

Radical Polymerization of *n*-Butyl Methacrylate Initiated by Stibonium Ylide

Sumita Srivastava, A. K. Srivastava

Department of Chemistry, H. B. T. I., Kanpur 208002, India

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ABSTRACT: 1,2,3,4-Tetraphenylcyclopentadiene triphenyl stibonium ylide initiated radical polymerization of *n*-butyl methacrylate (*n*-BMA) in dioxane at $(60 \pm 0.2)^\circ\text{C}$ for 90 min under nitrogen atmosphere has been carried out. The system follows nonideal kinetics, i.e., $R_p \propto [\text{ylide}]^{0.2} [n\text{-BMA}]^{1.8}$. The value of k_p^2/k_t and overall energy of activation have been computed as $0.133 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$, 33 kJ/mol, respectively. The FTIR spectrum shows a band at 1745 cm^{-1} due to acrylate group of *n*-BMA. The ^1H NMR spectrum shows a peak of two magnetically equivalent

protons of methylene group at 2.1 δ ppm. The DSC curve shows glass transition temperature (T_g) as 41°C . The presence of six hyperfine lines in ESR spectrum indicates that the system follows free radical polymerization and the initiation is brought about by phenyl radical. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 2457–2463, 2007

Key words: *n*-butyl methacrylate; nonideal kinetics; mechanism; polymerization; ylide; activation energy

INTRODUCTION

In the past few years, the industrial use of *n*-butyl methacrylate (*n*-BMA) polymers has grown enormously. The poly(*n*-BMA) finds applications in lubricating oils, additives, surface coatings, impregnates, adhesives, binders, sealers, and floor polishes. Because of a variety of industrial applications, poly(*n*-BMA) has been synthesized by several conventional water soluble initiators¹ like potassium persulphate, 2,2'-azobis (2-methyl propionamide) dihydrochloride (V-50), and 2,2'-azobis [2-(2-dimidazolin-2-yl) propane] dihydrochloride (VA-044). Further, the plasma-induced polymerization of *n*-BMA has been carried out by Simionescu et al.^{2,3} The field attracted a number of workers^{4,5} who reported ATRP polymerization of *n*-BMA. The water-born ATRP of *n*-BMA in homogeneous alcoholic media at room temperature has also been carried out by McDonald and Rannard.⁶ Vosloo et al.⁷ synthesized comb like poly(*n*-BMA) by using reversible addition-fragmentation chain transfer and activated ester. The effect of pluronic surfactants on the polymer diffusion rate in poly(*n*-BMA) latex films has been investigated by Ye et al.,⁸ whereas Beuermann⁹ studied the impact of hydrogen bonding on propagation kinetics in *n*-BMA radical polymerization. However, no ylide has

been examined as new initiator for the polymerization of *n*-BMA.

Because of the development of new polymerization techniques, the latter part of the century witnessed monomers and initiators, a revolution in the field of synthetic polymers. In this series, a new and extremely interesting field, polymer-ylide chemistry is of recent origin,^{10–14} i.e., synthesis of polymers initiated by ylides. Ylides (𑖧𑖧) are 1,2 dipolar compounds in which a positively charged heteroatom is connected to a carbanion. The search of published research revealed that the ylides containing N, P, As, and Bi have been used as new radical initiator(s) for the polymerization of vinyl monomers like styrene,¹⁵ vinyl acetate,¹⁶ methyl methacrylate,^{17,18} and methyl acrylate.¹⁹ The use of stibonium ylide in the domain of polymer science, because of the difficulties associated with their synthesis, is still scarce.²⁰ Stibonium ylide, because of the presence of $p\pi-d\pi$ bonding, is more stable than nitrogen ylide. To the best of our knowledge, stibonium ylide has never been used for the synthesis of poly(*n*-BMA). This article is an outcome of such efforts, which clearly demonstrate that 1,2,3,4-tetraphenylcyclopentadiene triphenyl stibonium ylide can be successfully used as an initiator for the synthesis of poly(*n*-BMA).

EXPERIMENTAL

Materials

n-Butyl methacrylate (*n*-BMA) (Lancaster:14637) and other solvents were purified by the usual methods.^{21,22}

Correspondence to: A. K. Srivastava (akspolym@rediffmail.com).

TABLE I
Effect of $[n\text{-BMA}]$ on the Rate of Polymerization (R_p) of n -Butyl Methacrylate Initiated by 1,2,3,4-Tetraphenylcyclopentadiene Triphenyl Stibonium Ylide in Dioxane

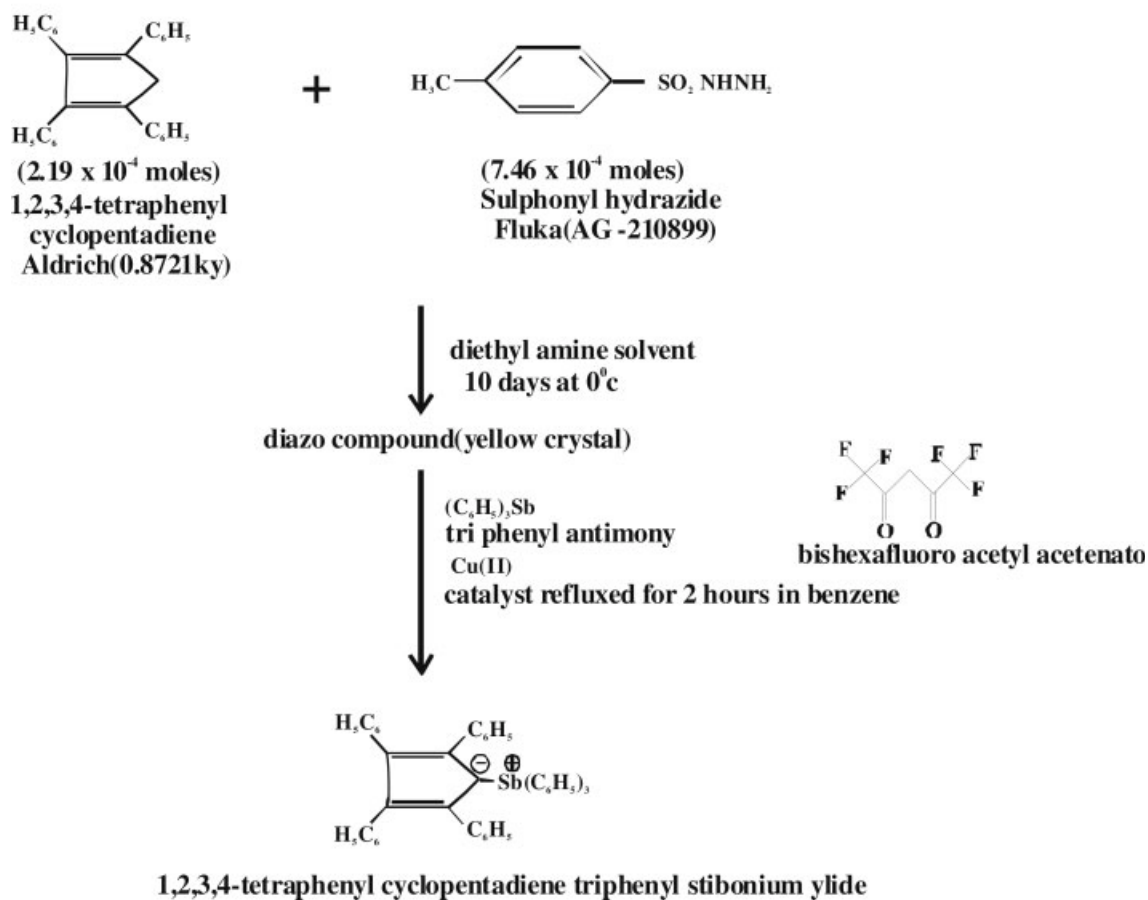
Sample no.	$[n\text{-BMA}]$ mol L ⁻¹	% Conversion	R_p (10 ⁶ mol L ⁻¹ s ⁻¹)	\bar{M}_v (10 ⁻⁵)
1	0.28	3.0	0.17	1.11
2	0.56	5.0	0.56	1.20
3	0.70	7.2	1.04	1.31
4	0.84	8.9	1.49	1.56
5	1.12	11.1	2.49	1.77

$[n\text{-BMA}] = 0.28$ to 1.12 mol L⁻¹.
 $[\text{Ylide}] = 3.08 \times 10^{-6}$ mol L⁻¹.
 Polymerization temp. = $(60 \pm 0.2)^\circ\text{C}$.
 Polymerization time = 90 min.

1,2,3,4-Tetraphenylcyclopentadiene (Aldrich: 0.8721 ky), p -toluene sulfonyl hydrazide (Fluka:AG-210899), triphenyl antimony (Merck-Schuchardt Art.821199), and

Cu(II) bishexafluoroacetyl acetanato (Merck) were used without further purification. The stibonium ylide was prepared by the method given by Glidewell and Lloyd.²³

Synthesis of triphenyl stibonium ylide



Polymerization procedure

The polymerization of n -BMA in 1,4-dioxane at $(60 \pm 0.2)^\circ\text{C}$ for 90 min under oxygen-free conditions was carried out dilatometrically to restrict the % conversion to 12.2. The polymer(s), precipitated with acidified methanol, were dried to constant weight. The rate of polymerization (R_p) was calcu-

lated from the slope of plot between % conversion versus time.

The intrinsic viscosity (dL/g) of the polymers was determined in benzene at $(25 \pm 0.1)^\circ\text{C}$ with an Ubbelohde viscometer to calculate the viscosity-average molecular weight \bar{M}_v , using values of the Mark-Houwink constant²⁴ (K and α) as 3.82×10^{-5} and 0.774, respectively.

TABLE II
Effect of [Ylide] on the Rate of Polymerization (R_p) of *n*-Butyl Methacrylate Initiated by 1,2,3,4-Tetraphenylcyclopentadiene Triphenyl Stibonium Ylide in Dioxane

Sample no.	[Ylide] (10^6 mol L^{-1})	% Conversion	R_p ($10^6 \text{ mol L}^{-1} \text{ s}^{-1}$)	M_v (10^{-5})
6	2.05	5.8	0.95	1.54
3	3.08	7.2	1.04	1.31
7	6.15	9.2	1.25	0.85
8	15.47	10.8	1.34	0.67
9	21.52	12.2	1.71	0.44

[Ylide] = 2.05 to $21.52 \times 10^{-6} \text{ mol L}^{-1}$.
[*n*-BMA] = 0.70 mol L^{-1} .
Polymerization temp. = $(60 \pm 0.2) \text{ C}$.
Polymerization time = 90 min.

Characterization

The Fourier transform infrared (FTIR) spectra were recorded with PerkinElmer, 599 B spectrophotometer. ^1H NMR spectra were recorded with a Varian 100 HA Jeol LA 400 spectrophotometer using C_6D_6 as a solvent and tetra methyl silane as an internal reference. The DSC runs were carried out using a VA.0B Dupont 2100 analyzer, sample weight 4.6800 mg, at a heating rate of $10^\circ\text{C}/\text{min}$. The TGA runs were carried out using a V5.1A Dupont 2100 analyzer, sample weight $\sim 10 \text{ mg}$, at a heating rate of $10^\circ\text{C}/\text{min}$. The ESR spectrum was recorded on X-band EPR 109 E-line century series spectrometer at room temperature.

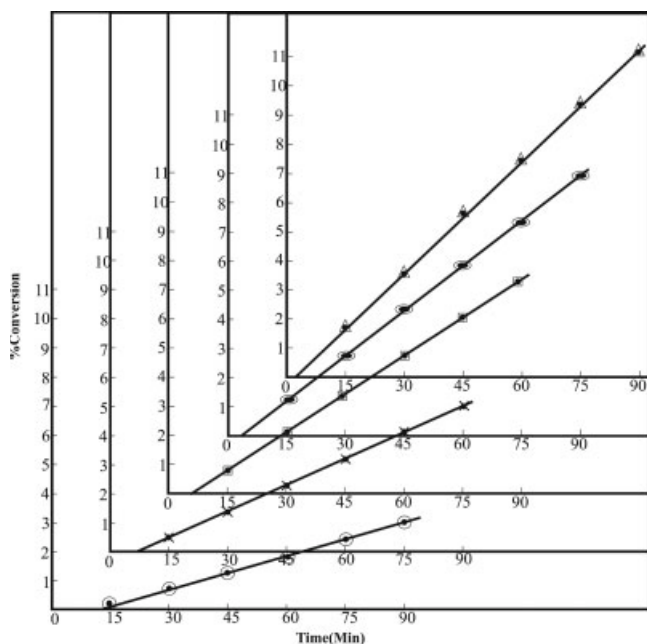


Figure 1 Percentage conversion versus time plots for the polymerization of *n*-butyl methacrylate [*n*-BMA]. [ylide] = $3.08 \times 10^{-6} \text{ mol L}^{-1}$, [*n*-BMA] = 0.28 to 1.12 mol L^{-1} , temp. = $60 \pm 0.2^\circ\text{C}$, total reaction time = 90 min.

RESULTS AND DISCUSSION

The kinetic studies were carried out by varying the concentration of initiator and monomer. The polymerization proceeded with an induction period of $3 \pm 2 \text{ min}$. The results are illustrated in Tables I and II and Figures 1–8.

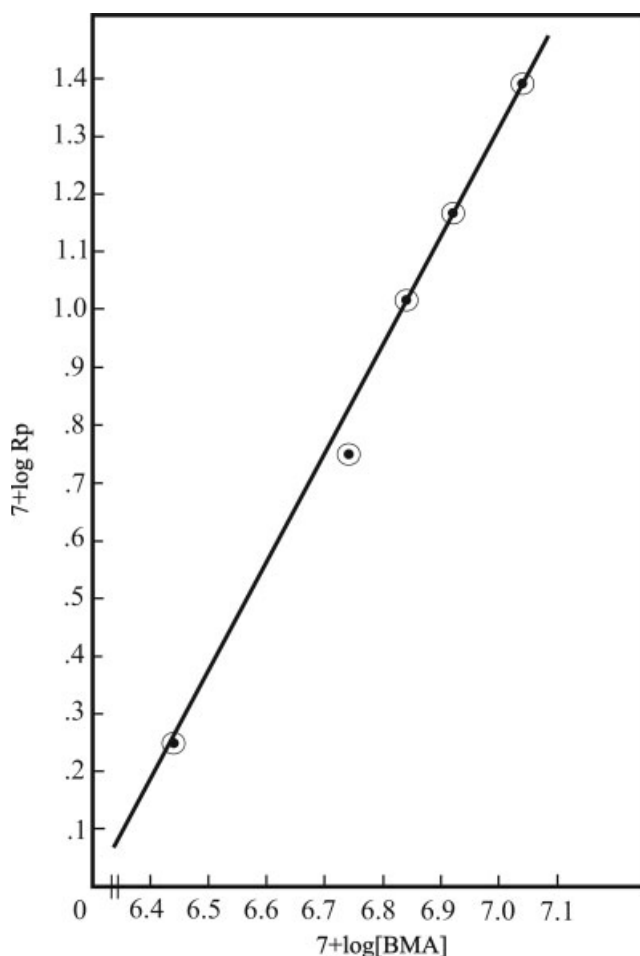


Figure 2 Relationship between $\log [n\text{-BMA}]$ and $\log R_p$ for the polymerization of *n*-butyl methacrylate [*n*-BMA]. [Ylide] = $3.08 \times 10^{-6} \text{ mol L}^{-1}$, [*n*-BMA] = 0.28 to 1.12 mol L^{-1} , temp. = $60 \pm 0.2^\circ\text{C}$, time = 90 min.

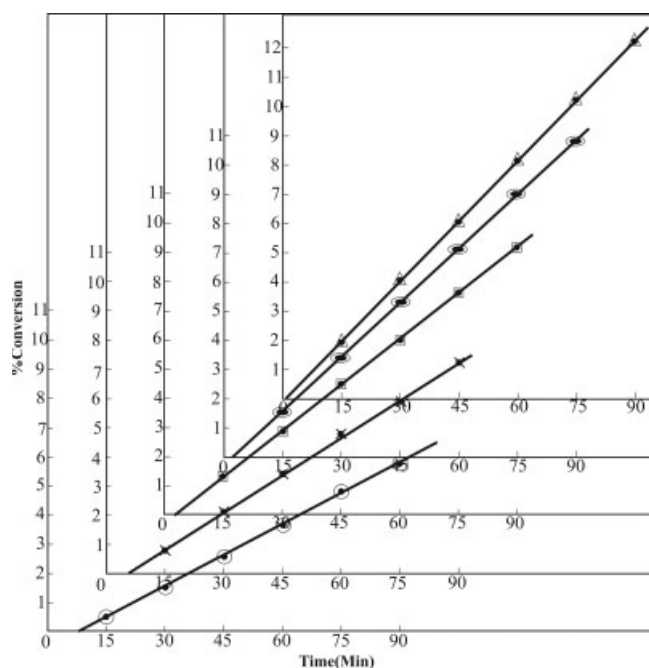


Figure 3 Percentage conversion versus time plots for polymerization of *n*-butyl methacrylate [*n*-BMA]. [Ylide] = 2.05 to 21.52×10^{-6} mol L⁻¹, [*n*-BMA] = 0.70 mol L⁻¹, temp. = $60 \pm 0.2^\circ\text{C}$, total reaction time = 90 min.

Effect of the monomer concentration

The effect of *n*-BMA concentration on the R_p and average molecular weight of the polymer was studied by varying the [*n*-BMA] from 0.28 to 1.12 mol L⁻¹ while keeping [ylide] constant at 3.08×10^{-6} mol L⁻¹ (Table I). The R_p increases as the monomer concentration is increased (Fig. 1). The monomer exponent value calculated from the slope of a linear plot of $\log R_p$ versus $\log [n\text{-BMA}]$ is 1.8 (Fig. 2). Likewise, the average molecular weight of the polymer also increases from 1.11×10^5 to 1.77×10^5 when the monomer concentration increases (Table I).

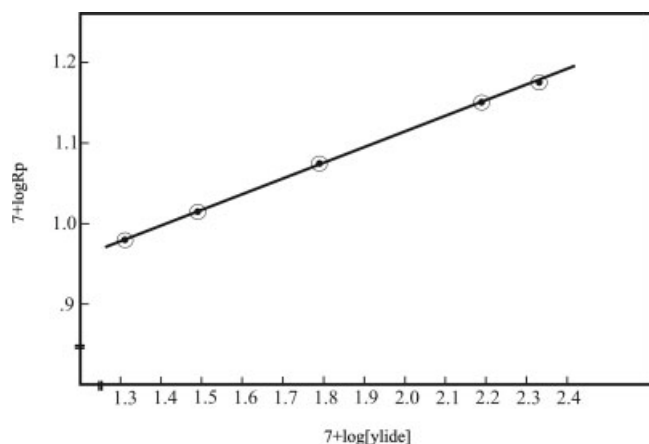


Figure 4 Relationship between $\log R_p$ and $\log [\text{ylide}]$ for the polymerization of *n*-butyl methacrylate [*n*-BMA]. [Ylide] = 2.05 to 21.52×10^{-6} mol L⁻¹, [*n*-BMA] = 0.70 mol L⁻¹, temp. = $60 \pm 0.2^\circ\text{C}$, time = 90 min.

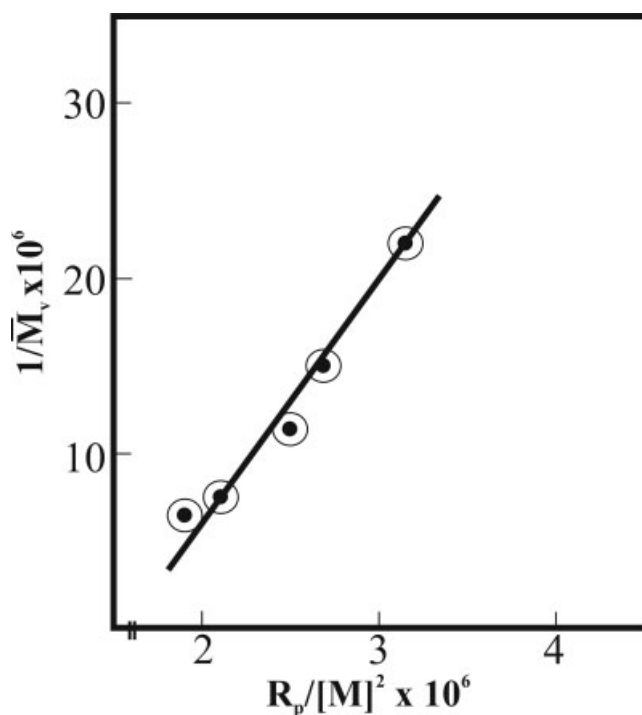


Figure 5 Relationship between $1/\bar{M}_v$ and $R_p/[M]^2$ for the polymerization of *n*-butyl methacrylate [*n*-BMA]. [Ylide] = 2.05 to 21.52×10^{-6} mol L⁻¹, [*n*-BMA] = 0.70 mol L⁻¹, temp. = $60 \pm 0.2^\circ\text{C}$, time = 90 min.

Effect of the initiator concentration

When the [ylide] was increased to 9.22×10^{-5} mol L⁻¹, keeping [*n*-BMA] constant at 0.70 mol L⁻¹, the

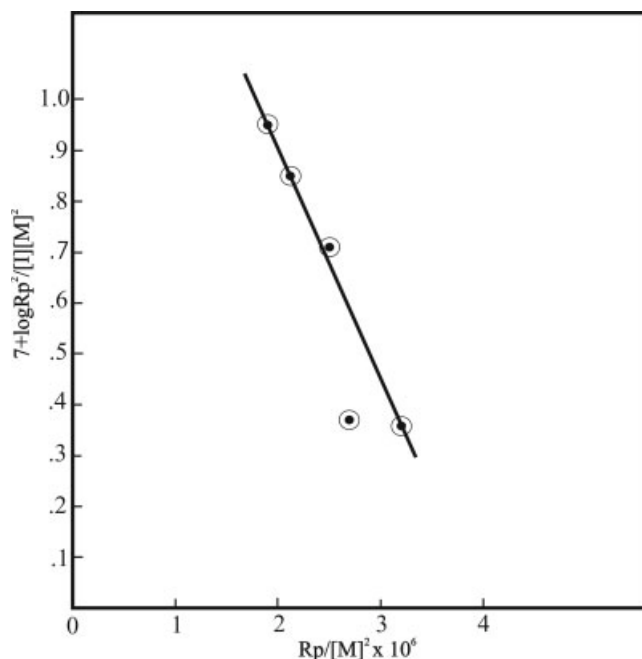


Figure 6 Relationship between $\log R_p^2/[I][M]^2$ and $R_p/[M]^2$. [Ylide] = 2.05 to 21.52×10^{-6} mol L⁻¹, [*n*-BMA] = 0.70 mol L⁻¹, temp. = $60 \pm 0.2^\circ\text{C}$, time = 90 min.

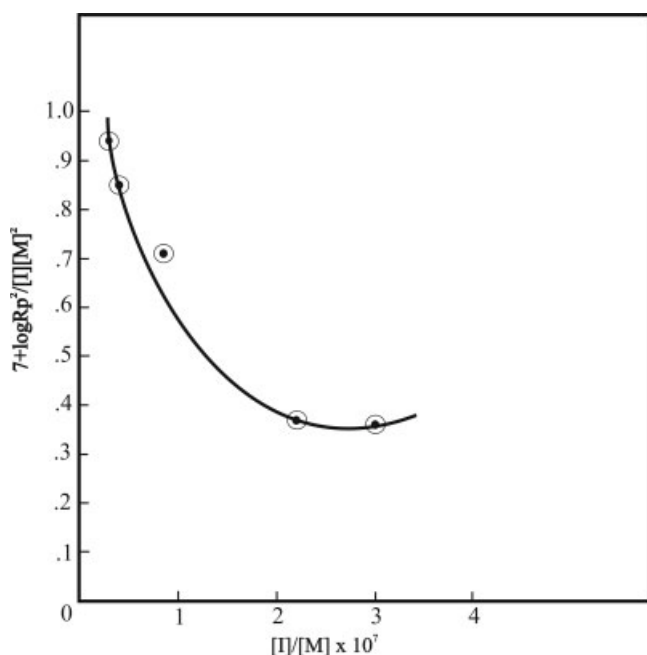


Figure 7 Relationship between $\log R_p^2/[I][M]^2$ and $[I]/[M]$. $[Y_{\text{ylide}}] = 2.05$ to 21.52×10^{-6} mol L⁻¹, $[n\text{-BMA}] = 0.70$ mol L⁻¹, temp. = $60 \pm 0.2^\circ\text{C}$, time = 90 min.

% conversion was 25.68%. Therefore, the effect of $[Y_{\text{ylide}}]$ on the R_p was examined by varying $[Y_{\text{ylide}}]$ from 2.05×10^{-6} to 21.52×10^{-6} mol L⁻¹ (Table II), which restricts the % conversion up to 12.2% to obtain good kinetic results. The polymerization rate increases as the ylide concentration is increased (Fig. 3). The initiator exponent calculated (by LSM) from the slope of the linear plot of $\log R_p$ vs. $\log [Y_{\text{ylide}}]$ is 0.2 (Fig. 4). The average molecular weight (\bar{M}_v) of

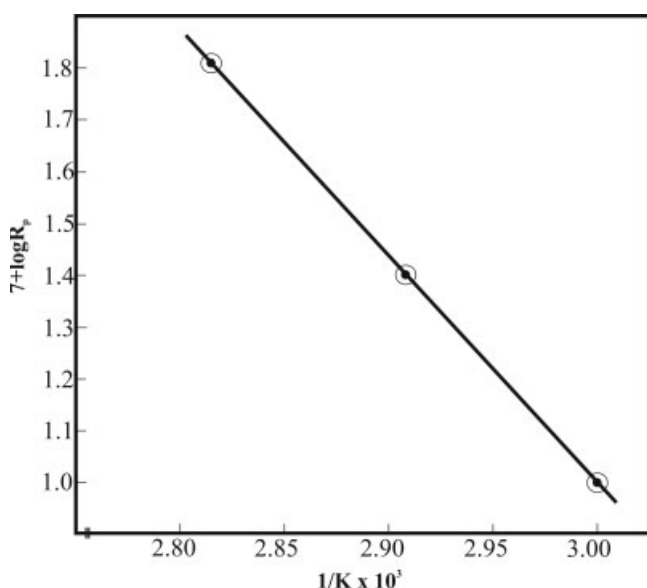


Figure 8 Arrhenius plot of $\log R_p$ versus polymerization temperature. $[Y_{\text{ylide}}] = 3.08 \times 10^{-6}$ mol L⁻¹, $[n\text{-BMA}] = 0.70$ mol L⁻¹, temp. = 60, 70, $85 \pm 0.2^\circ\text{C}$, time = 90 min.

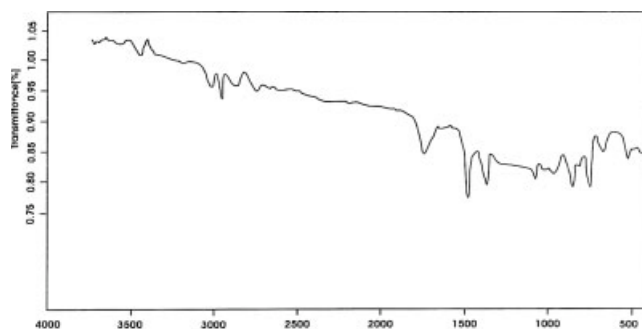


Figure 9 FTIR spectrum of poly(*n*-butyl methacrylate) (Sample 3).

polymers decreases as $[Y_{\text{ylide}}]$ increased concentration. The value of k_p^2/k_t (where k_p and k_t are propagation and termination rate constant), determined from the slope of the plot of $1/\bar{M}_v$ versus $R_p/[M]^2$ is 0.133×10^{-2} L mol⁻¹ s⁻¹ (Fig. 5).

The value of initiator and monomer exponent suggests that the system follows nonideal kinetics. It may be explained by analyzing the role of stibonium ylide as primary radical terminator as well as degradative chain transfer agent.

To analyze the effect of primary radical termination, a suitably modified expression given by Deb and Meyerhoff²⁵ in the following form is used:

$$\log \frac{R_p^2}{[Y][M]^2} = \log \frac{2f_k K_d K_p^2}{K_t} - 0.8684 \frac{K_{\text{prt}}}{K_Y \times K_p} \times \frac{R_p}{[M]^2}$$

where Y and M represent ylide and monomer, respectively. A plot of the left hand side of the above equation versus $R_p/[M]^2$ gave a negative slope (Fig. 6), indicating primary radical termination due to ylide for the present system.

The following equation, derived by Deb²⁶ and further simplified by Ghosh and Mitra²⁷ was used to examine the role of ylide as degradative chain transfer agent.

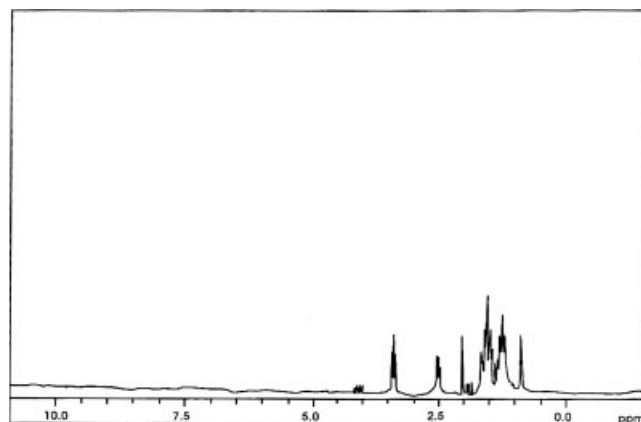


Figure 10 ¹H NMR spectrum of poly(*n*-butyl methacrylate) (Sample 3).

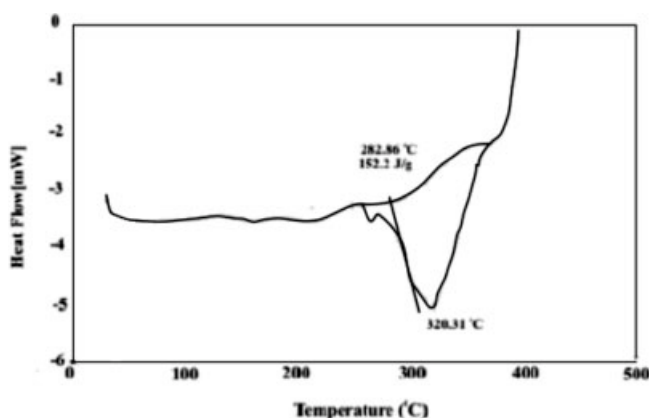


Figure 11 DSC curve of poly(*n*-butyl methacrylate) (Sample 3).

$$\log \frac{R_p^2}{[Y][M]^2} = \log \frac{2f_k k_d k_p^2}{K_t} - 0.434 \frac{k_p^2}{k_t} \times \frac{k_{rt} Y}{k_y Y k_p} \times C_1 \left(\frac{Y}{M} \right)$$

where C_1 is the ylide transfer constant. The plot of the left hand side of the above equation versus $[Y]/[M]$ also gave a negative slope (Fig. 7), suggesting degradative chain transfer reaction due to ylide.

Effect of temperature

The rate of polymerization was also measured at three different temperatures at a fixed monomer concentration (0.70 mol L^{-1}) and initiator concentration ($3.08 \times 10^{-6} \text{ mol L}^{-1}$). The rate of polymerization increases with the temperature and the overall activation energy (ΔE), calculated from the corresponding slope of the Arrhenius plot of $\log R_p$ versus $1/T$ (Fig. 8), is 33 kJ/mol .

SPECTRAL ANALYSIS

Fourier transform infrared spectroscopy

The FTIR spectrum of the poly(*n*-BMA) (Fig. 9) shows a band appeared at 1745 cm^{-1} due to acrylate

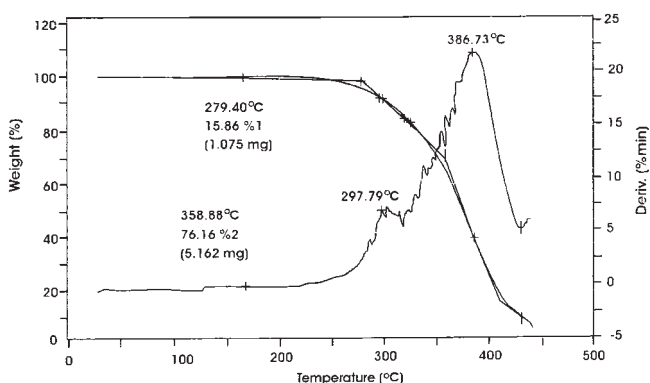


Figure 12 TGA curve of poly(*n*-butyl methacrylate) (Sample 3).

group of the polymer. The band at 1072 cm^{-1} is only noticed in syndiotactic²⁸ poly(*n*-BMA).

¹H NMR spectroscopy

The ¹H NMR spectrum of the polymer shows a peak of two magnetically equivalent protons of methylene group at $2.1 \delta \text{ ppm}$ (Fig. 10) indicating the syndiotactic²⁹ nature of the polymer. The acrylate protons appear as triplet at $3.5 \delta \text{ ppm}$.

THERMAL ANALYSIS

Differential scanning calorimetry

The DSC curve indicates the glass transition temperature of poly(*n*-BMA) as 41°C (Fig. 11). Lacabanne and coworkers³⁰ has observed that the T_g value of poly(*n*-BMA) is 33°C , whereas Patterson et al.³¹ measured it as 55°C . The T_g value reported in this work is in accordance with the literature.

The temperature T_{max} for maximum rate of crystallization has been calculated by the following equation.³²

$$T_{\text{max}} = T_g + \left(\frac{2}{3} \right) (T_m - T_g)$$

T_{max} for *n*-BMA is 227.20°C , where T_g and T_m values are 41 and 320.31°C , respectively.

Thermogravimetric analysis

The TGA curve for poly(*n*-BMA) (Fig. 12) exhibits weight loss with temperature.^{33,34} The polymer starts to decompose at 280°C . The thermal behavior data are as follows:

1. On set of major weight loss at 279°C is 15.86% and completion of major weight loss at 444°C .
2. Weight loss in the range $279\text{--}360^\circ\text{C}$ is 76.16%.
3. The volatilization temperature is 387°C .

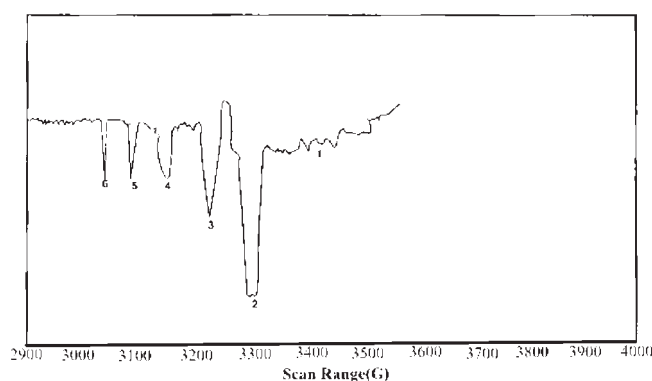
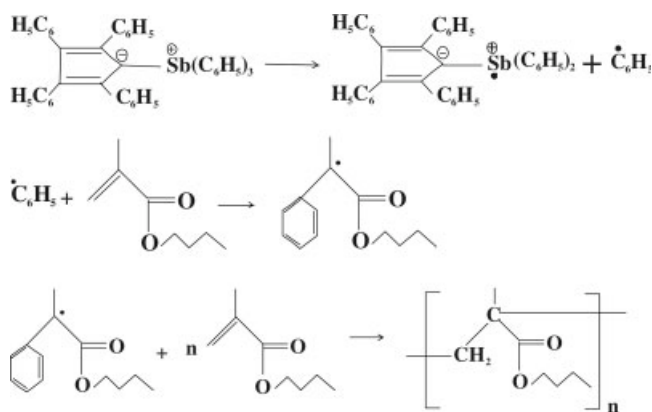


Figure 13 ESR spectrum.

MECHANISM

The kinetic study indicates that the system follows nonideal kinetics of radical polymerization. It has been reported in literature²⁰ that stibonium ylide undergoes bond fission between the hetero atom and the phenyl group to yield phenyl free radical, which is responsible for the initiation of the polymerization reaction. The radical mode of polymerization is further confirmed by the ESR spectrum³⁵ (Fig. 13), which shows six hyperfine lines and the hyperfine constant value is 3.73 G. Therefore, in the present case, the ylide dissociates to form phenyl radical as reported earlier for other system.^{36–38}

On the basis of the above-mentioned reaction, the following mechanism can be proposed.



CONCLUSIONS

From the earlier discussion, it is clear that 1,2,3,4-tetraphenyl cyclopentadiene triphenyl stibonium ylide is a new initiator for the synthesis of syndiotactic poly(*n*-BMA) having T_g value as 41°C. The presence of a band at 1072 cm^{-1} confirms syndiotactic nature of the polymer. The overall energy of activation is evaluated as 33 kJ/mol. The polymer is stable up to 280°C. The system follows nonideal kinetics due to primary radical termination and degradative chain transfer reaction. The rate of equation can be simply expressed as follows:

$$R_p \propto [\text{ylide}]^{0.2} [n - \text{BMA}]^{1.8}$$

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