

Copolymerization of Methyl Acrylate with Styrene Using Triphenylstibonium 1,2,3,4-Tetraphenylcyclopentadienylide as a Novel Radical Initiator

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ABSTRACT: The free-radical copolymerization of methyl acrylate with styrene initiated by triphenylstibonium 1,2,3,4-tetraphenylcyclopentadienylide under nitrogen blanket at $(60 \pm 0.1)^\circ\text{C}$ in 1,4-dioxane for 2 h has been carried out. The kinetic expression is $R_p \propto [\text{I}]^{0.14} [\text{MA}]^{0.70} [\text{Sty}]^{0.75}$. The system follows nonideal kinetics due to primary radical termination as well as degradative chain transfer reactions. The overall activation energy is 42 kJ mol^{-1} . The reactivity ratios calculated from Kelen–Tüdös method for r_1 (MA) and r_2 (Sty) are

0.16 ± 0.01 and 0.028 ± 0.005 respectively. These values suggest the alternating nature of the copolymer. The ylide dissociated to form a phenyl radical, which brings about copolymerization of methyl acrylate with styrene. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1731–1736, 2007

Key words: methyl acrylate; styrene; copolymerization; triphenylstibonium 1,2,3,4-tetraphenylcyclopentadienylide; nonideal kinetics; mechanism

INTRODUCTION

The use of ylide as a radical initiator in polymerization reaction is of recent origin.^{1,2} Recently reported ylides in the organic chemistry ($>\overset{\ominus}{\text{C}}-\overset{\oplus}{\text{X}}$) are nitrogen, phosphorus, arsonium, stibonium, bismuthonium, sulfonium, selenonium, and telluronium. Ylides have enabled to carry out the polymerization of various vinyl monomers,^{3,4} giving mostly syndiotactic homopolymers as well as alternating copolymers.^{5,6} Ylides have also been used to initiate homopolymerization of methyl acrylate^{7,8} by reducing the problem of Trommsdorff⁹ effect to some extent, whereby gel formation takes place due to the autoacceleration in the rate of polymerization reaction. Stibonium ylide has been reported to carry out the polymerization of methyl acrylate up to 31% conversion¹⁰ without the onset of gel effect.

Stibonium ylide, because of the solubility and synthetic problem whereby the ylide itself decomposed under the reaction conditions, was not much studied until recently. Lloyd and coworkers¹¹ brought a breakthrough in the preparation of ylides from diazo compound by using copper complexes as catalyst. It facilitated to carry out the reactions in solution, in a variety

of solvents much below the normal decomposition temperature of the diazo compound.

The proposed mechanism of Lloyd and Singer has enabled to conduct some interesting work using stibonium ylide in the organic chemistry. Among the few publications^{12–14} available, the work on copolymerization of methyl acrylate with styrene using stibonium ylide has not been studied yet. This has motivated us to carry out the experimental study of the kinetics and mechanism of methyl acrylate with styrene in dioxane using triphenylstibonium 1,2,3,4-tetraphenylcyclopentadienylide as radical initiator.

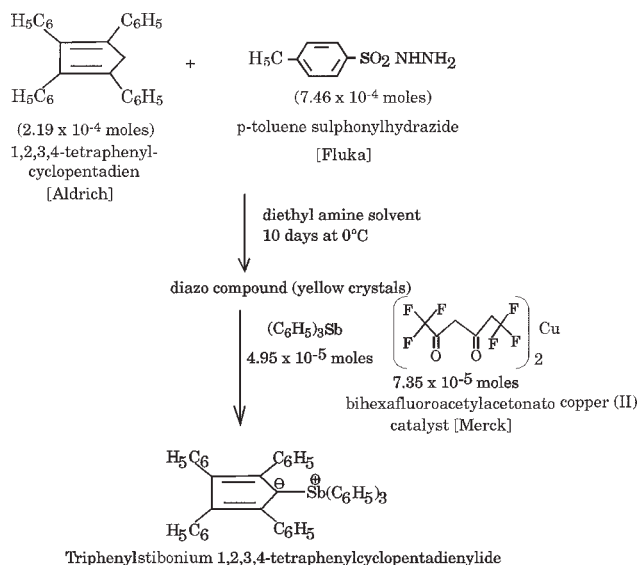
EXPERIMENTAL

Purification of monomers and solvents^{15,16} were carried out by standard methods. The synthesis of triphenylstibonium 1,2,3,4-tetraphenylcyclopentadienylide was carried out by the methods given by Lloyd and coworkers.¹¹ A solution containing 2.19×10^{-4} moles of 1,2,3,4-tetraphenylcyclopentadienylidene and 7.46×10^{-4} moles of *p*-toluene sulfonyl hydrazide in 6.3 mL diethylamine was kept at 0°C for 10 days. It was then followed by the addition of 3.5 mL water, 5 mL ether, and then dried over silica gel. The compound was finally washed with methanol to obtain yellow crystals of diazo compound. A solution of 2.64×10^{-4} moles of diazo compound, 7.35×10^{-5} moles of bis-hexafluoroacetylacetonato catalyst, and 4.95×10^{-5} moles of triphenylstibonium in 10 mL benzene were refluxed for 2 h. The evaporation of the solvent in vacuum resulted in triphenylstibonium 1,2,3,4-tetraphe-

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nylcyclopentadienylide. The reaction scheme is as follows:



Polymerization procedure

The polymerization reactions were carried out in 1,4 dioxane under oxygen-free conditions at $(60 \pm 0.1)^\circ\text{C}$ for 120 min using dilatometric apparatus (lower bulb capacity: 6 mL; diameter: 2 mm; capillary length: 5 cm). The advancement in the reaction was observed by the

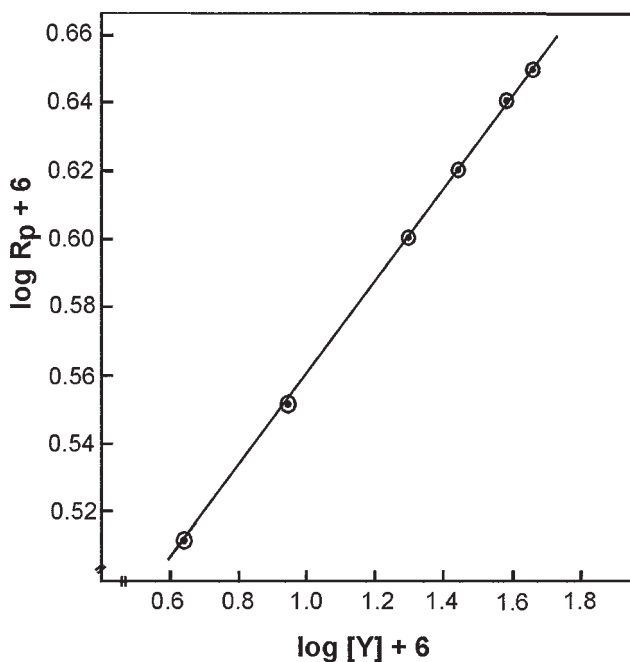


Figure 1 Plot between $\log R_p$ and $\log [\text{ylide}]$ for the copolymerization of methyl acrylate with styrene. $[\text{Ylide}] = 4.6\text{--}46.2 \times 10^{-6} \text{ mol L}^{-1}$, $[\text{MA}] = 1.48 \text{ mol L}^{-1}$; $[\text{Sty}] = 1.45 \text{ mol L}^{-1}$, time = 2 h, solvent = dioxane, temperature = $(60 \pm 0.1)^\circ\text{C}$.

change in the meniscus level per unit volume per unit time through cathetometer. The copolymer, precipitated in acidified methanol, was dried to constant weight and then refluxed with acetic acid and cyclohexane to remove the homopolymers, to calculate the percent conversion. Negligible weight loss was observed. The rate of polymerization was calculated from the slope of percentage conversion versus time plot.

The intrinsic viscosity (η) of the copolymers was determined in benzene at $(30 \pm 0.1)^\circ\text{C}$ using an Ubbelohde viscometer. These data were further used to calculate the viscosity average molecular weight (M_v) using Mark Houwink equation.

$$[\eta]_{\text{int}} = K[\overline{M}_v]^\alpha$$

where K and α are constant, whose values are 6.15×10^{-5} and 0.78,¹⁷ respectively. IR spectra of the copolymer were recorded on a PerkinElmer 599 B spectrophotometer using dichloromethane solvent. The nuclear magnetic resonance (NMR) spectra were recorded with the help of Varian 100 HA spectrometer, using CDCl_3 as solvent and tetramethylsilane as an internal reference.

RESULTS AND DISCUSSION

The results derived from the ylide-initiated copolymerization of methyl acrylate with styrene have been

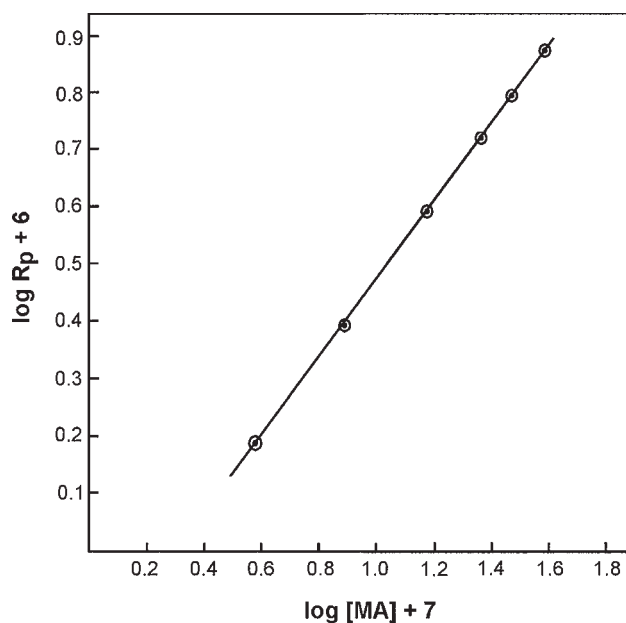


Figure 2 Plot between $\log R_p$ vs. $\log [\text{MA}]$ for the copolymerization of methyl acrylate with styrene. $[\text{Ylide}] = 18.5 \times 10^{-6} \text{ mol L}^{-1}$, $[\text{MA}] = 0.37\text{--}3.70 \text{ mol L}^{-1}$; $[\text{Sty}] = 1.45 \text{ mol L}^{-1}$, time = 2 h, solvent = dioxane, temperature = $(60 \pm 0.1)^\circ\text{C}$.

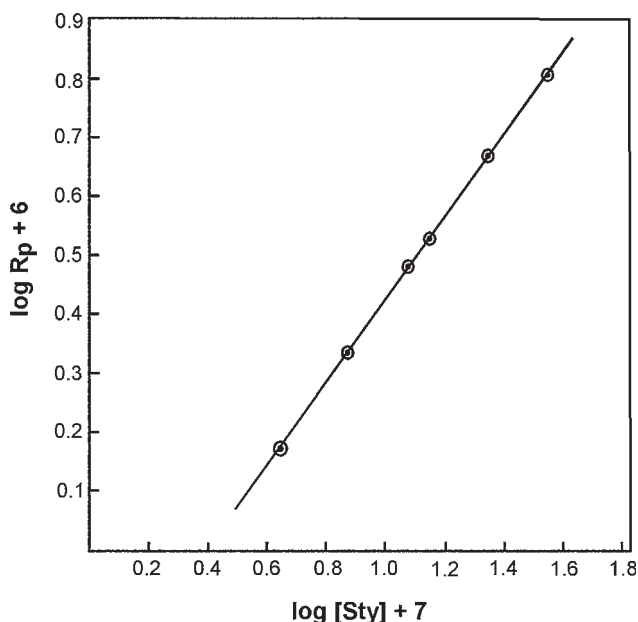


Figure 3 Plot between $\log R_p$ vs. $\log [\text{Sty}]$ for the copolymerization of methyl acrylate with styrene. $[\text{Ylide}] = 18.5 \times 10^{-6} \text{ mol L}^{-1}$, $[\text{MA}] = 1.48 \text{ mol L}^{-1}$; $[\text{Sty}] = 0.43\text{--}3.50 \text{ mol L}^{-1}$, time = 2 h, solvent = dioxane, temperature = $(60 \pm 0.1)^\circ\text{C}$.

summarized in Figures 1–9 and Tables I–IV. The reaction proceeds with the induction period of 1–14 min.

Effect of ylide

The use of stibonium ylide has facilitated the copolymerization of methyl acrylate with styrene without gelation caused by autoacceleration in the rate of polymerization. A maximum conversion of 24% was

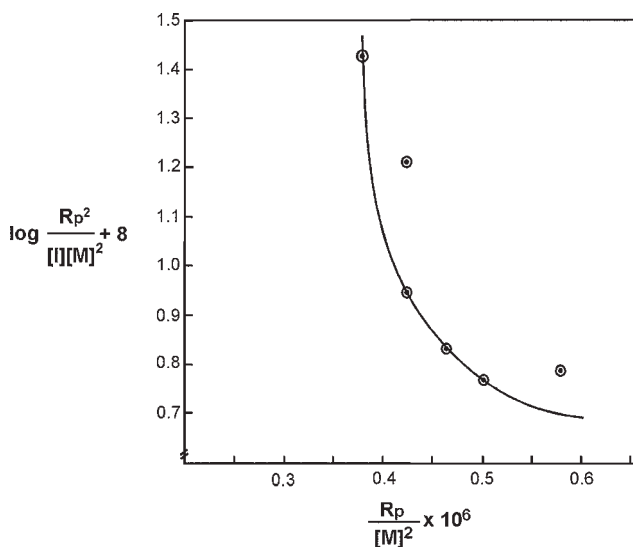


Figure 4 Plot between $\log R_p^2/[I][M]^2$ vs. $R_p/[M]^2$.

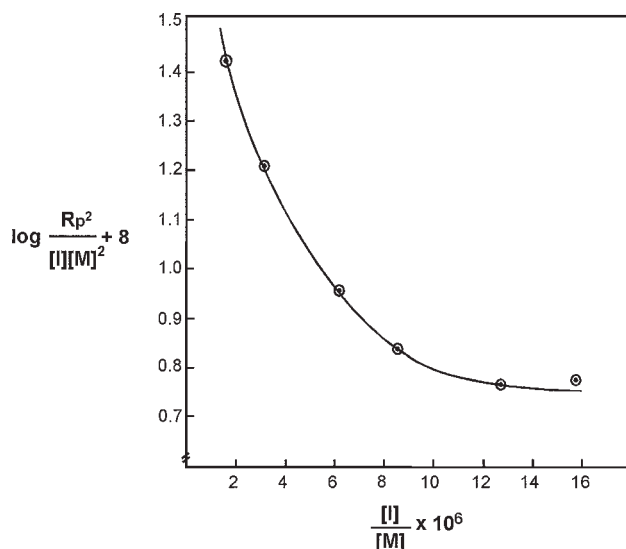


Figure 5 Plot between $\log R_p^2/[I][M]^2$ vs. $[I]/[M]$.

obtained upon carrying out the polymerization for 6 h, but we have limited the experiments for 2 h to restrict the conversion up to 10% to get good kinetic results. The effect of stibonium ylide on the rate of polymerization was studied by varying the concentration of ylide from $4.6 \times 10^{-6} \text{ mol L}^{-1}$ to $46.2 \times 10^{-6} \text{ mol L}^{-1}$ to limit the conversion up to 12%. A regular increase in the rate of polymerization was observed (Table I) and the initiator exponent value, obtained from the slope of the linear portion of $\log R_p$ vs. $\log [\text{ylide}]$ (Fig. 1), is 0.14 ± 0.01 , which is less than that expected for ideal radical kinetics (0.5).

Effect of monomer(s)

On varying concentration of methyl acrylate from 0.37 mol L^{-1} to 3.70 mol L^{-1} (Table II) keeping styrene and

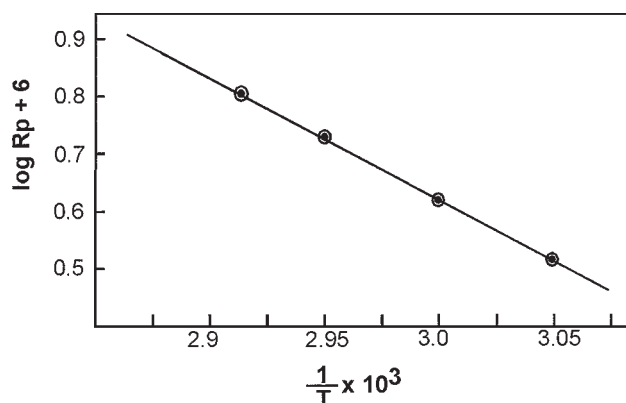


Figure 6 Plot of $\log R_p$ vs. $1/T$. $[\text{Ylide}] = 18.5 \times 10^{-6} \text{ mol L}^{-1}$, $[\text{MA}] = 1.48 \text{ mol L}^{-1}$; $[\text{Sty}] = 1.45 \text{ mol L}^{-1}$, time = 2 h, solvent = dioxane, temperature = $(60 \pm 0.1)^\circ\text{C}$.

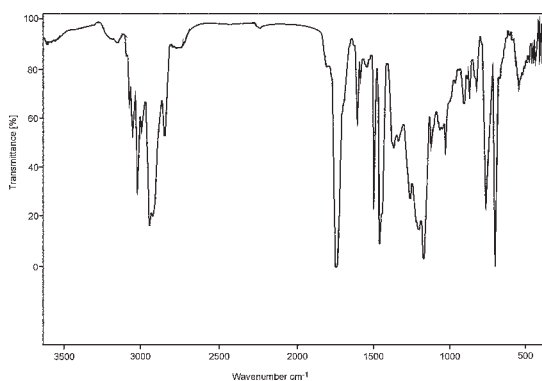


Figure 7 IR spectrum of the copolymer.

initiator constant at 1.45 mol L^{-1} and $18.5 \times 10^{-6} \text{ mol L}^{-1}$ respectively, an increase in the rate of polymerization was observed. Similar increase in polymerization was observed on varying the concentration of styrene from 0.43 mol L^{-1} to 3.5 mol L^{-1} (Table III) keeping methyl acrylate and initiator constant at 1.48 mol L^{-1} and $18.5 \times 10^{-6} \text{ mol L}^{-1}$, respectively. The monomer exponent value with respect to methyl acrylate and styrene obtained from the slope of the linear portion of $\log R_p$ vs. $\log [\text{monomer}]$ (Figs. 2–3) is 0.70 and 0.75 respectively.

The initiator and monomer(s) exponent value(s) suggest that the system follows nonideal¹⁸ radical kinetics. It may be due to the primary radical termination as well as degradative chain transfer reactions. Primary radical termination occurs due to the reaction between propagating radical and primary radical, instead of bimolecular termination. This result in the decrease in primary radical and, therefore, decrease in reaction rate. Primary radical termination is confirmed by the negative slope¹⁹ obtained from the plot between $\log R_p^2/[I][M]^2$ vs. $R_p/[M]^2$. The radicals formed from transfer reaction have equal affinity

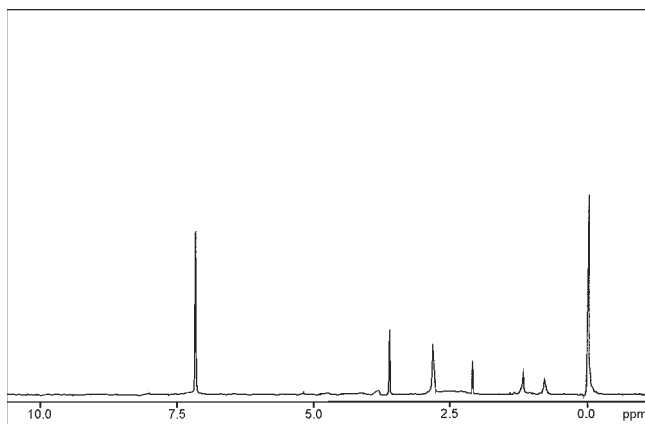


Figure 8 NMR spectrum of the copolymer.

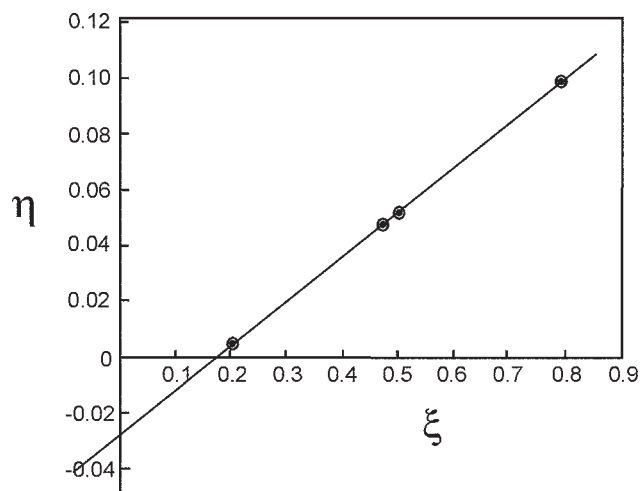


Figure 9 Kelen-Tüdös plot for determination of reactivity ratio.

for monomer as well as primary radical. The chain transfer reaction is caused by the reaction with primary radical, which results in decrease in the rate of polymerization as well as degree of polymerization and hence termed degradative chain transfer reaction. The negative slope obtained in MA-co-Sty system on plotting between $R_p^2/[I][M]$ and $[I]/[M]$ confirms the occurrence of degradative chain transfer reactions.

Effect of temperature

Polymerization reactions were also studied at 55, 65, and 70°C to calculate the energy of activation. The energy of activation, calculated from the slope of the Arrhenius plot of $\log R_p$ versus $1/T$ (Fig. 6), is 42 kJ mol^{-1} .

Characterization of the copolymers

Fourier transform infrared spectroscopy

The FTIR^{20,21} spectrum of the polymer (Fig. 7) shows the band at 1737 cm^{-1} due to the presence of acrylate

TABLE I
Effect of [ylide] on the Rate of Copolymerization of Methyl Acrylate with Styrene

[Ylide] (10^6 mol L^{-1})	% Conversion	R_p ($10^6 \text{ mol L}^{-1} \text{ s}^{-1}$)	\bar{M}_v
4.6	5.43	3.27	16,218
9.2	6.89	3.60	14,125
18.5	7.41	3.71	12,663
27.8	8.10	3.96	8,016
37.0	9.42	4.26	3,888
46.2	11.21	4.88	2,705

[MA] = 1.48 mol L^{-1} , [Sty] = 1.45 mol L^{-1} ; Polymerization time: 2 h; Polymerization temp: $60 \pm 0.1^\circ\text{C}$.

TABLE II
Effect of Methyl Acrylate [MA] on the Rate of Copolymerization of Methyl Acrylate with Styrene

[MA] (mol L ⁻¹)	% Conversion	$R_p \times 10^6$ (mol L ⁻¹ s ⁻¹)	\bar{M}_v
0.37	5.13	1.61	7,943.28
0.74	6.38	2.45	10,964.78
2.22	6.96	4.40	26,302.68
2.96	7.27	6.84	38,904.52
3.70	8.80	7.98	54,954.09

[Ylide] = 18.5×10^6 mol L⁻¹, [Sty] = 1.45 mol L⁻¹; polymerization time: 2 h, polymerization temp.: $60 \pm 0.1^\circ\text{C}$.

group, 1450–1600 cm⁻¹ (C=C stretching in aromatic rings) 3060 cm⁻¹ (aromatic C–H stretching), 2947 cm⁻¹ (aliphatic C–H stretching).

¹H-NMR

The ¹H-NMR spectrum of the polymer (Fig. 8) shows a singlet at 6.7–7.1 δ due to the phenyl protons and methoxy protons at 2.1 δ, 2.7–2.9 δ, and 3.4–3.8 δ, which indicates the alternating nature²² of the copolymer.

Copolymer composition

The copolymer composition is reported in Table IV. The mole fraction of MA and Sty was calculated from peak area due to methoxy protons and phenyl protons respectively.

The Kelen–Tüdös²³ method used for determining reactivity ratio r_1 and r_2 for the monomer pair is given below:

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

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

The value of α has been calculated by taking the square root of the product of the highest and the low-

TABLE III
Effect of Styrene [Sty] on the Rate of Copolymerization of Methyl Acrylate with Styrene

[Sty] (mol L ⁻¹)	% Conversion	$R_p \times 10^6$ (mol L ⁻¹ s ⁻¹)	\bar{M}_v
0.43	5.41	1.56	2,754.23
0.73	6.45	1.87	6,578.74
1.16	6.65	3.52	9,513.07
2.17	8.00	4.08	23,134.30
3.51	8.86	6.65	42,657.95

[Ylide] = 18.5×10^6 mol L⁻¹, [MA] = 1.48 mol L⁻¹; polymerization time: 2 h, polymerization temp.: $60 \pm 0.1^\circ\text{C}$.

est value of H for copolymerization series. The variable G and H have been determined by:

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

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

The graph plotted between η and ξ gives the value of r_1 and r_2 where r_1 is determined from the slope and r_2 is the intercept on the y -axis. The reactivity ratio^{24,25} values, calculated from the Kelen–Tüdös method (using LSM) is 0.16 ± 0.01 and 0.028 ± 0.005 for r_1 (MA) and r_2 (Sty) respectively, (Fig. 9). This suggests the alternating nature of the copolymer. The values of r_1 (MA) and r_2 (Sty) reported in literature²⁶ is 0.18 ± 0.02 and 0.75 ± 0.03 respectively, for random polymer. A search of literature¹² reveals that alternating copolymers were also obtained by free-radical copolymerization of methyl acrylate with styrene, using imidazolium-*p*-chlorophenacylide.

Mechanism

As reported earlier,²⁷ the stibonium ylide dissociates to yield a phenyl radical, which initiates the polymerization. The initiation steps are as follows:

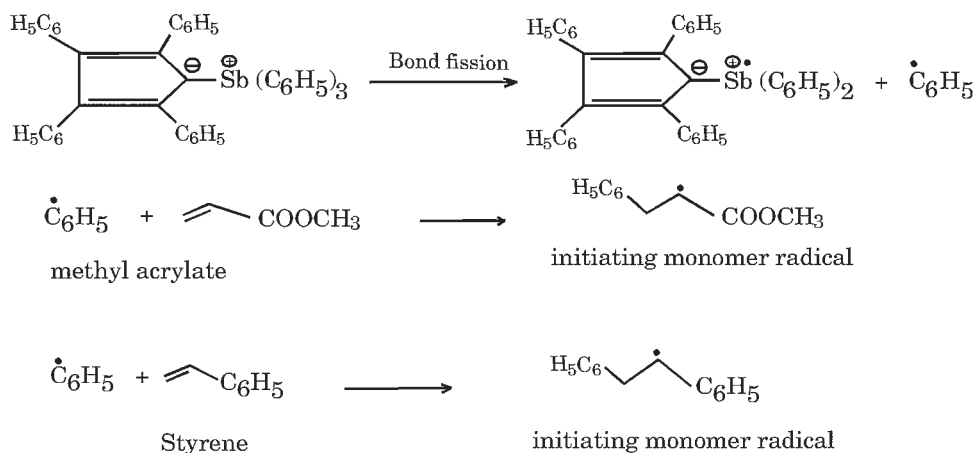


TABLE IV
Composition of the Copolymer

S. no.	Monomer feed [MA/Sty]	Copolymer feed [MA/Sty]	Mole fraction of MA in copolymer (M_1)	Mole fraction of Sty in copolymer (M_2)	η	ξ
1	0.51	1.27	0.56	0.44	0.006	0.21
2	2.05	1.44	0.59	0.41	0.098	0.79
3	1.02	1.33	0.57	0.43	0.052	0.50
4	0.68	0.67	0.40	0.60	0.047	0.47

[Ylide] = $18.5 (10^{-6} \text{ mol L}^{-1})$, polymerization time: 2 h, polymerization temp.: $60 \pm 0.1^\circ\text{C}$.

CONCLUSIONS

The copolymerization of methyl acrylate with styrene, initiated by triphenylstibonium 1,2,3,4-tetraphenylcyclopentadienylide follows nonideal kinetics due to primary radical termination as well as degradative chain transfer reaction. The resulted copolymer is alternate in nature.

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