [MMA]= 2.35 mol l^{-1}, [Sty] = 2.18 mol l^{-1}. Polymerization time = 10 hours, Polymerization temperature = 60 ± 1°C.

Table 3. Copolymer Composition

Run No.	Molar Ratios in Feed $\times$ = [M]/[S]	MMA Mol Fraction from Methoxy Protons	Styrene Mol Fraction from Phenyl Protons	Figure
1	1.32	0.55	0.44	7
4	1.12	0.008	0.007	8
5	1.23	0.54	0.45	9
3	1.07	0.065	0.056	10

Arrhenius plot (Figure 5) is 64 KJ mol^{-1}, which is in good agreement with reported values for radical copolymerization of MMA and Styrene.

Characterization of Copolymers: Spectral Analysis

Infra Red Spectroscopy

The IR spectra (Figure 6) (recorded on a Perkin-Elmer Spectrophotometer) of copolymer shows a band at 3000 cm^{-1} due to aromatic C-H stretch, at 1450 cm^{-1} due to aromatic C=C stretch, at 1732 cm^{-1} due to -C = O stretch of ester group and 2952 cm^{-1} due to C-H stretching of -CH$_3$ and -CH$_2$ groups.

Nuclear Magnetic Resonance Spectroscopy

The NMR spectra (recorded on a Jeol LA 400 Spectrophotometer; CdCl$_3$ solvent) of copolymers are shown in Figures 7-9. The phenyl protons appear at 6.6 d, the methyl protons at 0.9 d, and the methoxy protons at 3.3-3.4 d 3.1-3.3 d and at ~2.2 d. The appearance of methoxy protons as three split peaks as mentioned above, shows that the copolymer(s), prepared with (p-ABTAY) is of an alternating nature. The relative peak areas due to phenyl and methoxy protons have been used to calculate copolymer composition [11]. The Kelen-Tüdos approach is used for evaluation of reactivity ratios. r$_1$ and r$_2$ for the monomer pair according to:

$$\eta \; = \; r_1 \; \xi \; - \frac{r_2}{\alpha} \; (1 - \xi \;)$$

$$\text{where } \eta \; = \; \frac{G}{(\alpha + H)} \text{ and } \xi \; = \frac{H}{(\alpha + H)}$$

The transformed variables G and H are given by:
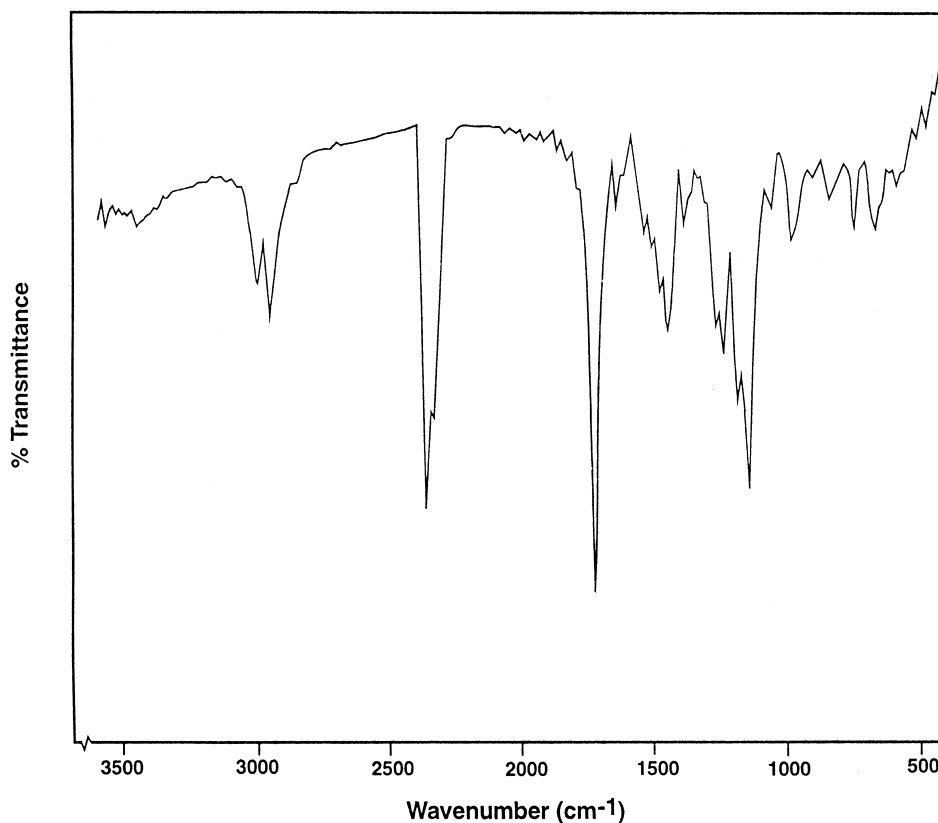
Figure 6. Infra red spectrum of poly (MMA-co-Sty) sample. [MMA] = 2.35 mol l^{-1}, [Sty] = 2.18 mol l^{-1}, [p-ABTAY] = 8.56 × 10-4 mol l^{-1}, Polymerization time = 10 hours, Polymerization temperature 60 ± 0.1°C.

$$G = \frac{[M_1]/[M_2] \ [(d[M_1]/d[M_2]) - 1]}{d[M_1]/d[M_2]}$$

$$H = \frac{([M_1]/[M_2]^2}{d[M_1]/d[M_2]}$$

The parameter a is calculated by taking the square root of the product of the lowest and highest values of H for the copolymerization series. The reactivity ratios were calculated by usingthe Kelen-Tüdos method are r_1MMA = .60, r_2 Sty = .35, respectively. These values are in good agreement with the values given in the literature [12].
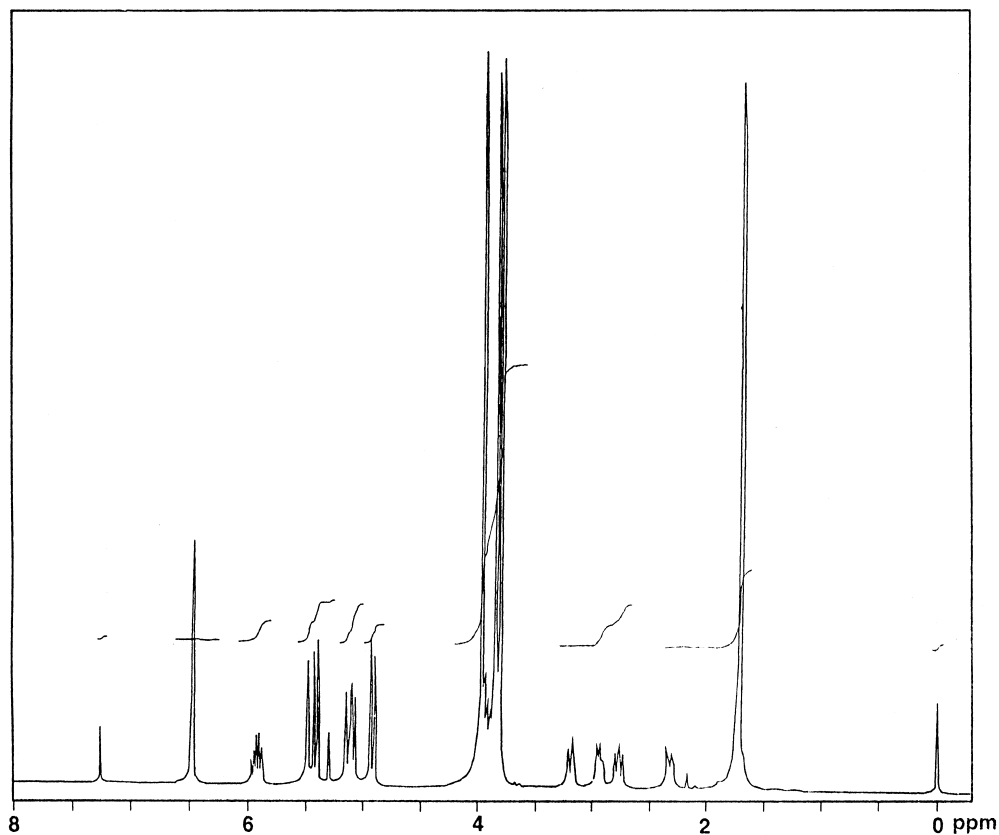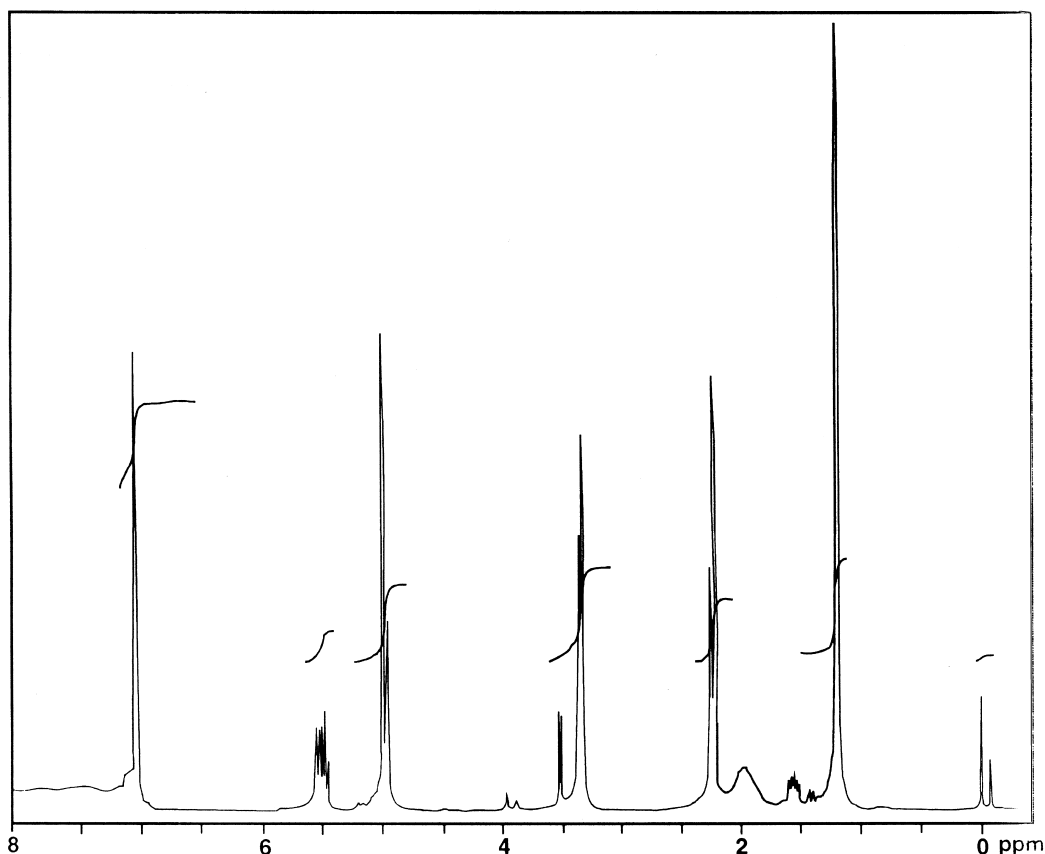
Figure 7. NMR spectrum of poly (MMA-co-Sty) sample, initiated by [p-ABTAY]. [p-ABTAY] = $8.56 \times 10\text{-}4$ mol l^{-1}, [MMA] = 2.35 mol l^{-1}, [Sty] = 1.75 mol l^{-1}, Polymerization temperature = 60°C, Polymerization time = 10 hours.

Stereochemistry

Theoretically, there are four kinds of triads along a copolymer chain, i.e., MMS, MMS, SMM, and SMS where S and M represent methylmethacrylate and styrene units, respectively. The following structures of each triad may be written consisting of four kinds of configurations, employing the representation of Nishioka *et al.* [13].
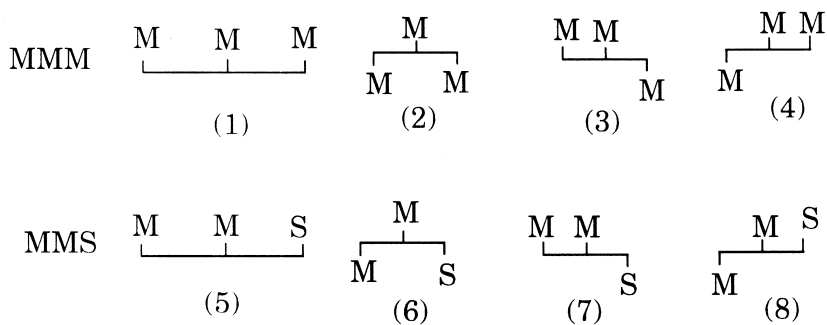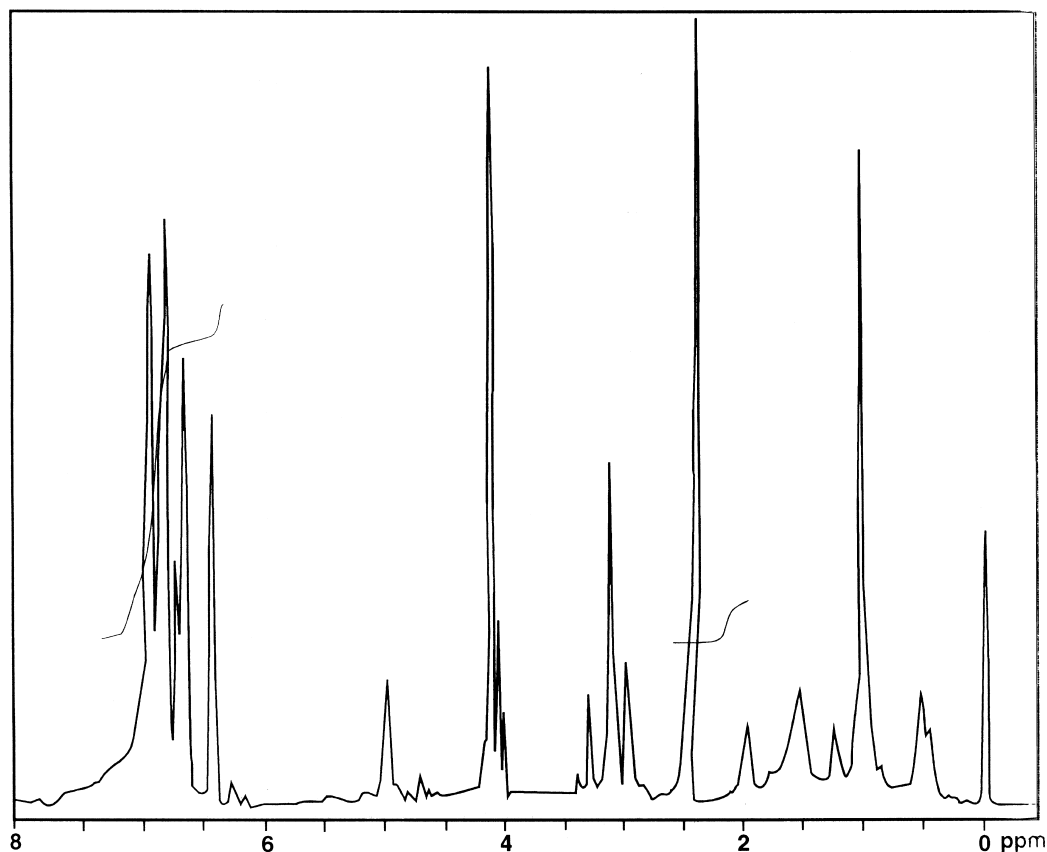
Figure 8. NMR spectrum of poly (MMA-co-Sty) sample, initiated by [p-ABTAY]. [p-ABTAY] = 8.56×10-4 mol l^{-1}, [MMA] = 2.46 mol l^{-1}, [Sty] = 2.18 mol l^{-1}, Polymerization temperature = 60°C, time = 10 hours.
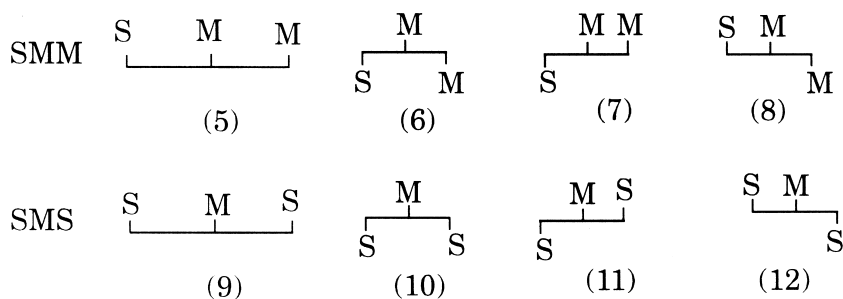
The appearance of methoxy protons as three peaks suggests that it is possible to distinguish three main kinds of MMA units spectroscopically, as suggested by Bovey [14]. The structures (1), (2), (3), (4), (6), (7), and (10) seem to constitute the peak at 3.4-3.3 d at the lowest field region of the methoxy resonance because
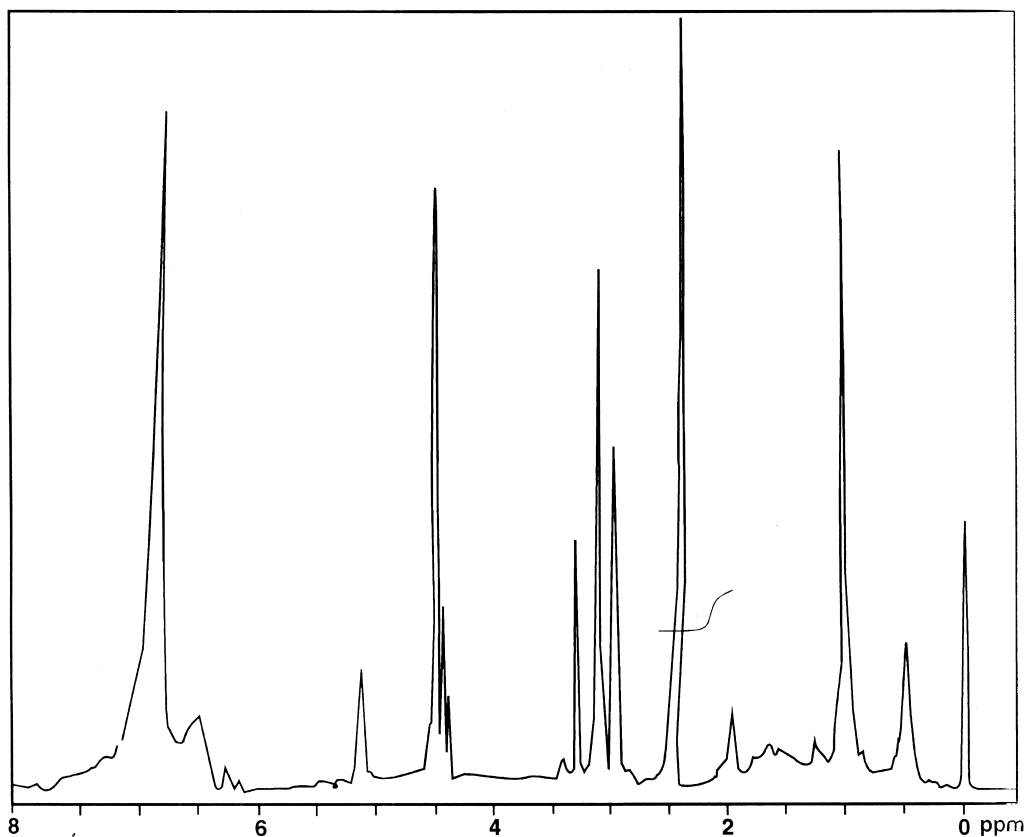
Figure 9. NMR spectrum of poly (MMA-co-Sty) sample, initiated by [p-ABTAY]. [p-ABTAY] = $8.56 \times 10\text{-}4$ mol l^{-1}, [MMA] = 2.7 mol l^{-1}, [Sty] = 2.18 mol l^{-1}, Polymerization temperature = 60°C, time = 10 hours.

the configuration of the neighboring S units in the structure (6), (7), and (10) are opposite to these of the central M units of interest so that the diamagnetic shielding by such S units may be little enough. Similarly, the triads (11) and (12) are responsible for the peak at 3.3-3.1 d, and triads (5), (8) and (9) are for the peak at 2.2 d, respectively.

Thus, on the basis of above evidence, it is concluded that the ylide (p-ABTAY) can be used as a radical initiator to obtain an alternating copolymer of MMA with Styrene. The advantage of the present initiator is that it yields alternating copolymer even without Lewis acids which are otherwise essential for conventional initiators.


Mechanism

(p-ABTAY) ylide is considered to be the resonance hybrid of the following resonating structure:

Figure 10.   NMR spectrum of poly (MMA-co-Sty) sample, initiated by [p-ABTAY]. [p-ABTAY] = 8.56×10^{-4} mol l^{-1}, [MMA] = 2.35 mol l^{-1}, [Sty] = 2.18 mol l^{-1}, Polymerization temperature = 60°C, time = 10 hours.
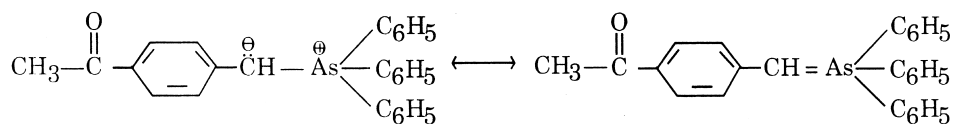

As reported in the literature [8], the ylide dissociates in the following manner yielding phenyl free radicals which is responsible for the initiation of the polymerization reaction. The initiation step is as follows:
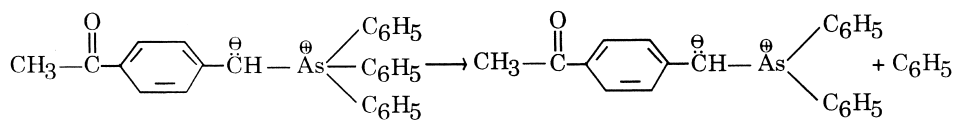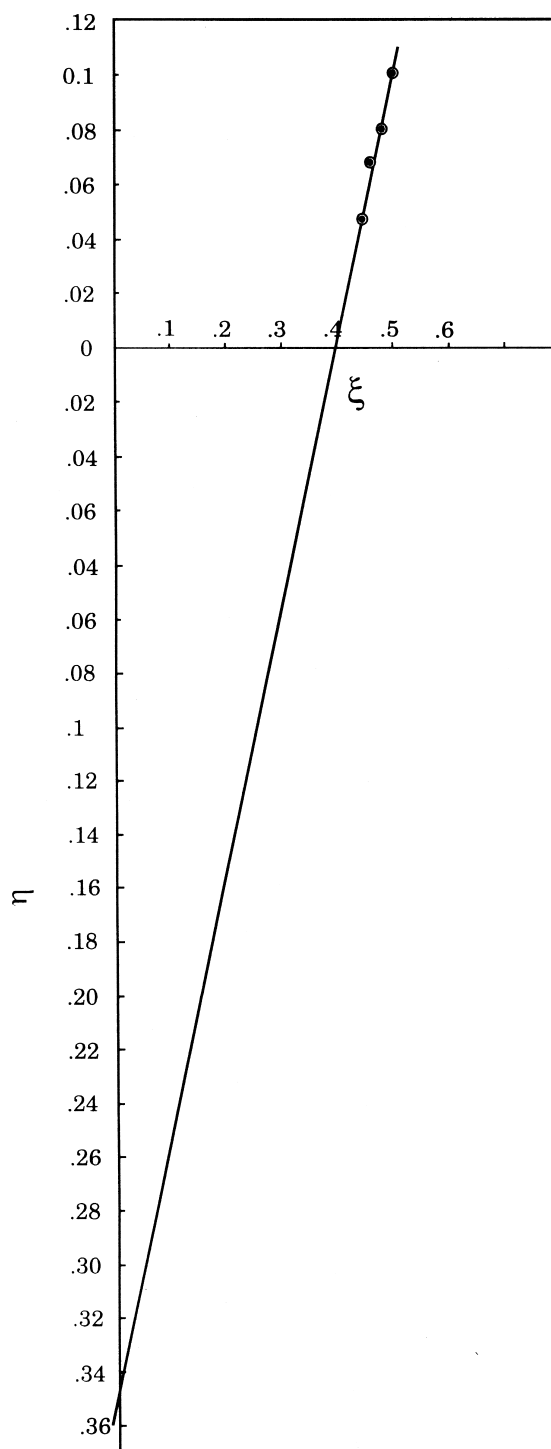
Figure 11. Reactivity ratios for poly (MMA-co-Sty) sample, by the Kelen-Tüdos method, [p-ABTAY] = 8.56×10^{-4}, Polymerization temperature $60 \pm 0.1°C$, Polymerization time = 10 hours.

Range : 10 keV

Total Counts = 131936   Linear   Auto - VS = 650
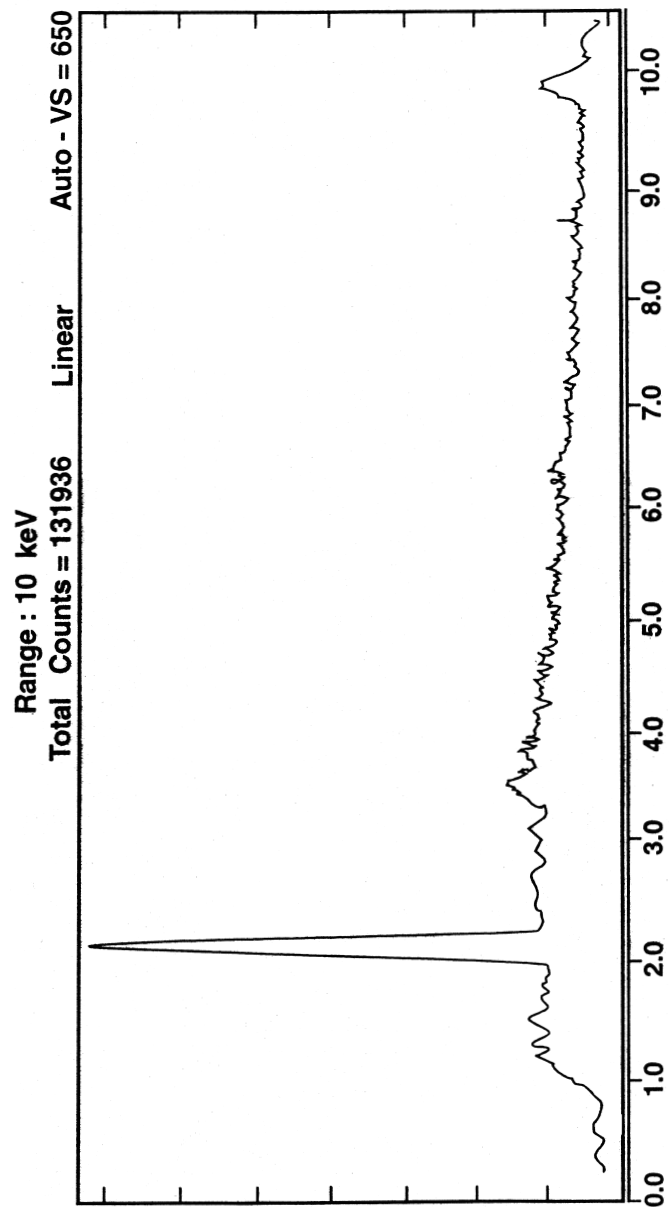
Figure 12. SEM of poly [MMA-co-Sty], [p-ABTAY] = 8.56 × 10-4 mol l⁻¹, [MMA] = 2.35 mol l⁻¹, [Sty] = 2.18 mol l⁻¹, Polymerization temperature = 60°C, Polymerization time = 10 hours.

SEM (Figure 10) analysis shows that arsenic is not incorporated in the polymer confirming the initiation with phenyl radicals only.

ACKNOWLEDGMENT

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