

# *p*-Acetylbenzylidene Triphenylarsonium Ylide Initiated Radical Polymerization of Methyl Acrylate

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**ABSTRACT:** Polymerization of methyl acrylate (MA), initiated by *p*-acetyl benzylidene triphenylarsonium ylide (*p*-ABTAY) in dioxan at  $(60 \pm 1)^\circ\text{C}$  for 1 h, follows nonideal kinetics ( $R_p \propto [I]^{0.21}[M]^{1.40}$ ) due to primary radical termination as well as degradative chain transfer reaction. The polymerization proceeded upto 20.49% conversion without gelation and results in the polymer of high molecular weight 98,000. The overall activation energy

and the value of  $k_p^2/k_t$  are  $14 \text{ kJ mol}^{-1}$  and  $18.75 \times 10^{-6} \text{ L mol}^{-1} \text{ s}^{-1}$ , respectively. The ylide dissociates to form phenyl radical, which initiates the polymerization of MA. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 1967–1972, 2008

**Key words:** MA; *p*-ABTAY; radical polymerization; kinetics; mechanism; activation energy

## INTRODUCTION

Looking down on the large amount of data available for polymerization of vinyl monomers, limited quantitative kinetic information is available on the homopolymerization of MA.<sup>1–7</sup> It is well known that polymerization of MA poses the problem of auto-acceleration<sup>8</sup> also referred to as Trommsdorff or gel effect. Mahadevan and Santhappa<sup>9</sup> also reported a maximum conversion of 10% with benzoylperoxide. Kice<sup>10</sup> also reported 12% conversion for bulk polymerization of MA with azobisisobutyronitrile (AIBN). Many new radical initiators, such as  $\beta$ -picolinium-*p*-chloro phenacylide ( $\beta$ -PCPY),<sup>11</sup> *p*-bromophenacyldimethyl sulphoniumylide,<sup>12</sup> triphenyl-bismuthonium 1, 2, 3, 4-tetraphenyl-cyclopentadienylide,<sup>13</sup> imidazolium-*p*-chlorophenacylide (ICPY),<sup>14</sup> triphenylstibonium 1,2,3,4-tetraphenyl-cyclopentadiene ylide,<sup>15</sup> have also been used as radical initiator for homopolymerization of MA to obtain 20%, 23%, 30%, 33%, 31% conversion without gelation, respectively. However, *p*-acetyl benzylidene triphenylarsonium ylide (*p*-ABTAY) has not been used for polymerization of MA. This article demonstrate that the *p*-ABTAY can be used as a new initiator to carry out polymerization upto 20.49% conversion without gelation and a polymer of high molecular weight (98,000) is obtained.

## EXPERIMENTAL

MA (Merck, Germany) was purified by treating it with alkali and distilled water, followed by vacuum distillation. The ylide (*p*-ABTAY) was prepared by the published<sup>16</sup> method.

### Polymerization procedure

The polymerization of MA was carried out in 1,4-dioxan at  $(60 \pm 1)^\circ\text{C}$  for 1 h using dilatometric technique (capillary = 2.0 mm, diameter and lower bulb capacity = 2.5 mL) under inert atmosphere of nitrogen. The polymer was precipitated in acidified methanol and dried to constant weight to calculate the percentage conversion. The rate of polymerization ( $R_p$ ) was calculated from the slope(s) of the percentage conversion versus the time plots.

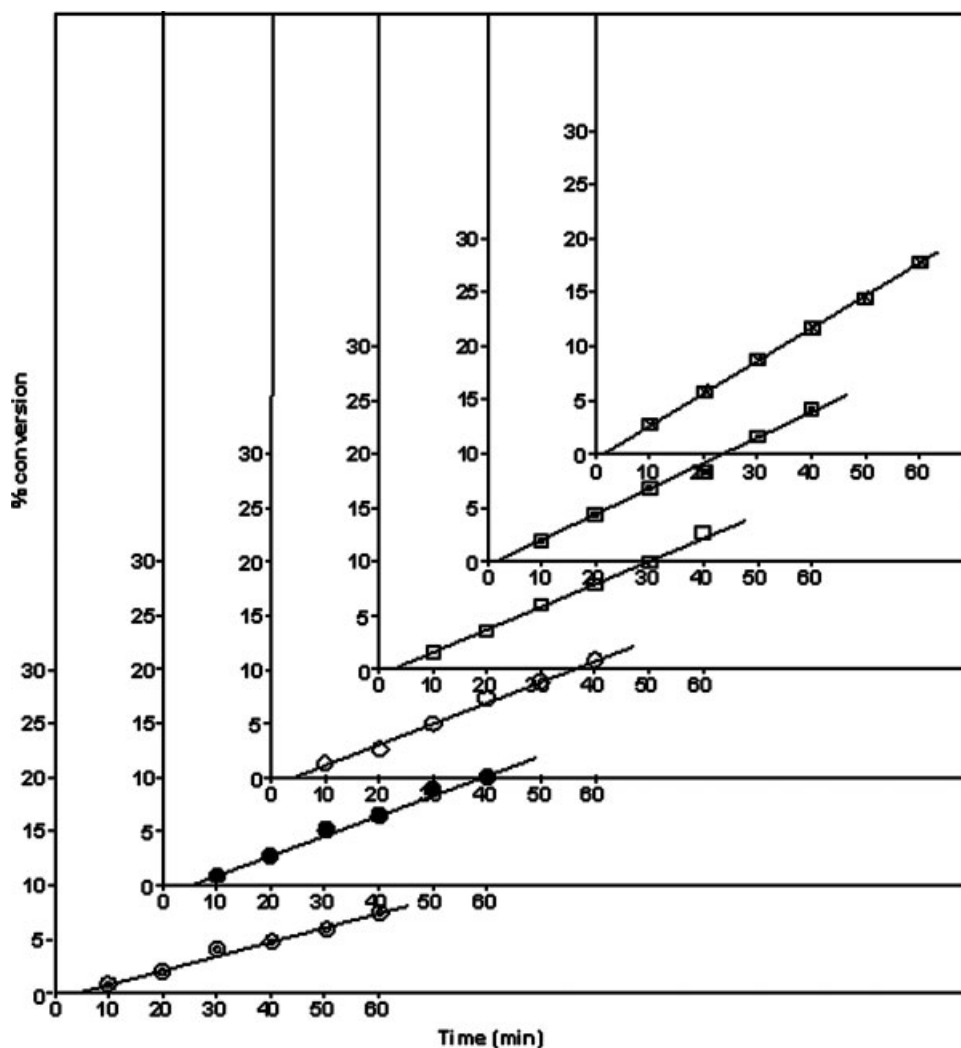
### Measurements

The intrinsic viscosity (dL/g) of the polymers was determined in benzene at  $(30 \pm 0.2)^\circ\text{C}$  using an Ubbelohde viscometer to calculate the viscosity average molecular weight ( $\bar{M}_v$ ) by using Mark–Houwink constant<sup>17</sup> ( $K$  and  $\alpha$  as  $4.50 \times 10^{-5}$  and 0.78), respectively.

### Characterization

The FTIR and <sup>1</sup>H-NMR spectra were recorded with the help of Perkin–Elmer 599B and Varian 100 HA Spectrometer, respectively, using CDCl<sub>3</sub> as solvent and tetramethyl silane as internal reference.

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**Figure 1** Percentage conversion versus time plots for polymerization of methyl acrylate [MA]. [Ylide] =  $2.85\text{--}57.1 \times 10^{-6}$  mol L<sup>-1</sup>, [MA] = 0.6861 mol L<sup>-1</sup>, temp. =  $(60 \pm 0.1)^\circ\text{C}$ , solvent = dioxan, time = 60 min.

The DSC runs were carried out using VA.0B Dupont 2100 analyzer, sample weight 5.3 mg, at a heating rate of  $10^\circ\text{C}/\text{min}$ .

## RESULT AND DISCUSSION

The ylide initiated polymerization upto 20.49% conversion without gelation and resulted in a polymer of high molecular weight (98,000). The results have been presented in Figures 1–8 and Table I.

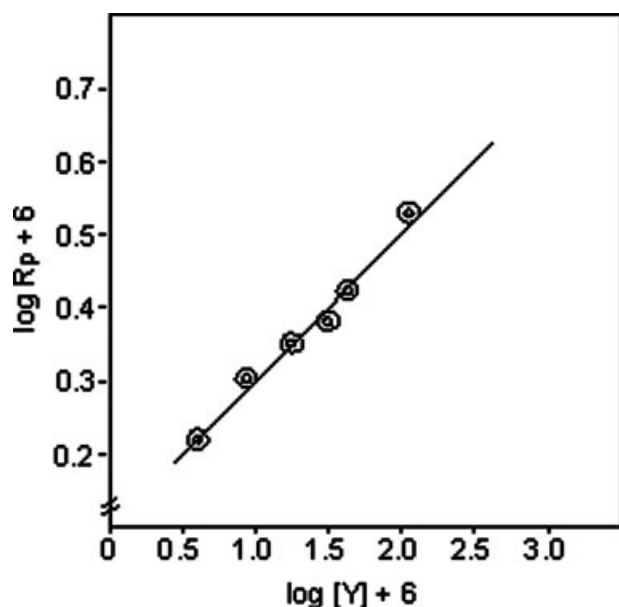
### Effect of initiator concentration [*p*-ABTAY]

The results of polymerization of MA in dioxane was carried out at  $(60 \pm 0.2)^\circ\text{C}$  for 1 h. The [ylide] was varied from  $2.85 \times 10^{-6}$  mol L<sup>-1</sup> to  $57.10 \times 10^{-6}$  mol L<sup>-1</sup>, while keeping [MA] constant as 0.6861 mol L<sup>-1</sup>. The results are presented in Table I. The  $R_p$  increased with increase in [ylide] and the order of reaction, calculated from slope of  $\log R_p$  versus  $\log$  [ylide], is 0.21.

It is less than expected for ideal kinetics in radical polymerization. The molecular weight ( $\bar{M}_v$ ) of the polymer(s) decreased with an increasing initiator concentration (Table I). The value of rate constant ratio  $k_p^2/k_t$  determined from the slope of the linear plot of  $1/\bar{M}_v$  versus  $R_p/[M]^2$ , is  $18.75 \times 10^{-6}$  L mol<sup>-1</sup> s<sup>-1</sup>. This value<sup>18</sup> agrees with the values of  $3.55 \times 10^{-6}$  to  $283 \times 10^{-6}$  L mol<sup>-1</sup> s<sup>-1</sup> reported for radical initiators.

### Effect of monomer concentration

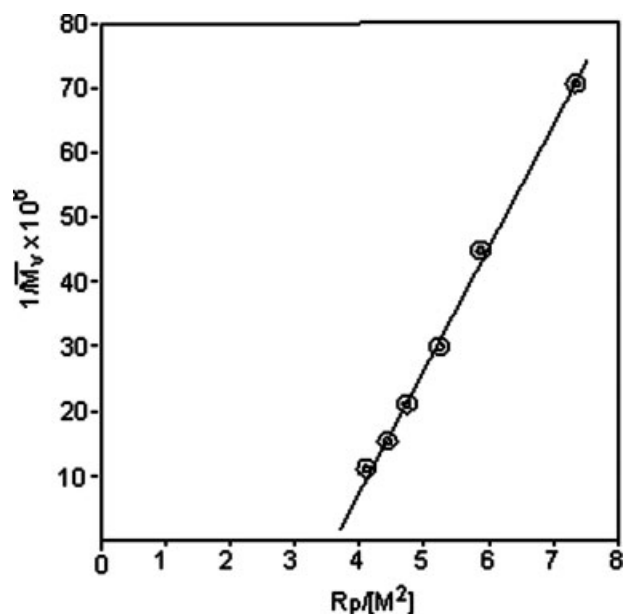
The effect of the concentration of MA on the  $R_p$  was investigated by varying [MA] from 0.4116 to 3.400 mol L<sup>-1</sup> while keeping [ylide] constant at  $8.56 \times 10^{-6}$  mol L<sup>-1</sup> (Table I). The  $R_p$  is a direct function of [MA]. A plot of  $\log R_p$  versus  $\log$  [MA] is linear giving an order of reaction with respect to MA as 1.40 (Fig. 4). This value is higher than expected for ideal kinetics. The ( $\bar{M}_v$ ) of the polymer increased with increasing [MA] (Table I).



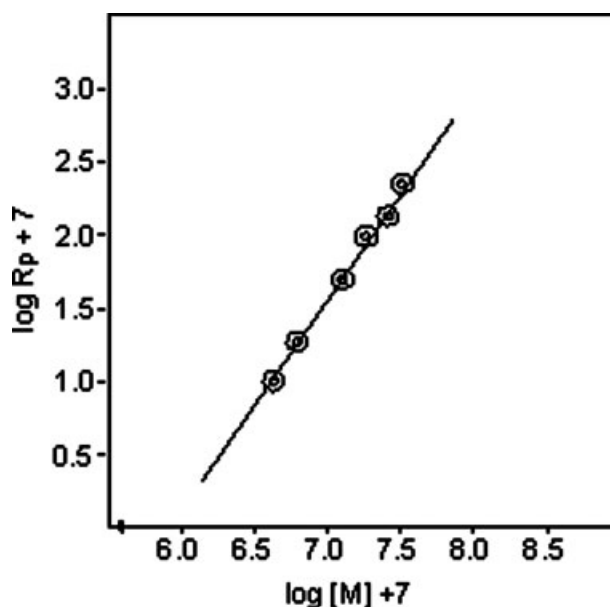
**Figure 2** Plot of  $\log R_p$  versus  $\log [Y]_{\text{lide}}$ ,  $[Y]_{\text{lide}} = 8.56 \times 10^{-6} \text{ mol L}^{-1}$ ,  $[MA] = 0.6861 \text{ mol L}^{-1}$ , temp. =  $(60 \pm 0.1)^\circ\text{C}$ , solvent = dioxan, time = 60 min.

The deviation in the values of initiator and monomer exponents suggests that the system follows non-ideal kinetics, which can be explained on the basis of primary radical termination and degradative chain transfer reactions. To analyze the effect of primary radical termination, the following expression, given by Deb and Meyerhoff,<sup>19</sup> is used.

$$\log \frac{R_p^2}{[I][M]^2} = \log \frac{2f_k k_d k_p^2}{k_t} - 0.864 \frac{k_{\text{prt}}}{k_t k_p} \frac{R_p}{[M]^2}$$

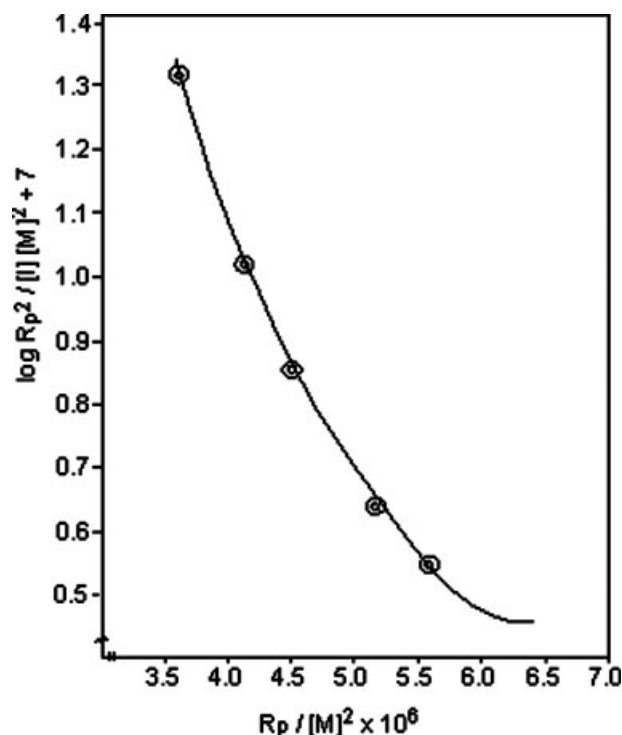


**Figure 3** Plot of  $1/\bar{M}_v$  versus  $R_p/[M]^2$ ,  $[Y]_{\text{lide}} = 8.56 \times 10^{-6} \text{ mol L}^{-1}$ ,  $[MA] = 0.6861 \text{ mol L}^{-1}$ , temp. =  $(60 \pm 0.1)^\circ\text{C}$ , solvent = dioxan, time = 60 min.

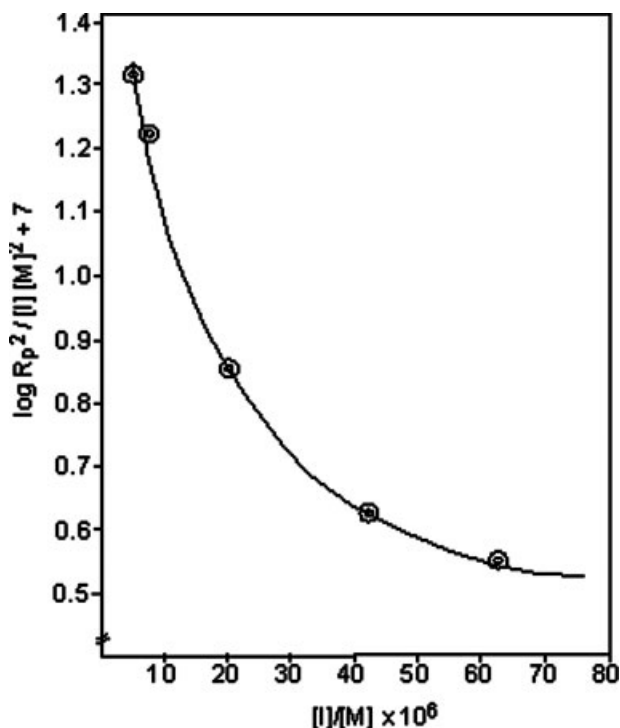


**Figure 4** Plot of  $\log R_p$  versus  $\log [MA]$ ,  $[Y]_{\text{lide}} = 8.56 \times 10^{-6} \text{ mol L}^{-1}$ ,  $[MA] = 0.6861 \text{ mol L}^{-1}$ , temp. =  $(60 \pm 0.1)^\circ\text{C}$ , solvent = dioxan, time = 60 min.

where  $f_k$  represents the fraction of free-radicals initiating chain growth,  $k_d$  is the initiator decomposition rate constant,  $k_p$  is the propagation rate constant, and  $k_{\text{prt}}$  is the primary radical termination constant,  $[M]$  is the monomer concentration.



**Figure 5** Plot of  $\log R_p^2 / [I][M]^2$  versus  $\log R_p/[MA]^2$ ,  $[Y]_{\text{lide}} = 8.56 \times 10^{-6} \text{ mol L}^{-1}$ ,  $[MA] = 0.6861 \text{ mol L}^{-1}$ , temp. =  $(60 \pm 0.1)^\circ\text{C}$ , solvent = dioxan, time = 60 min.

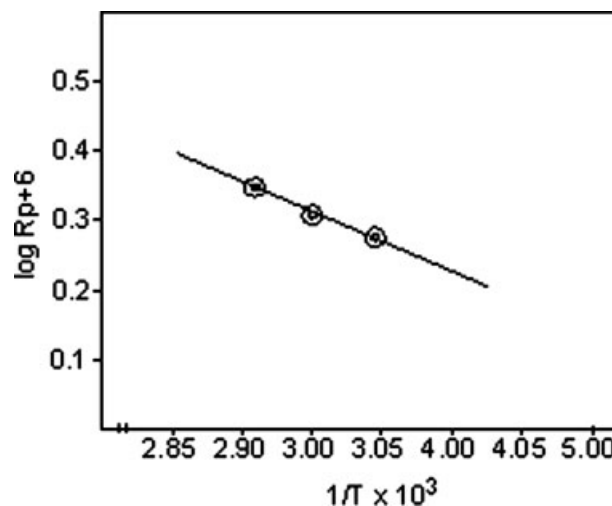


**Figure 6** Plot of  $\log R_p^2/[I][M]^2$  versus  $\log [I]/[M]$ ,  $[Y_{\text{lide}}] = 8.56 \times 10^{-6} \text{ mol L}^{-1}$ ,  $[MA] = 0.6861 \text{ mol L}^{-1}$ , temp. =  $(60 \pm 0.1)^\circ\text{C}$ , solvent = dioxan, time = 60 min.

The plot (Fig. 5) of the left-hand side of the aforementioned equation versus  $R_p/[M]^2$  gave a negative slope, indicating significant primary radical termination. It is generally assumed that the radical, formed as a result of transfer, has reactivity toward monomer equal to that of a primary radical obtained by cleavage of an initiator molecule. The effect of such transfer process decreases the overall degree of polymerization and changes the molecular weight distribution, but has no influence on the  $R_p$ . However, lower reactivities of the radical formed as a result of transfer would result in lower rate of polymerization this type of chain transfer is known as degradative chain transfer.<sup>20</sup> The equation given by Ghosh and Mitra<sup>21</sup> was used to examine degradative chain-transfer reaction as follows:

$$\log \frac{R_p^2}{[I][M]^2} = \log \frac{2f_k k_d k_p^2}{k_t} - 0.434 \frac{k_p^2 k_{\text{rti}}}{k_t k_{\text{ti}} k_p} C_1 \frac{[I]}{[M]}$$

where  $C_1$  is the initiator transfer constant,  $k_{\text{rti}}$  is the rate constant of degradative chain transfer to initiator and  $k_{\text{ti}}$  is the initiator rate constant. A plot (Fig. 6) of the left hand side of the preceding equation versus  $[I]/[M]$  gave a negative slope. It has been well reported in the literature<sup>22</sup> that the non-ideality, that is, primary radical termination and degradative chain transfer, both, causes delay in gelation.



**Figure 7** Arrhenius plot of  $R_p$  versus polymerization temperature,  $[Y_{\text{lide}}] = 8.56 \times 10^{-6} \text{ mol L}^{-1}$ ,  $[MA] = 0.6861 \text{ mol L}^{-1}$ , solvent = dioxan, time = 60 min.

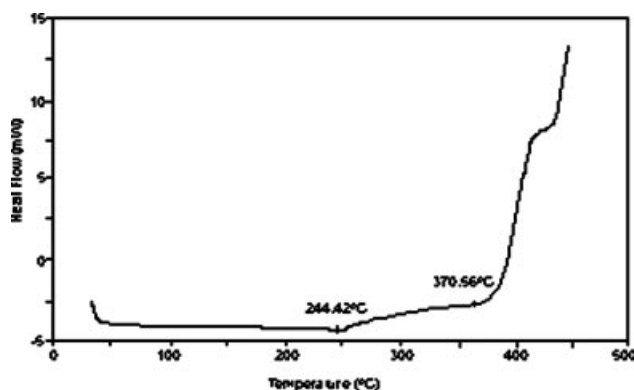
#### Effect of temperature

The rate of polymerization was measured at three different temperatures at a fixed monomer concentration  $0.6861 \text{ mol L}^{-1}$  and initiator concentration  $8.56 \times 10^{-6} \text{ mol L}^{-1}$ . The rate of polymerization increases with temperature and the overall activation energy ( $\Delta E$ ) for solution polymerization, calculated from the slope of the plot of  $\log R_p$  versus  $1/T$ , is  $14 \text{ kJ mol}^{-1}$  (Fig. 7).

#### Spectral analysis

##### Fourier transform infrared spectroscopy

The FTIR spectrum of the (PMA) shows the bands at  $2925 \text{ cm}^{-1}$  (C—H stretching),  $759\text{--}905 \text{ cm}^{-1}$  (bending),  $1381.2\text{--}1450 \text{ cm}^{-1}$  (C—H bending for  $\text{CH}_2$  and  $\text{CH}_3$  group), and  $1737 \text{ cm}^{-1}$  due to acrylate group of the polymer.



**Figure 8** DSC curve of polymethylacrylate (Sample 3).

**TABLE I**  
Effect of Initiator and Monomer Concentration on the  $R_p$

Sample No.	[ <i>p</i> -ABTAY] × 10 <sup>6</sup> (mol L <sup>-1</sup> )	[MA] (mol L <sup>-1</sup> )	% Conversion	$R_p \times 10^6$ mol L <sup>-1</sup> s <sup>-1</sup>	$\bar{M}_v$
1	2.85	0.6861	7.95	1.68	88125.40
2	8.56	0.6861	9.96	2.08	63231.38
3	14.3	0.6861	10.51	2.20	47499.50
4	28.5	0.6861	12.25	2.40	32848.17
5	42.8	0.6861	14.22	2.63	22400.10
6	57.1	0.6861	17.52	3.43	14200.25
7	8.56	0.4116	7.89	1.03	24500.20
8	8.56	0.6861	9.60	2.06	62300.40
9	8.56	1.372	11.51	4.80	68200.15
10	8.56	2.058	13.09	8.23	75000.43
11	8.56	2.744	16.48	13.72	80000.10
12	8.56	3.400	20.49	19.83	98000.10

Polymerization temperature = 60 ± 0.1°C.  
Polymerization time = 1 h.

<sup>1</sup>H-NMR magnetic resonance spectroscopy

The <sup>1</sup>H-NMR spectrum of the polymer shows a triplet at 1.85–2.16 δ due to CH<sub>2</sub> protons, thereby, indicating syndiotactic nature<sup>23</sup> of the polymer. The methoxy protons appear as triplet at 3.46 δ.

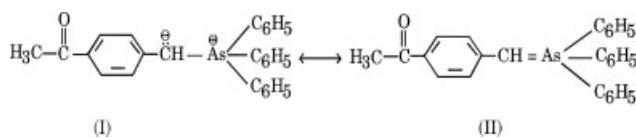
**Thermal analysis**

Differential scanning calorimetry

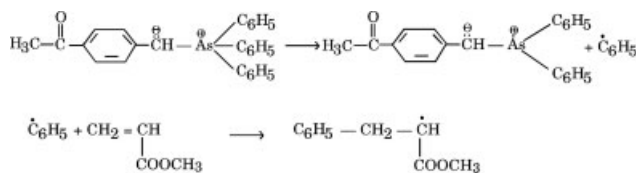
The  $T_g$  value of PMA, determined from DSC (Fig. 8), is 40°C. The literature<sup>24</sup> value is 10°C. The high  $T_g$  value of polymer may be attributed to syndiotactic nature of PMA because the  $T_g$  changes with tacticity,<sup>25</sup> molecular weight,<sup>26</sup> polarity in the main chain.<sup>27</sup>

Mechanism

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



As reported in the literature,<sup>28</sup> structure (I) dissociates in the following manner yielding phenyl free radical, which are responsible for the initiation of the polymerization. The initiation step is:



**CONCLUSION**

The polymerization of MA, initiated by (*p*-ABTAY) ylide in 1,4-dioxan, followed non ideal kinetics, due to primary radical termination as well as degradative chain transfer reaction. The polymer of high molecular weight (98,000) without gelation upto 20.49% conversion was obtained.

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