Chapter-IV
Results
And
Discussion
IV.1 Copolymerization of methyl acrylate with styrene using triphenylstibonium 1,2,3,4-tetraphenylcyclopentadienyliide as radical initiator*

The homopolymerization of methyl acrylate results in the autoacceleration which was explained by E. Trommosdorff and hence is also known as Trommosdorff effect. In this process, as the monomer is consumed, the concentration of polymer increases resulting in increase in viscosity and thus the probability of termination of two radical chain ends is minimized. Due to increasing viscosity, dissipation of the reaction heat becomes less effective resulting in autoacceleration and thus gel formation takes place. However, copolymerization of methyl acrylate with another monomer results in reduction in Trommosdorff effect and also facilitates the modification in the properties of the polymer.

Literature survey reveals that copolymerization of methyl acrylate with styrene\(^\text{340}\), acrylonitrile\(^\text{341}\), \(\beta\)-chloroethyl acrylate\(^\text{342}\), dichlorostyrenes\(^\text{343}\), acrolein\(^\text{344}\), vinyl chloride\(^\text{345}\) etc. has also been carried out. However, only one publication has been so far reported for copolymerization of MA with Sty using imidazolium-p-chlorophenacylidide\(^\text{89}\) as radical initiator and hence the present sub-chapter focuses on the synthesis, kinetics and mechanism of poly(MA-co-Sty) using triphenylstibonium 1,2,3,4-tetraphenylcyclopentadienyliide.

**Kinetics of copolymerization**

The copolymerization reactions were carried out using dilatometer technique under oxygen free conditions for 2hrs. at 60°C. The polymerization solution was prepared by dissolving monomers and initiator in dioxan. The copolymer(s) were precipitated with acidified methanol and dried under vacuum. The copolymer(s) were refluxed with cyclohexane and acetic acid to remove homopolymers of Sty and MA. Lastly, the copolymer(s) were dried to constant weight to obtain percent conversion.

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The reaction proceeded with the induction period of 1–14 min. The solution copolymerization of MA with Sty was carried out to maximum conversion of 12%. The results of kinetic investigations are summarized in Fig.IV.1.1–1.3.

**Effect of Initiator Concentration**

The effect of ylide on the rate of polymerization was observed by varying the [Ylide] concentration from $4.61 \times 10^{-6}$ mol L$^{-1}$ - $46.19 \times 10^{-6}$ mol L$^{-1}$ (Tab.IV.1.1). An increase in $R_p$ was observed upon increasing the [Ylide] concentration. The initiator exponent value, obtained from the slope of linear portion of log $R_p$ vs log [Ylide] (LSM), is $0.14 \pm 0.01$ (Fig.IV.1.4), which is far less than expected for ideal kinetics. The viscosity average molecular weight decreased on increasing the [Ylide] concentration.

**Effect of Monomer(s) Concentration (methyl acrylate and styrene)**

The effect of methyl acrylate was studied by varying [MA] concentration from 0.37 mol L$^{-1}$ - 3.70 mol L$^{-1}$ (Tab.IV.1.2) keeping [Sty] and [Ylide] concentration constant at 1.45 mol L$^{-1}$ and $18.50 \times 10^{-6}$ mol L$^{-1}$ respectively. The increase in [MA] concentration resulted in increase in $R_p$. The monomer exponent value, with respect to [MA] obtained from the slope of the linear portion of log $R_p$ vs log [MA] (using Least square method), is $0.70 \pm 0.05$ (Fig.IV.1.5). The effect of styrene was studied by varying [Sty] concentration from 0.43 mol L$^{-1}$ - 3.5 mol L$^{-1}$ (Tab.IV.1.2) while [MA] and [Ylide] concentration were kept constant as 1.48 mol L$^{-1}$ and $18.50 \times 10^{-6}$ mol L$^{-1}$ respectively. The $R_p$ is a direct function of [Sty]. A plot of log $R_p$ vs log [Sty] (LSM) is linear, giving the monomer exponent value with respect to styrene as $0.75 \pm 0.05$ (Fig.IV.1.6). The $\bar{M}_v$ increased on increasing the [MA] and [Sty] concentration.

The initiator and monomer(s) exponent value suggest that the system follows non-ideal kinetics, which may be attributed due to the primary radical termination and degradative chain transfer reactions.
Primary radical termination occurs due to reaction between propagating radical and primary radical, instead of bimolecular termination.

\[
P^* + H^* \xrightarrow{k_{pr}} \text{Polymer} \quad (IV.1.1)
\]

where \(M_0^*\) is the propagating radical and \(R^*\) is the radical produced from the initiator. The primary radical termination results in the decrease in primary radical and, therefore, decrease in reaction rate. Deb and Meyerhoff\(^{346}\) examined the primary radical termination using the following equation:

\[
\log \left( \frac{R_p^2}{[I][M]^2} \right) = \log \left( \frac{2 f_i k_d k_p^2}{k_t} \right) - 0.8684 \left( \frac{k_{pr}}{k_t k_p} \right) \left( \frac{R_p}{[M]^2} \right) \quad (IV.1.2)
\]

Primary radical termination is confirmed by the negative slope, obtained from the plot of \(\log R_p/[I][M]^2\) vs \(R_p/[M]^2\) (Fig.IV.1.7).

A degradative chain transfer reaction occurs when the radicals obtained from the transfer reaction have equal reactivity for the monomer as well as primary radical, resulting in an overall decrease in polymerization rate, and degree of polymerization.

\[
P^* + Y \xrightarrow{k_{ir}} \text{Polymer} + Y^* \quad (Initiator transfer) \quad (IV.1.3)
\]
\[
P^* + Y^* \xrightarrow{k_{pr}} \text{Polymer} \quad (Chain termination) \quad (IV.1.4)
\]
\[
M + Y^* \xrightarrow{k_{pr}} P_i^* \quad (reinitiation) \quad (IV.1.5)
\]

where \(P^*, M, Y\) represent polymer propagating radical, monomer and ylide respectively.

The degradative chain transfer effect is obtained by using the expression given by Ghosh and Mitra\(^{347}\):

\[
\ln \left( \frac{R_p^2}{[I][M]^2} \right) = \ln \left( \frac{2 f_i k_d k_p^2}{k_t} \right) - 2 \left( \frac{k_p^2 k_{pr}}{k_t k_d k_p} \right) C_i \left( \frac{[I]}{[M]} \right) \quad (IV.1.6)
\]
The negative slope, obtained by plotting the graph between \( \log \frac{R_p}{[I][M]^2} \) vs \( [I]/[M] \) (Fig.IV.1.8) confirm the degradative chain transfer reactions.

**Effect of temperature**

Polymerization reactions were also studied at 55°, 65° and 70°C to determine energy of activation. The activation energy, calculated from the slope of the Arrhenius plot of \( \log R_p \) vs \( 1/T \) (Fig.IV.1.9), is 42 kJ mol\(^{-1}\).

**Characterization of the copolymer**

(i) **Fourier Transform Infrared Spectroscopy**

The FTIR\(^{348,349}\) spectrum of poly(MA-co-Sty) (Fig.IV.1.10) shows the following bands:
- 3060 cm\(^{-1}\) – aromatic C–H stretching
- 2947 cm\(^{-1}\) – aliphatic C–H stretching
- 1737 cm\(^{-1}\) – >C=O stretching in acrylate group
- 1450-1600 cm\(^{-1}\) – C=C stretching in aromatic rings

(ii) **\( ^1H \) Nuclear Magnetic Spectroscopy**

The \( ^1H \)NMR spectrum of copolymer (Fig.IV.1.11) shows a singlet\(^{350}\) at 7.2 \( \delta \) ppm and three peaks at 2.1 \( \delta \) ppm, 2.5 \( \delta \) ppm and 3.4–3.8 \( \delta \) ppm. The presence of three peaks for methoxy protons of methyl acrylate and a singlet for styrene confirms the alternating nature of the polymer.

(iii) **\( ^{13}C \) Nuclear Magnetic Spectroscopy**

The \( ^{13}C \)NMR spectrum of poly(MA-co-Sty) (Fig.IV.1.12) shows the following peak:
- 20 \( \delta \) ppm – –CH\(_2\) (C\(_a\))
- 24 - 26 \( \delta \) ppm – –CH (C\(_b\), C\(_c\))
- 64 \( \delta \) ppm – –OCH\(_3\) (C\(_d\))
- 110-140 \( \delta \) ppm – –C\(_6\)H\(_5\) (C\(_e\))
- 171 \( \delta \) ppm – >C=O (C\(_f\))
(iv) Differential Scanning Calorimetry

The glass transition temperature \( T_g \) obtained from the DSC scan of poly (MA-co-Sty) (Fig.IV.1.13), is 65°C. The \( T_g \) of polymethyl acrylate and polystyrene is 10°C and 100°C respectively.

Copolymer Composition

Copolymerization reactions lead to four possible reactions due to the addition of propagating species with either \( M_1 \) or \( M_2 \) at the propagating end.

\[
\begin{align*}
\sim M_1^* + M_1 & \xrightarrow{k_{11}} \sim M_1 M_1^* \\
\sim M_1^* + M_2 & \xrightarrow{k_{12}} \sim M_1 M_2^* \\
\sim M_2^* + M_1 & \xrightarrow{k_{21}} \sim M_2 M_1^* \\
\sim M_2^* + M_2 & \xrightarrow{k_{22}} \sim M_2 M_2^*
\end{align*}
\]

The rate of monomer disappearance is given as:

\[
\begin{align*}
\frac{d[M_1]}{dt} &= k_{11} [M_1^*][M_1] + k_{21} [M_2^*][M_1] \\
\frac{d[M_2]}{dt} &= k_{12} [M_1^*][M_2] + k_{22} [M_2^*][M_1]
\end{align*}
\]

Dividing eq (IV.1.11) with eq (IV.1.12)

\[
\begin{align*}
\frac{d[M_1]}{d[M_2]} &= \frac{k_{11} [M_1^*][M_1] + k_{21} [M_2^*][M_1]}{k_{12} [M_1^*][M_2] + k_{22} [M_2^*][M_1]}
\end{align*}
\]

At steady state

\[ k_{21} [M_2^*][M_1] = k_{12} [M_1^*][M_2] \]

Dividing right hand side of the equation by \( k_2 [M_2][M_1] \)

\[
\begin{align*}
\frac{d[M_1]}{d[M_2]} &= \frac{k_{11} [M_1^*][M_1]}{k_{12} [M_2]} + \frac{k_{21} [M_2^*][M_1]}{k_{22} [M_2^*][M_1]}
\end{align*}
\]
The copolymer composition is thus obtained as-

\[
\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{r[M_1] + [M_2]}{[M_1] + r[M_2]}
\]  

where, \( M_1 \) and \( M_2 \) are concentration of monomers

Therefore,

\[ r_1 = \frac{k_{11}}{k_{12}} \quad r_2 = \frac{k_{22}}{k_{21}} \]

where \( k_{11} \) and \( k_{22} \) are the rate constants for the homopolymerization of two monomers, \( k_{12} \) and \( k_{21} \) are the rate constants for the reaction between two different monomers and \( r_1 \) and \( r_2 \) is reactivity ratios of the individual monomers which provide the measure of the preference for a propagating chain end radical to add its own monomer rather than the other monomer and \( r \) is copolymerization parameter.

The reactivity ratios were obtained from the plot of \( \eta \) vs \( \zeta \) using Kelen–Tüdos method \(^{204}\) which gave the value of \( r_1 \) and \( r_2 \), where \( r_1 \) was determined from the slope while \( r_2 \) was the intercept on the y-axis.

This treatment assumes that the consumption of the resulting copolymer depends mainly on the relative rates of each of these reactions, and for effective copolymerization to take place, the cross propagation reactions (IV.1.8) and (IV.1.9) should be more favoured than the self propagating steps (IV.1.7) and (IV.1.10).

Thus, random copolymer is formed when product of \( r_1 \) and \( r_2 \) is close to 1, alternating copolymer is favoured when product of \( r_1 \) and \( r_2 \) is close to zero. Mayo and Walling concluded that two monomers form alternating copolymer when there is a large difference between the polarities of each double bond. A vinyl monomer with an electron withdrawing substituent such as –CN or –COOH, which decreases the electron density on the double bond, will favour alternation with monomers possessing electron donating groups, such as –OR or –CO₂Me that contains electron rich double bonds. Thus, free radical copolymerization of a strong donor – acceptor pair predominantly form alternating structure.
The mole fraction of MA and Sty was calculated from the peak area due to methoxy protons and phenyl protons respectively (Tab.IV.1.3). The reactivity ratio, obtained from the plot of $\eta$ vs $\xi$ (LSM), is $0.16 \pm 0.01$ and $0.028 \pm 0.005$ for $r_1$(MA) and $r_2$(Sty) respectively (Fig.IV.1.14). The product of $r_1r_2$ is approaching zero, therefore, the copolymer is alternating in nature.

**Stereochemistry of the copolymer**

Stereochemically, there are four kind of triads formed in a copolymer chain namely MMM, MMS, SMM, SMS where M and S represent methyl acrylate and styrene units respectively. The schematic representation of these triads is given below:

(i) MMM : 
```
M M M
```

(ii) SMM : 
```
S M M
```

(iii) MMS : 
```
M M S
```

(iv) SMS : 
```
S M S
```

**Mechanism**

Literature survey reveals that triphenylstibonium ylide undergoes bond fission between the heteroatom and the phenyl group resulting in the formation of phenyl free radical that initiates the polymerization reaction. The ESR spectrum (Fig.IV.1.15) shows six hyperfine splitting lines confirming the formation of phenyl radical. These hyperfine splitting lines are formed due to the interaction between unpaired electrons and magnetic nuclei in paramagnetic species. The value of hyperfine splitting constant is calculated as 3.73 gauss which is close to the value (3.75 gauss) reported for phenyl radical.
Initiation:

\[
\text{H}_2\text{C}_6\text{H}_5 + \cdot\text{C}_6\text{H}_5 \rightarrow \text{H}_2\text{C}_6\text{H}_5 + \cdot\text{C}_6\text{H}_5 \quad \text{phenyl radical}
\]

\[
\text{CH}==\text{CH} + \cdot\text{C}_6\text{H}_5 \rightarrow \text{CH}==\text{CH}\text{C}_6\text{H}_5
\]

Initiating styrene radical

\[
\text{CH}==\text{CH} + \cdot\text{H}_2\text{C}_6\text{H}_5 \rightarrow \text{CH}==\text{CH}\text{C}_6\text{H}_5
\]

Initiating methyl acrylate radical

Propagation:

\[
\text{PR type 11}
\]

\[
\text{PR type 12}
\]

\[
\text{PR type 22}
\]

95
The copolymerization of methyl acrylate with styrene initiated by triphenylstibonium 1,2,3,4-tetraphenylcyclopentadienylide as radical initiator follows non-ideal kinetics and results in the formation of an alternating copolymer.
TABLE - IV.1.1

Effect of [Initiator] on the rate of copolymerization of methyl acrylate and styrene

<table>
<thead>
<tr>
<th>S.No.</th>
<th>[Ylide] x 10^6 (mol L^-1)</th>
<th>Conversion (%)</th>
<th>R_p x 10^6 (mol L^-1 s^-1)</th>
<th>M_v</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>4.61</td>
<td>5.43</td>
<td>3.27</td>
<td>16,218</td>
</tr>
<tr>
<td>2.</td>
<td>9.23</td>
<td>6.89</td>
<td>3.60</td>
<td>14,125</td>
</tr>
<tr>
<td>3.</td>
<td>18.50</td>
<td>7.41</td>
<td>3.71</td>
<td>12,663</td>
</tr>
<tr>
<td>4.</td>
<td>27.78</td>
<td>8.10</td>
<td>3.96</td>
<td>8,016</td>
</tr>
<tr>
<td>5.</td>
<td>37.02</td>
<td>9.42</td>
<td>4.26</td>
<td>3,888</td>
</tr>
<tr>
<td>6.</td>
<td>46.19</td>
<td>11.21</td>
<td>4.88</td>
<td>2,705</td>
</tr>
</tbody>
</table>

Temp = 60 ± 0.1°C, Time = 2 hrs., [MA] = 1.48 mol L^-1, [Sty] = 1.45 mol L^-1, Solvent = Dioxan
TABLE - IV.1.2
Effect of [Monomer(s)] on the rate of copolymerization of methyl acrylate and styrene

<table>
<thead>
<tr>
<th>S.No.</th>
<th>[MA] (mol L⁻¹)</th>
<th>[Sty] (mol L⁻¹)</th>
<th>Conversion (%)</th>
<th>( R_p \times 10^6 ) (mol L⁻¹ s⁻¹)</th>
<th>( \overline{M_v} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.37</td>
<td>1.45</td>
<td>5.13</td>
<td>1.61</td>
<td>7,943</td>
</tr>
<tr>
<td>2.</td>
<td>0.74</td>
<td>1.45</td>
<td>6.38</td>
<td>2.45</td>
<td>10,964</td>
</tr>
<tr>
<td>3.</td>
<td>2.22</td>
<td>1.45</td>
<td>6.96</td>
<td>4.40</td>
<td>26,302</td>
</tr>
<tr>
<td>4.</td>
<td>2.96</td>
<td>1.45</td>
<td>7.27</td>
<td>6.84</td>
<td>38,904</td>
</tr>
<tr>
<td>5.</td>
<td>3.70</td>
<td>1.45</td>
<td>8.80</td>
<td>7.98</td>
<td>54,954</td>
</tr>
<tr>
<td>6.</td>
<td>1.48</td>
<td>0.43</td>
<td>5.41</td>
<td>1.56</td>
<td>2,754</td>
</tr>
<tr>
<td>7.</td>
<td>1.48</td>
<td>0.72</td>
<td>6.45</td>
<td>1.87</td>
<td>6,578</td>
</tr>
<tr>
<td>8.</td>
<td>1.48</td>
<td>1.16</td>
<td>6.65</td>
<td>3.52</td>
<td>9,513</td>
</tr>
<tr>
<td>9.</td>
<td>1.48</td>
<td>2.17</td>
<td>8.00</td>
<td>4.08</td>
<td>23,134</td>
</tr>
<tr>
<td>10.</td>
<td>1.48</td>
<td>3.51</td>
<td>8.86</td>
<td>6.65</td>
<td>42,657</td>
</tr>
</tbody>
</table>

Temp = 60 ± 0.1°C, Time = 2 hrs., [Ylide] = 18.50 x 10⁻⁶ mol L⁻¹, Solvent = Dioxan
TABLE – IV.1.3
Copolymer composition

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Monomer feed ratio [MA/Sty]</th>
<th>Mole fraction in the copolymer</th>
<th>Ratio of mole fraction in the copolymer [MA/Sty]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>MA</td>
<td>Sty</td>
</tr>
<tr>
<td>1.</td>
<td>0.51</td>
<td>0.56</td>
<td>0.44</td>
</tr>
<tr>
<td>2.</td>
<td>2.05</td>
<td>0.59</td>
<td>0.41</td>
</tr>
<tr>
<td>3.</td>
<td>1.02</td>
<td>0.57</td>
<td>0.43</td>
</tr>
<tr>
<td>4.</td>
<td>0.68</td>
<td>0.40</td>
<td>0.60</td>
</tr>
</tbody>
</table>

Temp = 60 ± 0.1°C, [Ylide] = 18.50 x 10^{-6} mol L^{-1}, Time = 2 hrs., Solvent = Dioxan
Fig.IV.1.1: Percentage conversion vs time plot for the copolymerization of MA with Sty.

[MA] = 1.48 mol L\(^{-1}\),  \hspace{1cm} [Sty] = 1.45 mol L\(^{-1}\),

Temp = 60 ± 0.1°C, \hspace{1cm} Time = 2 hrs.
Fig. IV.1.2: Percentage conversion vs time plot for the copolymerization of MA with Sty.

[Ylide] = 18.50 x 10^{-6} \text{ mol L}^{-1}, \quad [\text{Sty}] = 1.45 \text{ mol L}^{-1},

Temp = 60 \pm 0.1^\circ\text{C}, \quad \text{Time} = 2 \text{ hrs.}
Fig. IV.1.3: Percentage conversion vs time plot for the copolymerization of MA with Sty.

[Sty] = 18.50 x 10^{-6} \text{ mol L}^{-1}, \quad [\text{MA}] = 1.48 \text{ mol L}^{-1},

\text{Temp} = 60 \pm 0.1^\circ \text{C}, \quad \text{Time} = 2 \text{ hrs.}
Fig.IV.1.4 : Relationship between log \( R_p \) vs log [Ylide] for the copolymerization of MA with Sty.

\[
[\text{MA}] = 1.48 \text{ mol L}^{-1}, \quad [\text{Sty}] = 1.45 \text{ mol L}^{-1},
\]

Temp = 60 ± 0.1°C,

Time = 2 hrs.

Fig.IV.1.5 : Relationship between log \( R_p \) vs log [MA] for the copolymerization of MA with Sty.

\[
[\text{Ylide}] = 18.50 \times 10^{-6} \text{ mol L}^{-1}, \quad [\text{Sty}] = 1.45 \text{ mol L}^{-1},
\]

Temp = 60 ± 0.1°C,

Time = 2 hrs.
Fig.IV.1.6:  Relationship between $\log R_p$ vs $\log [\text{Sty}]$ for the copolymerization of MA with Sty.

$[\text{Ylide}] = 18.50 \times 10^{-6} \text{ mol L}^{-1}$,  
$[\text{MA}] = 1.48 \text{ mol L}^{-1}$,
Temp $= 60 \pm 0.1^\circ\text{C}$,
Time $= 2$ hrs.

Fig.IV.1.7:  Relationship between $\log \frac{R_p^2}{[\text{I}][\text{M}]^2}$ vs $\frac{R_p}{[\text{M}]^2}$ for the copolymerization of MA with Sty.

Temp $= 60 \pm 0.1^\circ\text{C}$,
Time $= 2$ hrs.
**Fig.IV.1.8**: Relationship between $\log \frac{R_p^2}{[I][M]^2}$ vs $[I]/[M]$ for the copolymerization of MA with Sty.

Temp = $60 \pm 0.1^\circ C$, Time = 2 hrs.

**Fig.IV.1.9**: Arrhenius plot of log $R_p$ vs $1/T$ for the copolymerization of MA with Sty.

$[\text{Sty}] = 1.45 \text{ mol L}^{-1}$, $[\text{MA}] = 1.48 \text{ mol L}^{-1}$, $[\text{Ylide}] = 18.50 \times 10^{-6} \text{ mol L}^{-1}$, Temp = $60 \pm 0.1^\circ C$

Time = 2 hrs.
Fig.IV.1.10: FTIR spectrum of copolymer of MA with Sty.
Fig.IV.1.11: $^1$HNMR spectrum of copolymer of MA with Sty.

Fig.IV.1.12: $^{13}$CNMR spectrum of copolymer of MA with Sty.
Fig.IV.1.13: DSC curve of copolymer of MA with Sty.
Fig.IV.1.14: Kelen–Tüdos plot for copolymer of MA with Sty.
Fig.IV.1.15: ESR spectrum of copolymer of MA with Sty.
Kinetics of terpolymerization

The terpolymerization runs were studied dilatometrically in inert atmosphere of nitrogen for 1 hr at 60 ± 0.2°C. The terpolymer(s) were refluxed with cyclohexane, acetic acid and chloroform to remove homo and copolymer(s), if present, to obtain percent conversion.

The terpolymerization of styrene, methyl acrylate and acrylonitrile was restricted to maximum conversion of 8%. The reaction proceeded with the induction period of 1–4 min. The kinetic data are summarized in Fig.IV.2.1–2.4.

Effect of Initiator Concentration

The effect of triphenylstibonium 1,2,3,4-tetraphenylocyclopentadienyliide was investigated by varying the [Ylide] concentration from 1.53 x 10^-6 mol L^-1–7.72 x 10^-6 mol L^-1 (Tab.IV.2.1) while keeping [Sty], [MA] and [AN] concentration constant at 1.45 mol L^-1, 0.74 mol L^-1 and 0.76 mol L^-1 respectively. An increase in the \( R_p \) was observed on increasing the [Ylide] concentration. The slope of the graph of \( \log R_p \) vs \( \log [Ylide] \) (Fig.IV.2.5), gives the initiator exponent value as 0.27 ± 0.05, which is less than expected for ideal kinetics (0.5).

Effect of Monomer(s) Concentration (styrene, methyl acrylate and acrylonitrile)

The effect of styrene was observed by varying the [Sty] concentration from 0.58 mol L^-1–2.03 mol L^-1 (Tab.IV.2.2) keeping [MA], [AN] and [Ylide] concentration constant at 0.74 mol L^-1, 0.76 mol L^-1 and 4.62 x 10^-6 mol L^-1 respectively. The \( R_p \) is a direct function of [Sty]. The slope, calculated from \( \log R_p \) vs \( \log [Sty] \) (Fig.IV.2.6), gives the order with respect to [Sty] as 0.86 ± 0.05, which is slightly less than expected for ideal kinetics.

The influence of methyl acrylate was observed by varying [MA] concentration from 0.37 mol L^-1–1.11 mol L^-1 (Tab.IV.2.2), while keeping the [Sty], [AN] and [Ylide] concentration constant at 1.45 mol L^-1, 0.76 mol L^-1 and 4.62 x 10^-6 mol L^-1
respectively. The $R_p$ value increases on increasing the [MA] concentration. A plot of $\log R_p$ vs $\log [\text{MA}]$ (Fig.IV.2.7) is linear, giving the monomer exponent value with respect to methyl acrylate as $0.91 \pm 0.05$ which is slightly less than expected for ideal kinetics.

The effect of acrylonitrile was determined by varying the [AN] concentration from 0.51 mol L$^{-1}$–1.52 mol L$^{-1}$ (Tab.IV.2.2) with [Sty], [MA] and [Ylide] concentration constant at 1.45 mol L$^{-1}$, 0.74 mol L$^{-1}$ and 4.62 x 10$^{-6}$ mol L$^{-1}$ respectively. A regular increase in the rate of polymerization was observed upon increasing [AN] concentration. The order with respect to [AN], calculated from the slope of $\log R_p$ vs $\log [\text{AN}]$ (Fig.IV.2.8), is $0.88 \pm 0.05$ which is slightly less than expected for ideal kinetics. The intrinsic viscosity ($\eta_{\text{int}}$) was found to be the inverse function of [Ylide] concentration and direct function of [Sty], [MA] and [AN] concentration.

The deviation of initiator and monomer(s) exponent value suggest that the system follows non-ideal kinetics that may be attributed due to the primary radical termination as well as degradative chain transfer reaction.

The negative slope, obtained from the graph of $\log R_p/[I][M]^2$ vs $R_p/[M]^2$ (Fig.IV.2.9) indicate the primary radical termination$^{346}$. The slope of the plot of $\log R_p/[I][M]^2$ vs $[I]/[M]$ (Fig.IV.2.10), is negative indicating the degradative chain transfer reaction$^{347}$.

**Effect of temperature**

The polymerization reactions were also carried out at 55$^\circ$, 65$^\circ$ and 70$^\circ$C to determine the energy of activation. The activation energy, obtained from the slope of the linear graph of $\log R_p$ vs 1/T (Fig IV.2.11), is 47 kJ mol$^{-1}$.

**Characterization of the terpolymer**

(i) **Fourier Transform Infrared Spectroscopy**

The FTIR spectrum of the terpolymer (Fig.IV.2.12) shows the following bands:
3060 cm$^{-1}$ – aromatic C-H stretching  
2923 cm$^{-1}$ – aliphatic C-H stretching  
2237 cm$^{-1}$ – –CN group of acrylonitrile  
1732 cm$^{-1}$ – >C=O stretching in acrylate group  
1450-1600 cm$^{-1}$ – C=C stretching in aromatic rings

(ii) $^1$H Nuclear Magnetic Spectroscopy

The $^1$HNMR spectrum of terpolymer (Fig.IV.2.13) shows a singlet at 7.1 $\delta$ ppm for phenyl protons of styrene and triplet at 2.1 $\delta$ ppm, 2.5 $\delta$ ppm, 3.4-3.8 $\delta$ ppm for methoxy protons of methyl acrylate.

(iii) $^{13}$C Nuclear Magnetic Spectroscopy

The $^{13}$CNMR spectrum of terpolymer (Fig.IV.2.14) shows the following peaks:

\begin{align*}
29-56 \delta \text{ ppm} & \quad -\text{CH}_2 \text{ and } -\text{CH (C}_a\text{C}_t) \\
72 \delta \text{ ppm} & \quad -\text{OCH}_3 (\text{C}_g) \\
117 \delta \text{ ppm} & \quad -\text{CN (C}_h) \\
120-140 \delta \text{ ppm} & \quad -\text{C}_6\text{H}_2 (\text{C}_i) \\
171 \delta \text{ ppm} & \quad >\text{C}=\text{O (C}_j) \\
\end{align*}

(iv) Differential Scanning Calorimetry

The DSC scan of terpolymer (Fig.IV.2.15) was used to determine the glass transition temperature ($T_g$). The $T_g$ value gives an indication of the temperature region at which a polymeric material transforms from a rigid solid to a soft viscous state. The $T_g$ of the terpolymer calculated from DSC is 59°C. The $T_g$ values reported for homopolymer of PMA, PSty and PAN are 10°C, 100°C and 97°C respectively.

Terpolymer Composition

Terpolymerization involves nine propagating steps$^{222}$ as follows due to the addition of propagating species with M$_1$, M$_2$ and M$_3$.  

114
The rate of disappearance of particular monomer may be given as:

\[ -\frac{d[M_1]}{dt} = k_{11}[M_1^*][M_1] + k_{21}[M_2^*][M_1] + k_{31}[M_3^*][M_1] \]  

\[ -\frac{d[M_2]}{dt} = k_{12}[M_1^*][M_2] + k_{22}[M_2^*][M_2] + k_{32}[M_3^*][M_2] \]  

\[ -\frac{d[M_3]}{dt} = k_{13}[M_1^*][M_3] + k_{23}[M_2^*][M_3] + k_{33}[M_3^*][M_3] \]  

As the absolute values of the concentration of radicals are unknown, therefore, derivation of composition equation is achieved by assuming the ‘steady state’.

\[ k_{12}[M_1^*][M_2] + k_{13}[M_1^*][M_3] = k_{21}[M_2^*][M_1] + k_{31}[M_3^*][M_1] \]  

\[ k_{22}[M_2^*][M_2] + k_{23}[M_2^*][M_3] = k_{12}[M_1^*][M_2] + k_{32}[M_3^*][M_2] \]  

\[ k_{31}[M_3^*][M_2] + k_{32}[M_3^*][M_3] = k_{13}[M_1^*][M_3] + k_{23}[M_2^*][M_3] \]
The above relationship states that radicals are consumed at the equal rate to that of their formation by the reaction of the other two radical types with the appropriate monomer.

The combination of the two sets of equations gives the copolymer composition relationship for the ratio of monomers for terpolymer as:

\[
\frac{d[M_1]}{d[M_2]} : \frac{d[M_3]}{d[M_1]} : M_1 : M_2 : M_3
\]

where \(m_1, m_2, m_3\) are the monomer incorporated in the polymer and \(M_1, M_2, M_3\) are the unreacted monomers. The rate constants are given as:

\[
\begin{align*}
    r_{12} &= \frac{k_{11}}{k_{12}} \\
    r_{13} &= \frac{k_{11}}{k_{13}} \\
    r_{21} &= \frac{k_{22}}{k_{21}} \\
    r_{23} &= \frac{k_{22}}{k_{23}} \\
    r_{31} &= \frac{k_{33}}{k_{31}} \\
    r_{32} &= \frac{k_{33}}{k_{32}}
\end{align*}
\]

The reactivity ratios were calculated using Kelen–Tüdos method\textsuperscript{204}, whereby styrene content was calculated from the peak area of phenyl protons, methyl acrylate content from the peak area of methoxy proton and acrylonitrile content from the nitrogen percentage (Table IV.2.3) obtained through elemental analysis.

The terpolymer consists of two electron acceptor monomers i.e. methyl acrylate and acrylonitrile and an electron donor i.e. styrene. The kinetic data reveals that sum of the mole fractions of electron acceptors (MA + AN) and electron donor (Sty), is nearly equimolar (Table IV.2.4). The reactivity ratios obtained from Kelen–Tüdos method (LSM), give the values 0.25 ± 0.05 and 0.22 ± 0.05 for \(r_1(\text{Sty})\) and \(r_2(\text{MA})\) respectively (Fig.IV.2.16). The reactivity ratios calculated for \(r_{12}, r_{13}, r_{21}, r_{23}, r_{31}\) and \(r_{32}\) (LSM) are 0.45, 0.35, 0.08, 0.11, 0.07 and 0.10 respectively (Fig.IV.2.17–2.19).
Mechanism

The ESR spectrum (Fig.IV.2.20) confirms the formation of phenyl radicals, which further reacts with the monomer forming initiating monomer radical that continues to react with other monomer molecules resulting in the growth of the polymer chain. The possible mechanism for the terpolymerization of [Sty], [MA] and [AN] is given below:

**Initiation:**

![Initiation Diagram]

**Propagation:**

![Propagation Diagram]
Termination:

By coupling:

\[
\begin{align*}
\sim \mathrm{CH}_2\sim \mathrm{CH} + \cdot \mathrm{CH} & \rightarrow \sim \mathrm{CH}_2\sim \mathrm{CH} \\
\mathrm{H}_2\mathrm{CO} & \\
\sim \mathrm{CH}_2\sim \mathrm{CH} + \cdot \mathrm{CH} & \rightarrow \sim \mathrm{CH}_2\sim \mathrm{CH} \\
\mathrm{H}_2\mathrm{CO} & \\
\sim \mathrm{CH}_2\sim \mathrm{CH} + \cdot \mathrm{CH} & \rightarrow \sim \mathrm{CH}_2\sim \mathrm{CH} \\
\mathrm{H}_2\mathrm{CO} & \\
\end{align*}
\]

By disproportionation:

\[
\begin{align*}
\sim \mathrm{CH}_2\sim \mathrm{CH} + \cdot \mathrm{CH} & \rightarrow \sim \mathrm{CH}_2\sim \mathrm{CH} + \sim \mathrm{CH}_2\sim \mathrm{CH} \\
\mathrm{H}_2\mathrm{CO} & \\
\sim \mathrm{CH}_2\sim \mathrm{CH} + \cdot \mathrm{CH} & \rightarrow \sim \mathrm{CH}_2\sim \mathrm{CH} + \sim \mathrm{CH}_2\sim \mathrm{CH} \\
\mathrm{H}_2\mathrm{CO} & \\
\sim \mathrm{CH}_2\sim \mathrm{CH} + \cdot \mathrm{CH} & \rightarrow \sim \mathrm{CH}_2\sim \mathrm{CH} + \sim \mathrm{CH}_2\sim \mathrm{CH} \\
\mathrm{H}_2\mathrm{CO} & \\
\end{align*}
\]
Conclusions

The terpolymerization of styrene, methyl acrylate and acrylonitrile initiated by triphenylstibonium 1,2,3,4-tetraphenylcyclopentadienylide undergoes radical mode of polymerization and follows non-ideal kinetics. The sum of the mole fractions of the electron acceptor monomers (MA + AN) and electron donor monomer (Sty) is equimolar.
IV.2 Kinetics and mechanism of triphenylstibonium ylide initiated terpolymerization of styrene, methyl acrylate and acrylonitrile*

Terpolymerization of multiple monomers allows for the synthesis of new polymeric material with properties very different from the individual monomers. Terpolymerization is an effective solution to obtain the products desired with greater durability and dimensional stability by using different combination of monomers. Terpolymerization offers wide variations in monomer reactivity with radicals.

Leibersohn and Konh\textsuperscript{352} synthesized poly(styrene–acrylonitrile–styryl isocyanate) by radical initiation and determined the monomer feed and terpolymer composition. Maiti \textit{et al}.$^{353}$ reported that acrylonitrile–butadiene–styrene terpolymer blending with polyvinyl chloride improved its thermal stability. The increase in the rubber content of the polymer blends increased their impact strength and ductibility. The terpolymerizations of styrene–methyl acrylate–methacrylonitrile, styrene–ethyl acrylate–methacrylonitrile, styrene–methyl acrylate–acrylonitrile and styrene–ethyl acrylate–acrylonitrile were also examined in the presence of ethylaluminium sesquichloride\textsuperscript{354} (EASC). The terpolymers were found to contain equimolar amounts of styrene and acceptor monomers. It was found that the complexed acceptor monomers had higher reactivities than the free monomers toward styryl radicals in all the four terpolymerization systems. Examination of the early literature reveals that the terpolymerization of styrene–acrylonitrile with vinyl monomers like acrylic acid\textsuperscript{355}, butadiene\textsuperscript{356}, tri-n-butyltin-4-acryloyloxy benzoate\textsuperscript{357} as well as terpolymerization of Sty–AN with some metal acrylates like chromium acrylate\textsuperscript{358}, copper acrylate\textsuperscript{358} and terpenes like α-terpineol\textsuperscript{359} have been reported. However, the literature lacks report on the present system. Therefore, the present studies were undertaken.

*A part of this work has been published in Designed Monomers and Polymers, 10 (1), 19-35 (2007), Impact Factor-0.890*
### TABLE – IV.2.1

Effect of [Initiator] on the rate of terpolymerization of methyl acrylate, styrene and acrylonitrile

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>[Ylide] x 10^6 (mol L⁻¹)</th>
<th>Conversion (%)</th>
<th>R_p x 10^6 (mol L⁻¹ s⁻¹)</th>
<th>η_int (dL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>1.53</td>
<td>5.50</td>
<td>4.27</td>
<td>0.21</td>
</tr>
<tr>
<td>2.</td>
<td>3.10</td>
<td>5.75</td>
<td>4.90</td>
<td>0.16</td>
</tr>
<tr>
<td>3.</td>
<td>4.62</td>
<td>6.41</td>
<td>5.46</td>
<td>0.13</td>
</tr>
<tr>
<td>4.</td>
<td>6.15</td>
<td>7.16</td>
<td>5.61</td>
<td>0.10</td>
</tr>
<tr>
<td>5.</td>
<td>7.72</td>
<td>7.56</td>
<td>6.29</td>
<td>0.09</td>
</tr>
</tbody>
</table>

Temp = 60 ± 0.2°C, Time = 2 hrs., Solvent = Dioxan,

[Sty] = 1.45 mol L⁻¹, [MA] = 0.74 mol L⁻¹, [AN] = 0.76 mol L⁻¹
TABLE – IV.2.2

Effect of [Monomer(s)] on the rate of terpolymerization of methyl acrylate, styrene and acrylonitrile

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>[Sty] (mol L(^{-1}))</th>
<th>[MA] (mol L(^{-1}))</th>
<th>[AN] (mol L(^{-1}))</th>
<th>Conversion (%)</th>
<th>(R_p \times 10^6) (mol L(^{-1}) s(^{-1}))</th>
<th>(\eta_{int}) (dL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.</td>
<td>0.58</td>
<td>0.74</td>
<td>0.76</td>
<td>4.19</td>
<td>2.44</td>
<td>0.05</td>
</tr>
<tr>
<td>7.</td>
<td>0.87</td>
<td>0.74</td>
<td>0.76</td>
<td>5.40</td>
<td>3.95</td>
<td>0.08</td>
</tr>
<tr>
<td>8.</td>
<td>1.16</td>
<td>0.74</td>
<td>0.76</td>
<td>5.93</td>
<td>4.83</td>
<td>0.12</td>
</tr>
<tr>
<td>9.</td>
<td>1.74</td>
<td>0.74</td>
<td>0.76</td>
<td>6.77</td>
<td>6.26</td>
<td>0.18</td>
</tr>
<tr>
<td>10.</td>
<td>2.03</td>
<td>0.74</td>
<td>0.76</td>
<td>7.08</td>
<td>7.66</td>
<td>0.24</td>
</tr>
<tr>
<td>11.</td>
<td>1.45</td>
<td>0.37</td>
<td>0.76</td>
<td>5.59</td>
<td>4.36</td>
<td>0.04</td>
</tr>
<tr>
<td>12.</td>
<td>1.45</td>
<td>0.55</td>
<td>0.76</td>
<td>5.83</td>
<td>4.61</td>
<td>0.07</td>
</tr>
<tr>
<td>13.</td>
<td>1.45</td>
<td>0.92</td>
<td>0.76</td>
<td>7.17</td>
<td>6.73</td>
<td>0.14</td>
</tr>
<tr>
<td>14.</td>
<td>1.45</td>
<td>1.11</td>
<td>0.76</td>
<td>9.04</td>
<td>8.31</td>
<td>0.16</td>
</tr>
<tr>
<td>15.</td>
<td>1.45</td>
<td>0.74</td>
<td>0.51</td>
<td>5.00</td>
<td>4.19</td>
<td>0.12</td>
</tr>
<tr>
<td>16.</td>
<td>1.45</td>
<td>0.74</td>
<td>1.01</td>
<td>7.60</td>
<td>6.82</td>
<td>0.17</td>
</tr>
<tr>
<td>17.</td>
<td>1.45</td>
<td>0.74</td>
<td>1.27</td>
<td>8.01</td>
<td>7.67</td>
<td>0.20</td>
</tr>
<tr>
<td>18.</td>
<td>1.45</td>
<td>0.74</td>
<td>1.52</td>
<td>9.12</td>
<td>10.02</td>
<td>0.28</td>
</tr>
</tbody>
</table>

Temp = 60 ± 0.2°C, Time = 2 hrs., Solvent = Dioxan, \([Ylide] = 4.62 \times 10^{-6} \text{ mol L}^{-1}\)
**TABLE – IV.2.3**

Elemental analysis data*

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Carbon (%)</th>
<th>Hydrogen (%)</th>
<th>Nitrogen (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.</td>
<td>72.48</td>
<td>4.09</td>
<td>3.38</td>
</tr>
<tr>
<td>6.</td>
<td>63.70</td>
<td>3.39</td>
<td>2.22</td>
</tr>
<tr>
<td>10.</td>
<td>68.44</td>
<td>5.09</td>
<td>4.86</td>
</tr>
<tr>
<td>11.</td>
<td>70.34</td>
<td>3.09</td>
<td>3.88</td>
</tr>
<tr>
<td>14.</td>
<td>67.45</td>
<td>4.00</td>
<td>4.73</td>
</tr>
<tr>
<td>15.</td>
<td>66.62</td>
<td>3.84</td>
<td>2.39</td>
</tr>
<tr>
<td>18.</td>
<td>71.09</td>
<td>3.38</td>
<td>4.46</td>
</tr>
</tbody>
</table>

*Elementar Vario EL III Carlo Erba 1108*
### TABLE IV.2.4

**Terpolymer composition**

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Monomer feed ratio [Sty/(MA+AN)]</th>
<th>Mole fraction of the terpolymer</th>
<th>Ratio of mole fraction in the terpolymer [Sty/(MA+AN)]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>[Sty]</td>
<td>[MA]</td>
</tr>
<tr>
<td>1.</td>
<td>0.97</td>
<td>0.465</td>
<td>0.500</td>
</tr>
<tr>
<td>2.</td>
<td>0.39</td>
<td>0.410</td>
<td>0.567</td>
</tr>
<tr>
<td>3.</td>
<td>1.35</td>
<td>0.508</td>
<td>0.442</td>
</tr>
<tr>
<td>4.</td>
<td>1.28</td>
<td>0.465</td>
<td>0.495</td>
</tr>
<tr>
<td>5.</td>
<td>0.78</td>
<td>0.445</td>
<td>0.504</td>
</tr>
<tr>
<td>6.</td>
<td>1.16</td>
<td>0.483</td>
<td>0.492</td>
</tr>
<tr>
<td>7.</td>
<td>0.64</td>
<td>0.467</td>
<td>0.487</td>
</tr>
</tbody>
</table>

Temp = 60 ± 0.2°C, Time = 2 hrs.,

[Ylide] = 4.62 x 10⁻⁶ mol L⁻¹, Solvent = Dioxan
Fig.IV.2.1: Percentage conversion vs time plot for the terpolymerization of MA, Sty and AN.

\[
\begin{align*}
[\text{Sty}] &= 1.45 \text{ mol L}^{-1}, \\
[\text{AN}] &= 0.76 \text{ mol L}^{-1}, \\
[\text{MA}] &= 0.74 \text{ mol L}^{-1}, \\
\text{Temp} &= 60 \pm 0.2^\circ\text{C}, \\
\text{Time} &= 1 \text{ hr}.
\end{align*}
\]
Fig. IV.2.2: Percentage conversion vs time plot for the terpolymerization of MA, Sty and AN.

\[ [\text{Sty}] = 1.45 \text{ mol L}^{-1}, \quad [\text{Ylide}] = 4.62 \times 10^{-6} \text{ mol L}^{-1}, \]

\[ [\text{AN}] = 0.76 \text{ mol L}^{-1}, \quad \text{Temp} = 60 \pm 0.2^\circ \text{C}, \]

Time = 1 hr.
Fig. IV.2.3: Percentage conversion vs time plot for the terpolymerization of MA, Sty and AN.

\[ [\text{MA}] = 0.74 \text{ mol L}^{-1}, \quad [\text{Ylide}] = 4.62 \times 10^{-6} \text{ mol L}^{-1}, \]

\[ [\text{AN}] = 0.76 \text{ mol L}^{-1}, \quad \text{Temp} = 60 \pm 0.2^\circ \text{C}, \]

Time = 1 hr.
Fig. IV.2.4: Percentage conversion vs time plot for the terpolymerization of MA, Sty and AN.

[Sty] = 1.45 mol L$^{-1}$,

[MA] = 0.74 mol L$^{-1}$,

[Ylide] = $4.62 \times 10^{-6}$ mol L$^{-1}$,

Temp = 60 ± 0.2°C,

Time = 1 hr.
Fig.IV.2.5 : Relationship between log $R_p$ vs log $[Ylide]$ for the terpolymerization of MA, Sty and AN.

$[\text{Sty}] = 1.45 \text{ mol L}^{-1}$, \quad $[\text{MA}] = 0.74 \text{ mol L}^{-1}$,

$[\text{AN}] = 0.76 \text{ mol L}^{-1}$, \quad Temp = 60 ± 0.2°C,

Time = 1 hr.

Fig.IV.2.6 : Relationship between log $R_p$ vs log $[\text{Sty}]$ for the terpolymerization of MA, Sty and AN.

$[\text{MA}] = 0.74 \text{ mol L}^{-1}$, \quad $[\text{Ylide}] = 4.62 \times 10^{-6} \text{ mol L}^{-1}$,

$[\text{AN}] = 0.76 \text{ mol L}^{-1}$, \quad Temp = 60 ± 0.2°C,

Time = 1 hr.
Fig.IV.2.7 : Relationship between log $R_p$ vs log [MA] for the terpolymerization of MA, Sty and AN.

$[\text{Sty}] = 1.45 \ \text{mol L}^{-1}, \quad [\text{Ylide}] = 4.62 \times 10^{-6} \ \text{mol L}^{-1},$

$[\text{AN}] = 0.76 \ \text{mol L}^{-1}, \quad \text{Temp} = 60 \pm 0.2^\circ \text{C},$

Time = 1 hr.

Fig.IV.2.8 : Relationship between log $R_p$ vs log [AN] for the terpolymerization of MA, Sty and AN.

$[\text{Sty}] = 1.45 \ \text{mol L}^{-1}, \quad [\text{Ylide}] = 4.62 \times 10^{-6} \ \text{mol L}^{-1},$

$[\text{MA}] = 0.74 \ \text{mol L}^{-1}, \quad \text{Temp} = 60 \pm 0.2^\circ \text{C},$

Time = 1 hr.
Fig. IV.2.9: Relationship between $\log \frac{R_p^2}{[I][M]^2}$ vs $R_p/[M]^2$ for the terpolymerization of MA, Sty and AN.
Temp = 60 ± 0.2°C, Time = 1 hr.

Fig. IV.2.10: Relationship between $\log \frac{R_p^2}{[I][M]^2}$ vs $[I]/[M]$ for the terpolymerization of MA, Sty and AN.
Temp = 60 ± 0.2°C, Time = 1 hr.
Fig. IV.2.11: Arrhenius plot of log $R_p$ vs $1/T$ for the terpolymerization of MA, Sty and AN.

$[\text{Sty}] = 1.45 \text{ mol L}^{-1}$, \hspace{1cm} $[\text{MA}] = 0.74 \text{ mol L}^{-1}$,

$[\text{AN}] = 0.76 \text{ mol L}^{-1}$, \hspace{1cm} $[\text{Ylide}] = 18.5 \times 10^{-6} \text{ mol L}^{-1}$,

Temp = $60 \pm 0.2^\circ\text{C}$ \hspace{1cm} Time = $1 \text{ hr}$.
Fig.IV.2.12: FTIR spectrum of terpolymer of MA, Sty and AN.
Fig.IV.2.13: $^1$HNMR spectrum of terpolymer of MA, Sty and AN.

Fig.IV.2.14: $^{13}$CNMR spectrum of terpolymer of MA, Sty and AN.
Fig. IV.2.15: DSC curve of terpolymer of MA, Sty and AN.
Fig.IV.2.16: Kelen–Tüdos plot for terpolymer of MA, Sty and AN.

Fig.IV.2.17: Kelen–Tüdos plot for terpolymer of MA, Sty and AN with Sty variation.
Fig.IV.2.18 : Kelen–Tüdos plot for terpolymer of MA, Sty and AN with MA variation.

Fig.IV.2.19 : Kelen–Tüdos plot for terpolymer of MA, Sty and AN with AN variation.
Fig. IV.2.20: ESR spectrum of terpolymer of MA, Sty and AN.
IV.3 Photopolymerization of methyl methacrylate initiated by triphenylbismuthonium ylide as radical initiator

Polymethyl methacrylate finds application as impact resistance substitute for glass, in medical technologies and implants as well as for artistic and aesthetic uses. PMMA is less dense ($\rho=1150-1190 \text{ kg m}^{-3}$) as compared to glass ($\rho=2400-2800 \text{ kg m}^{-3}$). PMMA also known as acrylic is used in lens, light covers, glazing, bathroom fittings, outdoor signs, skylights, toys etc. due to excellent clarity, UV resistance, good abrasion resistance, hardness, stiffness, low water absorption, low smoke emission and good track and arc resistance. In the medical field, PMMA is used as replacement of interocular lenses in the eye when original lens has been removed in treatment of the cataract. In orthopaedics, PMMA bone cement is used to fix implants into the bone and to remodel lost bone. Dentures are often made of PMMA and can be colour matched to patients teeth. Acrylic paint essentially comprises of PMMA. It is also used as glass substitute in picture framing due to low cost, light weight, shatter resistant nature. Other uses include manufacturing of electric guitars and basses, laser discs, backlight tattoo ink etc.

Kinetics of homopolymerization

The photopolymerization of methyl methacrylate was studied under Philips (125 W) high pressure mercury lamp (path length = 10 cm, 440 nm interference filter) with a light intensity of $2.53 \times 10^{-4} \text{ Lux}$, for 12 hrs. at 20 ± 0.1°C. The polymer was precipitated with acidified methanol. The polymerization of methyl methacrylate was restricted to the maximum conversion of 12%. The reaction proceeds with the maximum induction period of 90 min. The results are summarized in Fig.IV.3.1-3.2.

Effect of Initiator Concentration

The effect of ylide on the rate of polymerization ($R_p$) was investigated by varying the [Ylide] concentration from $1.77 \times 10^{-6} \text{ mol L}^{-1}$ to $17.66 \times 10^{-6} \text{ mol L}^{-1}$

*Presented in ‘Polymer 2006’ National Conference on Frontiers in Polymer Science and Technology in Kolkata organized by Polymer Science Unit, IACS and The Society for Polymer Science, India from 10-12th Feb,2006.
while keeping the [MMA] concentration constant at 2.69 mol L⁻¹. An increase in the $R_p$ was observed upon increasing the ylide concentration. The initiator exponent value, calculated from the slope of log $R_p$ vs log [Ylide] (Fig.IV.3.3), is 0.5.

The $\overline{M}_v$ decreases with increase in [Ylide] concentration. The plot of $1/\overline{M}_v$ vs $[\text{Ylide}]^{0.5}$ (Fig.IV.3.4) passes through the origin indicating bimolecular termination. The value of $k_p^2/k_t$, obtained from the slope of plot between $1/\overline{M}_v$ vs $R_p/[M]^2$ (Fig.IV.3.5), is $4.48 \times 10^{-5}$ L mol⁻¹ s⁻¹

**Effect of Methyl methacrylate**

The effect of methyl methacrylate on the rate of polymerization was examined by varying [MMA] concentration from 1.35 mol L⁻¹–4.04 mol L⁻¹ (Tab.IV.3.2) for a fixed [Ylide] concentration ($8.83 \times 10^{-6}$ mol L⁻¹). The $R_p$ is a direct function of [MMA]. A plot of log $R_p$ vs log [MMA] (Fig.IV.3.6), is linear and the order of reaction with respect to methyl methacrylate is unity. The $\overline{M}_v$ of PMMA increases on increasing the [MMA] concentration.

Ylide initiated polymerization involves the radical as reactive species in the course of reaction. The radical chain polymerization involves three steps namely initiation, propagation and termination.

**Initiation-** The homolytic decomposition of the initiator results in the generation of free radicals which are responsible for starting the reaction.

$$\text{I} \xrightarrow{k_d} \text{R}^* + \text{R}^* \quad \text{(IV.3.1)}$$

where I is the initiator, $\text{R}^*$ is the free radical also known as initiator radical / primary radical and $k_d$ is the initiator decomposition rate constant. The rate of decomposition ($R_d$) of the initiator is related to the initiator concentration by the equation:

$$- \frac{d[I]}{dt} = R_d = 2k_d[I] \quad \text{(IV.3.2)}$$

A factor of 2 is used as one molecule of initiator decomposes to form a pair of radicals.

The free radicals generated by the decomposition of the initiator attack the monomer and start the initiation process yielding a new free radical.
\[
R^* + M \xrightarrow{k_i} RM^*
\]  
(IV.3.3)

where \(M\) is the monomer and \(k_i\) is the initiator rate constant. Therefore, the rate of initiation is given as:

\[
-\frac{d[M]}{dt} = R_i = k_i[R^*][M]
\]  
(IV.3.4)

The free radicals due to high reactivity attack the monomer as soon as they are formed and begin the initiation process. Assuming that the rate of formation of free radicals is equal to the rate of disappearance of the same, therefore, \(R_i\) is equal to \(R_d\) and hence \(R_i\) may be written as:

\[
R_i = 2k_i[I]
\]  
(IV.3.5)

The above equation is valid when all the free radicals generated are effective in initiating the polymer growth. In actual practice, some of them are ineffective as they are lost as side products by way of recombination. If we denote the fraction of free radicals effective in initiating the polymer chain growth by \(f\), then \(R_i\) can be modified as:

\[
R_i = 2k\_f[I]
\]  
(IV.3.6)

where \(f\) is the frequency factor whose value is between 0.6 – 1.0.

**Propagation:** The addition of monomer molecule to the reactive species is repeated as many more monomer molecules are successfully added to continuously propagate the reactive centre.

\[
M^* + M \xrightarrow{k_p} M\_1^*
\]  
(IV.3.7)

\[
M\_1^* + M_2 \xrightarrow{k_p} M\_2^*
\]  
(IV.3.8)

\[
M\_2^* + M_3 \xrightarrow{k_p} M\_3^*
\]  
(IV.3.9)

\[
M\_n^* + M \xrightarrow{k_p} M\_n\_1^*
\]  
(IV.3.10)

where \(k_p\) is the propagation rate constant.

The rate of propagation is given by:

\[
-\frac{d[M]}{dt} = R_p = k_p[M^*][M]
\]  
(IV.3.11)

where \([M^*]\) is the concentration of reactive free radical sites and \([M]\) is the monomer concentration.
**Termination** - The last step in polymerization is termination which may take place either by combination of two growing chains (i.e. coupling) or by disproportionation.

\[ M_n^* + M_m^* \xrightarrow{k_{tc}} M_{n+m} \]  
\[ M_n^* + M_m^* \xrightarrow{k_{td}} M_n + M_m \]

where \( k_{tc} \) and \( k_{td} \) are the rate constants for termination by coupling and disproportionation respectively.

The corresponding rate equation for the termination process is given by:

\[ -\frac{d[M]}{dt} = R_t = 2k_h[M^*]^2 \]  

Assuming the steady state, where the number of chain growths initiated equals the number of chain growth arrested, the rate of initiation is equal to the rate of termination, i.e.,

\[ R_i = R_t \]

Therefore,

\[ [M^*]^2 = \frac{k_d[I]}{k_i} \]

\[ [M^*] = \left( \frac{k_d[I]}{k_i} \right)^{1/2} \]

From (IV.3.11), the value of \([M^*]\) is:

\[ [M^*] = \frac{R_p}{k_p[M]} \]

Substituting the value of \([M^*]\) in (IV.3.16)

\[ \frac{R_p}{k_p[M]} = \left( \frac{k_d[I]}{k_i} \right)^{1/2} \]

\[ R_p = k_p \left( \frac{k_i}{k_t} \right)^{1/2} (f[I])^{1/2} [M] \]

This equation states that for ideal kinetics, the rate of polymer formation is proportional to the first power of monomer concentration and also to the square root of the initiator concentration.
Effect of temperature

Polymerization runs were also performed at 25° and 30°C to obtain activation energy. The $R_p$ is a direct function of temperature and the energy of activation determined from the slope of Arrhenius plot of log $R_p$ vs 1/T (Fig.IV.3.7), is 52 kJ mol⁻¹.

Characterization of the polymer

(i) Fourier Transform Infrared Spectroscopy

The FTIR spectrum of PMMA (Fig.IV.3.8) shows the following bands:

- 2995 cm⁻¹ – aliphatic C-H stretching
- 1735 cm⁻¹ – >C=O stretching in acrylate group
- 1150-1275 cm⁻¹ – ester (C-O-C) stretching

The presence of band at 1060 cm⁻¹ indicates the syndiotactic™ nature of the polymer.

(ii) ¹H Nuclear Magnetic Spectroscopy

The ¹HNMR spectrum of PMMA (Fig.IV.3.9) shows the following peaks:

- 0.9 δ ppm – due to –CH₃ group
- 1.8 δ ppm – due to –CH₂ group
- 3.8 δ ppm – due to –OCH₃ group

(iii) ¹³C Nuclear Magnetic Spectroscopy

The ¹³CNMR spectrum of PMMA (Fig.IV.3.10) shows the following peaks:

- 13 δ ppm – -CH₃ (Cₐ)
- 22 δ ppm – -CH₂ (Cₖ)
- 34 δ ppm – >C (Cₖ)
- 50 δ ppm – -OCH₃ (Cₐ)
- 171 δ ppm – >C=O (Cₖ)

The extra peaks may be accounted to the small amount of isotactic and atactic PMMA formed along with syndiotactic PMMA during polymerization process.
(iv) Differential Scanning Calorimetry

$T_g$ values reported in the literature for atactic PMMA is $105^\circ C^{362}$ and $103^\circ C^{363}$. A large difference in glass transition temperature is found between isotactic PMMA and syndiotactic PMMA with $T_g$ values of $45^\circ C$ and $130^\circ C$ respectively. The $T_g$ value decreases in the series as:

$T_g$ (syndiotactic) > $T_g$ (atactic) > $T_g$ (isotactic)

Higher $T_g$ in syndiotactic PMMA can be attributed to higher chain stiffness or stronger intermolecular interaction between polar vinyl groups because of the different chain packing.

The $T_g$ value calculated from the DSC scan (Fig. IV.3.11) of PMMA, is $120^\circ C$ and is very close to the $T_g$ value reported for syndiotactic PMMA. Hence, the PMMA formed is syndiotactic in nature. The temperature for maximum rate of crystallization ($T_{max}$) is calculated by the following equation:

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

The $T_{max}$ calculated from DSC is $280^\circ C$.

Mechanism

The polymerization reaction was inhibited by the presence of hydroquinone ($1.5 \times 10^{-3}$ mol L$^{-1}$) which confirmed the radical mode of termination. It has already been reported in the literature and confirmed by ESR spectrum (Fig. IV.3.12) that the ylide dissociates to give phenyl radical$^{364}$ which initiates the polymerization. The mechanism is as follows:

**Initiation:**

\[
\begin{align*}
\text{Bi}(\text{C}_6\text{H}_5)_3 & \xrightarrow{\text{initiating methyl methacrylate radical}} \text{Bi}(\text{C}_6\text{H}_5)_2 + \text{C}_6\text{H}_5^* \\
\text{H,C,} & \text{C} \equiv \text{C,H}_2 & \text{C}_6\text{H}_5^* & \text{phenyl radical} \\
\text{H,C,} & \text{C} \equiv \text{C,H}_2 & \text{C}_6\text{H}_5 & \text{C}_6\text{H}_5^* & \text{phenyl radical}
\end{align*}
\]
Propagation:
\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{C}^* + \text{CH}_2=\text{CH} & \rightarrow \text{H}_3\text{C} - \text{C}^* - \text{CH}_2\text{C} - \text{CH}_3
\end{align*}
\]

Termination:
By coupling:
\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{C}^* + \text{CH}_3\text{CH}_2\text{C}^* & \rightarrow \text{H}_3\text{C} - \text{C}^* - \text{CH}_2\text{C} - \text{CH}_3
\end{align*}
\]
By disproportionation:
\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{C}^* + \text{CH}_2=\text{CH} & \rightarrow \text{H}_3\text{C} - \text{C}^* - \text{CH}_2\text{C} - \text{CH}_3 + \text{H}_2\text{C}=\text{CH}_3
\end{align*}
\]

Conclusions
The photoinduced radical polymerization of methyl methacrylate, initiated by triphenylbismuthonium 1,2,3,4-tetraphenylcyclopentadienylide obeys ideal kinetics and the polymer formed is syndiotactic in nature with the \(T_g\) value of 120°C.
TABLE – IV.3.1

Effect of [Initiator] on the rate of homopolymerization of methyl methacrylate

<table>
<thead>
<tr>
<th>S.No.</th>
<th>[Ylide] x 10^6 (mol L^-1)</th>
<th>Conversion (%)</th>
<th>R_p x 10^7 (mol L^-1 s^-1)</th>
<th>(\bar{M}_v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>1.77</td>
<td>3.17</td>
<td>2.20</td>
<td>64,525</td>
</tr>
<tr>
<td>2.</td>
<td>5.30</td>
<td>4.99</td>
<td>3.44</td>
<td>38,462</td>
</tr>
<tr>
<td>3.</td>
<td>8.83</td>
<td>7.80</td>
<td>5.16</td>
<td>30,303</td>
</tr>
<tr>
<td>4.</td>
<td>14.13</td>
<td>9.42</td>
<td>6.05</td>
<td>23,256</td>
</tr>
<tr>
<td>5.</td>
<td>17.66</td>
<td>11.95</td>
<td>7.47</td>
<td>20,833</td>
</tr>
</tbody>
</table>

Temp = 20 ± 0.1°C, 
Time = 12 hrs., 
Solvent = Dioxan, 
[MMA] = 2.69 mol L^-1
### TABLE – IV.3.2

**Effect of [methyl methacrylate] on the rate of homopolymerization**

<table>
<thead>
<tr>
<th>S.No.</th>
<th>[MMA] (mol L(^{-1}))</th>
<th>Conversion (%)</th>
<th>(R_p \times 10^7) (mol L(^{-1}) s(^{-1}))</th>
<th>(\overline{M_v})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>1.35</td>
<td>7.02</td>
<td>2.59</td>
<td>9,241</td>
</tr>
<tr>
<td>2.</td>
<td>2.02</td>
<td>7.44</td>
<td>3.87</td>
<td>20,433</td>
</tr>
<tr>
<td>3.</td>
<td>2.69</td>
<td>7.80</td>
<td>5.16</td>
<td>30,303</td>
</tr>
<tr>
<td>4.</td>
<td>3.36</td>
<td>8.38</td>
<td>6.63</td>
<td>36,731</td>
</tr>
<tr>
<td>5.</td>
<td>4.04</td>
<td>8.83</td>
<td>8.19</td>
<td>49,386</td>
</tr>
</tbody>
</table>

Temp = 20 ± 0.1°C, Time = 12 hrs., Solvent = Dioxan, [ylide] = 8.83 \times 10^{-6} \text{ mol L}^{-1}
Fig. IV.3.1: Percentage conversion vs time plot for the homopolymerization of MMA.

\[ [\text{MMA}] = 2.69 \text{ mol L}^{-1}, \quad \text{Temp} = 20 \pm 0.1^\circ C, \]

Time = 12 hrs.
Fig. IV.3.2: Percentage conversion vs time plot for the homopolymerization of MMA.

$$[\text{Ylide}] = 8.83 \times 10^{-6} \text{ mol L}^{-1}, \quad \text{Temp} = 20 \pm 0.1^\circ\text{C},$$

Time = 12 hrs.
Fig.IV.3.3 : Relationship between log $R_p$ vs log [Ylide] for the homopolymerization of MMA.

$[MMA] = 0.74 \text{ mol L}^{-1}$, $\text{Temp} = 20 \pm 0.1^\circ \text{C}$,
$\text{Time} = 12 \text{ hrs.}$

Fig.IV.3.4 : Relationship between $1/M_v$ vs $[\text{Ylide}]^{0.5}$ for the homopolymerization of MMA.

$[MMA] = 0.74 \text{ mol L}^{-1}$, $\text{Temp} = 20 \pm 0.1^\circ \text{C}$,
$\text{Time} = 12 \text{ hrs.}$
Fig.IV.3.5 : Relationship between $1/M_v$ vs $R_p/[M]^2$ for the homopolymerization of MMA.

$[\text{MMA}] = 0.74 \text{ mol L}^{-1}, \quad \text{Temp} = 20 \pm 0.1 ^\circ \text{C},$

$\text{Time} = 12 \text{ hrs.}$

Fig.IV.3.6 : Relationship between $\log R_p$ vs $\log [\text{MMA}]$ for the homopolymerization of MMA.

$[\text{Ylide}] = 8.83 \times 10^{-6} \text{ mol L}^{-1}, \quad \text{Temp} = 20 \pm 0.1 ^\circ \text{C},$

$\text{Time} = 12 \text{ hrs.}$
Fig.IV.3.7 : Arrhenius plot of log $R_p$ vs $1/T$ for the homopolymerization of MMA.

$[\text{MMA}] = 2.69 \text{ mol L}^{-1}$, \hspace{1cm} $[\text{Ylide}] = 8.83 \times 10^{-6} \text{ mol L}^{-1}$

Temp = 20 $\pm$ 0.1$^\circ$C, \hspace{1cm} Time = 12 hrs.
Fig. IV.3.8: FTIR spectrum of PMMA.
Fig. IV.3.9: $^1$HNMR spectrum of PMMA.

Fig. IV.3.10: $^{13}$CNMR spectrum of PMMA.
Fig.IV.3.11: DSC curve of PMMA.
Fig.IV.3.12 : ESR spectrum of PMMA.
IV.4 Solution copolymerization of n-butyl methacrylate with styrene initiated by stibonium ylide

The copolymerization of styrene with n-butyl methacrylate is extensively studied as the latter component increases the rate of polymerization and is chosen for reasons of safety and price. The copolymer of styrene with n-butyl methacrylate is used in the manufacturing of recording tapes and toners for photocopiers.

A search of literature reveals that copolymerization of n-butyl methacrylate with comonomers like styrene, methyl methacrylate, ethyl acrylate, methyl acrylate and α-ethyl hexylacrylate, vinylidene chloride, methacrylonitrile using conventional radical initiators like AIBN / BPO has been carried out. However, the copolymerization of n-butyl methacrylate with styrene using ylide as radical initiator has not been studied yet. Therefore, the present sub-chapter emphasizes on the synthesis, kinetics and mechanism of poly(n-BMA-co-Sty) with triphenylstibonium ylide.

Kinetics of Copolymerization

The copolymerization of n-butyl methacrylate and styrene were carried out in dilatometer using triphenylstibonium 1,2,3,4-tetraphenylcyclopentadienylide as radical initiator under nitrogen blanket at 80 ± 0.2°C for 3 hrs. The decline in the meniscus level per unit volume per unit time was observed through cathetometer. The copolymer(s) were precipitated with acidified methanol and vacuum dried to constant weight. The copolymer(s) were treated with cyclohexane and acetonitrile to remove the traces of homopolymers, if any, and finally percent conversion was determined. Negligible weight loss was observed. The reaction proceeded with the maximum induction period of 12 min. The kinetic data of copolymerization obtained experimentally are summarized in Fig.IV.4.1-4.3.

Effect of initiator Concentration

The influence of ylide was observed by varying the [Ylide] concentration

*A part of this sub-chapter is under communication to International Journal.
from $4.12 \times 10^{-6}$ mol L$^{-1}$–$37.08 \times 10^{-6}$ mol L$^{-1}$ (Tab.IV.4.1), while keeping the [n-BMA] and [Sty] concentration constant at 1.47 mol L$^{-1}$ and 1.45 mol L$^{-1}$ respectively. The $R_p$ is direct function of [Ylide] concentration. The initiator exponent value obtained from the slope of graph of log $R_p$ vs log [Ylide] (Fig.IV.4.4), is 0.5 which is in agreement with the value of ideal kinetics. The $\eta_{int}$ value decreased on increasing the concentration of ylide.

**Effect of Monomer(s) Concentration (n-butyl methacrylate and styrene)**

The effect of n-butyl methacrylate was investigated by varying the [n-BMA] concentration from 0.63 mol L$^{-1}$–1.89 mol L$^{-1}$ (Tab.IV.4.2) with [Sty] and [Ylide] concentration fixed at 1.45 mol L$^{-1}$ and $20.6 \times 10^{-6}$ mol L$^{-1}$ respectively. The $R_p$ shows a regular increase on increasing [n-BMA] concentration. The slope of the plot between log $R_p$ vs log [n-BMA] (Fig.IV.4.5) give the monomer exponent value with respect to [n-BMA] as unity.

The effect of styrene was observed by varying the [Sty] concentration from 0.87 mol L$^{-1}$–2.61 mol L$^{-1}$ (Tab.IV.4.2), while keeping the [n-BMA] and [Ylide] concentration constant at 1.47 mol L$^{-1}$ and $20.6 \times 10^{-6}$ mol L$^{-1}$ respectively. The $R_p$ increases on increasing the [Sty] concentration. The order of the reaction with respect to styrene calculated from the slope of the graph plotted between log $R_p$ vs log [Sty] (Fig.IV.4.6) is unity, thereby, obeying the ideal kinetics. An increase in the $\eta_{int}$ value was observed on increasing the [n-BMA] and [Sty] concentration.

**Effect of temperature**

Activation energy was calculated by carrying out the polymerization at 55°, 65° and 70°C. The energy of activation obtained from the slope of the Arrhenius plot of log $R_p$ vs 1/T (Fig.IV.4.7), is 38 kJ mol$^{-1}$.

**Characterization of the copolymer**

(i) Fourier Transform Infrared Spectroscopy

The FTIR spectrum of poly(n-BMA-co-Sty) (Fig.IV.4.8) shows the following bands:
- 3060 cm$^{-1}$ – aromatic C-H stretching
- 2957 cm$^{-1}$ – aliphatic C-H stretching
1724 cm\(^{-1}\) – C=O stretching in acrylate group
1450-1600 cm\(^{-1}\) – C=C stretching in aromatic rings

(ii) \(^1\)H Nuclear Magnetic Spectroscopy

The \(^1\)HNMR spectrum of poly(n-BMA-co-Sty) (Fig.IV.4.9) shows the peak at 3.4 – 3.8 δ ppm for -OCH\(_2\) in n-butyl methacrylate and 7.4 δ ppm for styrene protons.

(iii) \(^{13}\)C Nuclear Magnetic Spectroscopy

The \(^{13}\)CNMR spectrum of copolymer (Fig.IV.4.10) shows the following peaks:

\begin{align*}
14 \delta \text{ ppm} & \quad \text{CH}_3 (C_a) \\
20 \delta \text{ ppm} & \quad \text{CH}_3 (C_b) \\
64 \delta \text{ ppm} & \quad \text{OCH}_3 (C_c) \\
110-140 \delta \text{ ppm} & \quad \text{C}_6\text{H}_5 (C_d) \\
171 \delta \text{ ppm} & \quad >\text{C}=\text{O} (C_e)
\end{align*}

Copolymer Composition

The relative peak area of -OCH\(_2\) and phenyl protons in n-butyl methacrylate and styrene respectively were used to calculate the copolymer composition. The mole fraction for n-BMA and Sty (Tab.IV.4.3) is nearly equimolar indicating the formation of alternating copolymer. The reactivity ratios calculated using Kelen–Tüdos method (Fig.IV.4.11), is 0.11 ± 0.01 and 0.083 ± 0.01 for \(r_1\)(n-BMA) and \(r_2\)(Sty) respectively.

Mechanism

The values of reactivity ratios suggest the alternating mode of copolymerization in the present case. Three mechanisms\(^{371}\) have been proposed to explain the alternating copolymerization:

1) Ternary molecular complex (TMC) mechanism
2) Cross-propagation mechanism
3) Complex radical mechanism

In copolymerization of styrene with n-butyl methacrylate, the formation of alternating copolymer is explained by TMC mechanism. It was found that the viscosity of the copolymer decreased upon increasing the [CCl\(_4\)] concentration. This observation excluded the cross propagation as well as complex radical
mechanism since \([\text{CCl}_4]\) has no effect on the molecular weight\(^{372}\) of the copolymer formed by cross propagation and complex radical mechanism.

In TMC mechanism\(^{373-375}\), a ternary molecular complex is postulated to form among the Lewis acid, the acceptor monomer and the electron donor monomer. The TMC acts as a unit and polymerizes to yield an alternating copolymer. The structure given below shows the formation of TMC between the electron acceptor monomer (n-BMA), ylide and electron donor monomer (Sty).

\[
\begin{align*}
\text{C}_6\text{H}_5-\text{CH} & \quad \text{CH} \\
\text{C} & \quad \text{COO(CH}_3)_2\text{CH}_3
\end{align*}
\]

The ylide initiated polymerization proceeds through free radical mechanism as confirmed through ESR (Fig.IV.4.12). The phenyl radical formed from the ylide reacts with monomer to generate initiating monomer radical which further reacts with monomer molecule resulting in the polymer chain growth.

**Initiation**:

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{C}_6\text{H}_5 \\
\text{H}_3\text{C} & \quad \text{C}_6\text{H}_5
\end{align*}
\]

Initiating butyl methacrylate radical

\[
\begin{align*}
\text{CH}_3 & \quad \text{C} \quad \text{CH}_3 \\
\text{H}_3\text{C}_6\text{O} & \quad \text{C}
\end{align*}
\]

Initiating styrene radical
Propagating:

\[
\begin{align*}
\text{CH}_2=\text{CH}-\cdot & + \text{CH}_2=\text{CH} \\
\text{H,C,O} & \longrightarrow \text{H,C,O} \\
\text{H}_2 & \\
\end{align*}
\]

(PR type 11)

\[
\begin{align*}
\text{CH}_2=\text{CH}-\cdot & + \text{CH}_2=\text{CH} \\
\text{H,C,O} & \longrightarrow \text{H,C,O} \\
\end{align*}
\]

(PR type 12)

\[
\begin{align*}
\text{CH} \cdot & + \text{CH}_2=\text{CH} \\
\text{H,C,O} & \longrightarrow \text{H,C,O} \\
\end{align*}
\]

(PR type 22)

Terminating:

By coupling:

\[
\begin{align*}
\text{CH}_2=\cdot & + \text{CH}=\text{CH} \\
\text{H,C,O} & \longrightarrow \text{H,C,O} \\
\end{align*}
\]

By disproportionation:

\[
\begin{align*}
\text{CH}_2=\cdot & + \text{CH}=\text{CH} \\
\text{H,C,O} & \longrightarrow \text{H,C,O} \\
\end{align*}
\]

Conclusions

The copolymerization of n-butyl methacrylate with styrene initiated by triphenylstibonium 1,2,3,4-tetraphenylocyclopentadienylide follows ideal kinetics and results in an alternating copolymer through ternary molecular complex mechanism.
TABLE – IV.4.1

Effect of [Initiator] on the rate of copolymerization of n-butyl methacrylate and styrene

<table>
<thead>
<tr>
<th>S.No.</th>
<th>[Ylide] x 10^6 (mol L⁻¹)</th>
<th>Conversion (%)</th>
<th>R_p x 10^6 (mol L⁻¹ s⁻¹)</th>
<th>η_int (dL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>4.12</td>
<td>6.35</td>
<td>1.70</td>
<td>0.28</td>
</tr>
<tr>
<td>2.</td>
<td>12.36</td>
<td>9.13</td>
<td>2.58</td>
<td>0.19</td>
</tr>
<tr>
<td>3.</td>
<td>20.60</td>
<td>9.81</td>
<td>2.78</td>
<td>0.10</td>
</tr>
<tr>
<td>4.</td>
<td>28.84</td>
<td>13.77</td>
<td>3.55</td>
<td>0.08</td>
</tr>
<tr>
<td>5.</td>
<td>37.08</td>
<td>14.39</td>
<td>3.89</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Temp = 80 ± 0.2°C, Time = 3 hrs., η_int = dL/g
[n-BMA] = 1.47 mol L⁻¹, [Sty] = 1.45 mol L⁻¹, Solvent = Dioxan
TABLE – IV.4.2

Effect of [Monomer(s)] on the rate of copolymerization of
n-butyl methacrylate and styrene

<table>
<thead>
<tr>
<th>S.No.</th>
<th>[n-BMA] (mol L(^{-1}))</th>
<th>[Sty] (mol L(^{-1}))</th>
<th>Conversion (%)</th>
<th>(R_p \times 10^6) (mol L(^{-1}) s(^{-1}))</th>
<th>(\eta_{int}) (dL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
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<td>1.45</td>
<td>6.97</td>
<td>1.42</td>
<td>0.06</td>
</tr>
<tr>
<td>2.</td>
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<td>1.45</td>
<td>8.04</td>
<td>1.92</td>
<td>0.09</td>
</tr>
<tr>
<td>3.</td>
<td>1.89</td>
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<td>12.51</td>
<td>3.66</td>
<td>0.21</td>
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<td>4.</td>
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<td>0.87</td>
<td>8.12</td>
<td>1.82</td>
<td>0.08</td>
</tr>
<tr>
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<td>2.03</td>
<td>11.17</td>
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<td>0.13</td>
</tr>
<tr>
<td>6.</td>
<td>1.47</td>
<td>2.61</td>
<td>12.05</td>
<td>4.96</td>
<td>0.23</td>
</tr>
</tbody>
</table>

Temp = 80 ± 0.2°C, Time = 3 hrs., [Ylide] = 20.60 \(\times 10^{-6}\) mol L\(^{-1}\), Solvent = Dioxan
### TABLE - IV.4.3

Copolymer composition

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Monomer feed ratio [n-BMA/Sty]</th>
<th>Mole fraction in the copolymer</th>
<th>Ratio of mole fraction in the copolymer [n-BMA/Sty]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>n-BMA</td>
<td>Sty</td>
</tr>
<tr>
<td>1.</td>
<td>1.30</td>
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<td>0.50</td>
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<td>2.</td>
<td>1.69</td>
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<td>3.</td>
<td>0.43</td>
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<tr>
<td>4.</td>
<td>0.72</td>
<td>0.48</td>
<td>0.52</td>
</tr>
</tbody>
</table>

Temp = $80 \pm 0.2^\circ C$,  
Time = 3 hrs.,  
[Ylide] = $20.60 \times 10^{-6}$ mol L$^{-1}$,  
Solvent = Dioxan
Fig.IV.4.1: Percentage conversion vs time plot for the copolymerization of n-BMA with Sty.

[\text{n-BMA}] = 1.47 \text{ mol L}^{-1},    [\text{Sty}] = 1.45 \text{ mol L}^{-1},

Temp = 80 \pm 0.2^\circ C,    Time = 3 hrs.
Fig.IV.4.2 : Percentage conversion vs time plot for the copolymerization of n-BMA with Sty.

[Ylide] = 20.60 x 10^{-6} \text{ mol L}^{-1}, \quad [\text{Sty}] = 1.45 \text{ mol L}^{-1},

Temp = 80 \pm 0.2^\circ \text{C}, \quad \text{Time} = 3 \text{ hrs.}
Fig. IV.4.3: Percentage conversion vs time plot for the copolymerization of n-BMA with Sty.

[Ylide] = 20.60 x 10^{-6} \text{ mol L}^{-1}, \quad [\text{n-BMA}] = 1.47 \text{ mol L}^{-1},

Temp = 80 \pm 0.2^\circ \text{C}, \quad \text{Time} = 3 \text{ hrs.}
Fig.IV.4.4 : Relationship between log $R_p$ vs log [Ylide] for the copolymerization of n-BMA with Sty.

[n-BMA] = 1.47 mol L$^{-1}$, [Sty] = 1.45 mol L$^{-1}$,  
Temp = 80 ± 0.2°C,  
Time = 3 hrs.

Fig.IV.4.5 : Relationship between log $R_p$ vs log [n-BMA] for the copolymerization of n-BMA with Sty.

[Ylide] = 20.60 x 10$^{-5}$ mol L$^{-1}$,  
[Sty] = 1.45 mol L$^{-1}$,  
Temp = 80 ± 0.2°C,  
Time = 3 hrs.
Fig.IV.4.6: Relationship between $\log R_p$ vs $\log [\text{Sty}]$ for the copolymerization of n-BMA with Sty.

[$[\text{Ylide}] = 20.60 \times 10^{-5}$ mol L$^{-1}$, $[\text{n-BMA}] = 1.47$ mol L$^{-1}$, 
Temp $= 80 \pm 0.2^\circ$C, Time $= 3$ hrs.]

Fig.IV.4.7: Arrhenius plot of $\log R_p$ vs $1/T$ for the copolymerization of n-BMA with Sty.

[$[\text{Sty}] = 1.45$ mol L$^{-1}$, $[\text{n-BMA}] = 1.47$ mol L$^{-1}$, 
$[\text{Ylide}] = 20.60 \times 10^{-5}$ mol L$^{-1}$, 
Temp $= 80 \pm 0.2^\circ$C, Time $= 3$ hrs.]

169
Fig. IV.4.8: FTIR spectrum of copolymer of Sty with n-BMA.
Fig.IV.4.9: $^1$HNMR spectrum of copolymer of Sty with n-BMA.

Fig.IV.4.10: $^{13}$CNMR spectrum of copolymer of Sty with n-BMA.
Fig IV.4.11: Kelen–Tüdos plot for copolymer of n-BMA with Sty.
Fig. IV.4.12: ESR spectrum of copolymer of Sty with n-BMA.
IV.5 Triphenylbismuthonium ylide initiated polymerization of n-butyl methacrylate*

Poly n-butyl methacrylate is a base material for coatings and adhesives. It is used in resins, solvent, coatings, adhesives, oil additives, dental products, textile emulsions, leather and paper finishing.

The living radical polymerization of n-BMA\(^{376}\) was conducted under ATRP conditions in an emulsion using water soluble initiators like potassium persulfate (KPS), 2,2'-azobis(2-methyl propionamide) dihydrochloride. Several publications\(^{377,378}\) have also been reported for ATRP polymerization of n-BMA. Beuermann\(^{379}\) examined the impact of hydrogen bonding on propagation kinetics in n-BMA radical polymerization. However, only one publication\(^{164}\) has been reported for the polymerization of n-BMA using triphenylstibonium ylide. The present paper focuses on the studies of synthesis, kinetics and mechanism of poly n-butyl methacrylate initiated by triphenylbismuthonium 1,2,3,4-tetrphenylcyclopentadien ylide.

**Kinetics of Homopolymerization**

The polymerization reactions were carried out using triphenylbismuthonium 1,2,3,4-tetrphenylcyclopentadienylide as radical initiator at 60 ± 0.1°C for 2hrs. in dioxan. The polymerization solution was filled in dilatometer and amount of liquid displaced was noted through cathetometer. The polymer was precipitated with acidified methanol and dried to constant weight. The maximum induction period determined from percent conversion vs time graph, is 12 min. The kinetic data for triphenylbismuthonium initiated polymerization on n-butyl methacrylate is summarized in Fig.IV.5.1-5.2.

**Effect of Initiator Concentration**

The influence of triphenylbismuthonium ylide was investigated by varying the \([\text{Ylide}]\) concentration from 1.65 \(\times\) 10\(^{-5}\) mol L\(^{-1}\)--4.12 \(\times\) 10\(^{-5}\) mol L\(^{-1}\) (Tab.IV.5.1), while keeping the \([\text{n-BMA}]\) concentration constant at 1.26 mol L\(^{-1}\).

\*A part of this work is under communication to International Journal.
The Rp is the direct function of [Ylide]. The initiator exponent value, calculated from the slope of \( \log R_p \) vs \( \log [\text{Ylide}] \) (Fig.IV.5.3), is \( 0.17 \pm 0.02 \) which is far less than expected for ideal kinetics.

The viscosity average molecular weight decreased upon increasing the [Ylide] concentration. The plot of \( 1/\bar{M}_v \) vs \( [\text{Ylide}]^{0.5} \) (Fig.IV.5.4) does not pass through the origin indicating some additional mode of termination operating with usual bimolecular termination. The additional initiator dependent termination process may be primary radical termination or termination via degradative transfer. The value of \( k_p^2/k_t \), obtained from the slope of plot between \( 1/\bar{M}_v \) vs \( R_p[M]^2 \) (Fig.IV.5.5), is \( 2.2 \times 10^{-4} \) L mol\(^{-1}\) s\(^{-1}\).

**Effect of n-butyl methacrylate**

The effect of the concentration of n-butyl methacrylate on the rate of polymerization was studied by varying [n-BMA] concentration from 0.42 mol L\(^{-1}\) – 2.10 mol L\(^{-1}\) (Tab.IV.5.2) with [Ylide] concentration constant at \( 2.47 \times 10^{-5} \) mol L\(^{-1}\). An increasing trend in the rate of polymerization was observed on increasing the [n-BMA] concentration. The order with respect to [n-BMA], calculated from the slope of graph of \( \log R_p \) vs \( \log [\text{n-BMA}] \) (Fig.IV.5.6), is \( 1.23 \pm 0.05 \) which is greater than the expected for ideal kinetics. The \( \bar{M}_v \) increased with increase in the [n-BMA] concentration.

The system follows non–ideal kinetics which could be attributed to primary radical termination and degradative chain transfer reactions, as discussed in the previous sub-chapters.

The negative slope, obtained from the graph of \( \log R_p/[I][M]^2 \) vs \( R_p/[M]^2 \) (Fig.IV.5.7) indicate the primary radical termination\(^{346}\).

The plot of \( \log R_p/[I][M]^2 \) vs \( [I]/[M] \) (Fig.IV.5.8) gave negative slope, indicating the degradative chain transfer reaction\(^{347}\).

**Effect of temperature**

Polymerization runs were performed at 55°, 60° and 65°C to calculate the energy of activation. The activation energy calculated from the Arrhenius plot of \( \log R_p \) vs \( 1/T \) (Fig.IV.5.9), is 37 kJ mol\(^{-1}\).
Characterization of the polymer

(i) Fourier Transform Infrared Spectroscopy

The FTIR spectrum of poly n-butyl methacrylate (Fig.IV.5.10) shows the following bands:
- $2958 \text{ cm}^{-1}$ – aliphatic C-H stretching
- $1728 \text{ cm}^{-1}$ – C=O stretching in acrylate group
- $1340-1485 \text{ cm}^{-1}$ – C-H bending

The presence of band at $1068 \text{ cm}^{-1}$ indicates the syndiotactic$^{380}$ nature of the polymer.

(ii) $^1\text{H}$ Nuclear Magnetic Spectroscopy

The $^1\text{HNMR}$ spectrum of poly n-butyl methacrylate (Fig.IV.5.11) gives the triplet for $-\text{OCH}_2$ at 3.4 $\delta$ ppm. The other peaks in the region of 0.9-2.1 $\delta$ ppm are due to $-\text{CH}_3$ and $-\text{CH}_2$ groups. The presence of two magnetically equivalent protons of methylene group$^{381}$ at 2.1 $\delta$ ppm indicates the syndiotactic nature of the polymer.

(iii) $^{13}\text{C}$ Nuclear Magnetic Spectroscopy

The $^{13}\text{CNMR}$ spectrum of poly n-butyl methacrylate (Fig.IV.5.12) shows the following peaks:
- $14 \delta$ ppm – $-\text{CH}_3$ ($C_a$)
- $22 \delta$ ppm – $-\text{CH}_3$ ($C_b$)
- $29 \delta$ ppm, $34 \delta$ ppm – $-\text{CH}_2$ ($C_c$, $C_d$)
- $45 \delta$ ppm – $\rightarrow C$ ($C_e$)
- $57 \delta$ ppm – $-\text{OCH}_2$ ($C_f$)
- $171 \delta$ ppm – $\rightarrow\text{C}=\text{O}$ ($C_a$)

(iv) Differential Scanning Calorimetry

The DSC (Fig.IV.5.13) of poly n-butyl methacrylate gives $T_g$ value as $45^\circ\text{C}$. The $T_g$ value reported in the literature$^{382}$ is $14^\circ\text{C}$ and $55^\circ\text{C}$ for atactic and syndiotactic poly n-butyl methacrylate. Lacabanne et al.$^{383}$ also found $T_g$ of poly n-butyl methacrylate as $33^\circ\text{C}$ without showing tacticity. Since the $T_g$ value
calculated is close to the 45°C, therefore, it is concluded that the poly n-butyl methacrylate is syndiotactic in nature. The slight deviation in T_g value may be accounted to the tacticity, molecular weight, and the polarity in the main chain.

(iv) Thermal Gravimetric Analysis

The TGA curve (Fig.IV.5.14) of poly n-butyl methacrylate reveals that the polymer is stable up to the temperature of 280°C and starts to decompose thereafter. The thermal behaviour is as follows:

1) A major weight loss observed at 279°C is 15.86%, while at the temperature of 444°C, the complete weight loss occurs.
2) Weight loss in the range of 279 - 360°C is 76.16%.
3) Volatization temperature obtained from the TGA curve is 386°C

Mechanism

As discussed in the previous sub-chapters, the ESR spectrum shows six hyperfine splitting lines with hyperfine splitting constant value as 3.73 gauss which is in agreement to the value reported in the literature for phenyl radical (Fig.IV.5.15). Literature reveals that one phenyl group in Ph_3 Bi is cleaved by Palladium (II) chloride and olefins to produce phenyl radical. Hence, it is concluded that the initiation is brought about by the phenyl radical.

Initiation:
**Propagation:**

\[
\text{C}_6\text{H}_5\text{CH}_2\text{C}^\cdot \ + \ \text{CH}_2=\text{CH} \rightarrow \text{CH}_2=\text{CHC}_6\text{H}_5^\cdot
\]

**Termination:**

**By coupling:**

\[
\text{H}_2\text{C}=\text{CH}^\cdot + \text{CH}_3 \rightarrow \text{CH}_2=\text{CHCH}_3
\]

**By disproportionation:**

\[
\text{H}_2\text{C}=\text{CH}^\cdot + \text{CH}_3 \rightarrow \text{CH}_2=\text{CH}^\cdot + \text{CH}_3\text{CH}=\text{CH}_2
\]

**Conclusions**

The triphenylbismuthonium ylide initiated homopolymerization of n-butyl methacrylate follows non-ideal kinetics and resulting polymer is syndiotactic in nature.
### TABLE – IV.5.1

Effect of [Initiator] on the rate of homopolymerization of n-butyl methacrylate

<table>
<thead>
<tr>
<th>S.No.</th>
<th>[Ylide] x 10^5 (mol L^-1)</th>
<th>Conversion (%)</th>
<th>R_p x 10^6 (mol L^-1 s^-1)</th>
<th>( \overline{M_v} )</th>
</tr>
</thead>
<tbody>
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<td>1.65</td>
<td>6.88</td>
<td>1.39</td>
<td>94,543</td>
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<td>2.47</td>
<td>7.44</td>
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<td>43,478</td>
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<td>3.</td>
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<td>8.56</td>
<td>1.60</td>
<td>34,483</td>
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<tr>
<td>4.</td>
<td>4.12</td>
<td>9.30</td>
<td>1.62</td>
<td>25,481</td>
</tr>
</tbody>
</table>

Temp = 60 ± 0.1°C, Time = 2 hrs., Solvent = Dioxan, \([n-BMA] = 1.26\ \text{mol}\ \text{L}^{-1}\)
TABLE – IV.5.2

Effect of \textit{[n-butyl methacrylate]} on the rate of homopolymerization

<table>
<thead>
<tr>
<th>S.No.</th>
<th>[n-BMA] (mol L^{-1})</th>
<th>Conversion (%)</th>
<th>( R_p \times 10^7 ) (mol L^{-1} s^{-1})</th>
<th>( \overline{M_v} )</th>
</tr>
</thead>
<tbody>
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<td>1.</td>
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<td>6.14</td>
<td>3.85</td>
<td>26,302</td>
</tr>
<tr>
<td>2.</td>
<td>0.84</td>
<td>6.70</td>
<td>8.65</td>
<td>34,668</td>
</tr>
<tr>
<td>3.</td>
<td>1.26</td>
<td>7.44</td>
<td>14.90</td>
<td>43,478</td>
</tr>
<tr>
<td>4.</td>
<td>1.68</td>
<td>8.85</td>
<td>21.28</td>
<td>69,153</td>
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<td>2.10</td>
<td>9.80</td>
<td>23.70</td>
<td>96,736</td>
</tr>
</tbody>
</table>

Temp = 60 ± 0.1°C,  
Time = 2 hrs.,  
Solvent = Dioxan,  
\([\text{Ylide}] = 2.47 \times 10^{-5} \text{ mol L}^{-1}\)
Fig. IV.5.1: Percentage conversion vs time plot for the polymerization of n-BMA.

\[ [\text{n-BMA}] = 2.69 \text{ mol L}^{-1}, \quad \text{Temp} = 60 \pm 0.1^\circ \text{C}, \]

Time = 2 hrs.
Fig. IV.5.2: Percentage conversion vs time plot for the polymerization of n-BMA.

[Ylide] = 2.47 x 10^{-5} \text{ mol L}^{-1}, \quad \text{Temp} = 60 \pm 0.1^\circ \text{C},

Time = 2 \text{ hrs.}
Fig IV.5.3: Relationship between log $R_p$ vs log [Ylide] for the polymerization of n-BMA.

$n$-[BMA] = 2.69 mol L$^{-1}$, 
Temp = 60 ± 0.1°C, 
Time = 2 hrs.

Fig IV.5.4: Relationship between $1/M_v$ vs [Ylide]$^{0.5}$ for the polymerization of n-BMA.

$n$-[BMA] = 2.69 mol L$^{-1}$, 
Temp = 60 ± 0.1°C, 
Time = 2 hrs.
Fig.IV.5.5 : Relationship between $1/\bar{M}$ vs $R_p/[M]^2$ for the polymerization of n-BMA.

$[n\text{-BMA}] = 2.69 \text{ mol L}^{-1}$, \hspace{1cm} Temp = 60 ± 0.1°C, \hspace{1cm} Time = 2 hrs.

Fig.IV.5.6 : Relationship between $\log R_p$ vs $\log [n\text{-BMA}]$ for the polymerization of n-BMA.

$[\text{Ylide}] = 2.47 \times 10^{-5} \text{ mol L}^{-1}$, \hspace{1cm} Temp = 60 ± 0.1°C, \hspace{1cm} Time = 2 hrs.
**Fig. IV.5.7:** Relationship between $\log \frac{R_p^2}{[I][M]^2}$ vs $\log \frac{R_p}{[M]^2}$ for the polymerization of n-BMA.

Temp = 60 ± 0.1°C, Time = 2 hrs.

**Fig. IV.5.8:** Relationship between $\log \frac{R_p^2}{[I][M]^2}$ vs $[I]/[M]$ for the polymerization of n-BMA.

Temp = 60 ± 0.1°C, Time = 2 hrs.
Fig IV.5.9: Arrhenius plot of log $R_p$ vs $1/T$ for the homopolymerization of n-BMA.

$[\text{n-BMA}] = 2.69 \text{ mol L}^{-1}, \quad [\text{Ylide}] = 2.47 \times 10^{-5} \text{ mol L}^{-1}$

Temp = $60 \pm 0.1^\circ\text{C}$, \quad Time = 2 hrs.
Fig. IV.5.10: FTIR spectrum of poly n-butyl methacrylate.
Fig.IV.5.11: $^1$HNMR spectrum of poly n-butyl methacrylate.

Fig.IV.5.12: $^{13}$CNMR spectrum of poly n-butyl methacrylate.
Fig.IV.5.13: DSC curve of poly n-butyl methacrylate.

Fig.IV.5.14: TGA curve of poly n-butyl methacrylate.
Fig. IV.5.15: ESR spectrum of poly n-butyl methacrylate.
IV.6: Synthesis and properties of semi interpenetrating polymer network from poly(methyl acrylate-co-styrene) and acrylamide using triphenylbismuthonium ylide.*

In past few decades, there has been widespread interest in multicomponent polymer systems including polyblends, block and graft copolymers and interpenetrating polymer networks. IPN are composed of two (or more) chemically distinct networks held together by their trapped mutual entanglements rather than covalent bond grafting. The crosslinked polymers have varied applications throughout the chemical industry including rubber, latexes, urethanes, epoxides, aqueous fluid absorbers, high impact plastics, vibration damping material, high temperature alloys etc. IPNs are typical representations of hybrid binders that make it possible to achieve a much more complex combination of different polymer structures.

Recent work on IPN include the studies on synthesis and swelling behaviour of polyvinyl alcohol / poly(acrylamide-co-potassium methacrylate)\(^{388}\), polyacrylamide / polyacrylic acid \(^{389}\), poly N-isopropylacrylamide / β-cyclodextrin \(^{390}\), polyvinyl alcohol / poly(acrylamide-co-acrylic acid) \(^{391}\) etc.

A search of literature shows that a number of radical initiators such as benzoin \(^{392}\) (photoinitiation), potassium persulfate \(^{393}\), benzyol peroxide \(^{394}\), AIBN \(^{395}\), and ammonium persulfate \(^{396}\) have been used for the synthesis of IPNs. However, very few publications are available for the synthesis and characterization of IPNs using ylide as initiator. The present sub-chapter deals with the synthesis and characterization of IPN of poly(MA-co-Sty) with acrylamide (AAm) using triphenylstibonium 1,2,3,4-tetraphenylcyclopentadienylide.

**Synthesis of IPN**

Poly(methyl acrylate-co-Styrene) was prepared from 1.45 mol L\(^{-1}\) styrene, 1.47 mol L\(^{-1}\), methyl acrylate and 6.1 \times 10^{-2} mol L\(^{-1}\) AIBN at 70 ± 0.2°C for 1hr.

*A part of this paper is under communication to International Journal*
The polymerization reactions were carried out using solution polymerization technique. The polymerization solution consists of polymer, monomer, ylide and divinylbenzene in dioxan. The reaction was carried out in nitrogen atmosphere at $80 \pm 0.2^\circ$C for 1hr. The polymer was precipitated with methanol and dried to constant weight.

The percentage swelling of various IPN samples determined in DMF, dioxan, benzene, toluene and percentage extractable material in DMF are summarized in Tab.IV.6.1.

**Effect of [Ylide]**

The effect of [Ylide] on the properties of semi-interpenetrating polymer network (SIPN) (Tab.IV.6.2) was studied by varying the concentration of triphenylbismuthonium 1,2,3,4-tetraphenylcyclopentadienyliide from $0.41 \times 10^{-5}$–$3.77 \times 10^{-5}$ mol L$^{-1}$. An increase in [Ylide] concentration results in the increase in yield, percentage swelling in DMF and crosslink density of the IPN.

**Effect of poly[MA-co-Sty]**

The concentration of [poly(MA-co-Sty)] was examined by varying the concentration of polymer from $2.36 \times 10^{-5}$–$6.84 \times 10^{-5}$ mol L$^{-1}$ (Tab.IV.6.3). The increase in [poly(MA-co-Sty)] concentration showed increase in the percentage yield and the semi-IPN properties i.e. percentage swelling in DMF, crosslink density and Young’s modulus. This is due to the restricted crosslinking in the presence of [poly(MA-co-Sty)] which results in overall increase in concentration of crosslinking sites of copolymer with increase in [poly(MA-co-Sty)].

**Effect of Acrylamide [AAm]**

The effect of acrylamide was studied by varying the concentration of [AAm] from $2.31 \times 10^{-2}$–$6.08 \times 10^{-2}$ mol L$^{-1}$ (Tab.IV.6.4). The data showed that the [AAm] is directly proportional to the yield and inversely proportional to percentage swelling and molecular weight between crosslinks.
Effect of divinylbenzene [DVB]

The concentration of DVB was varied from 0.71–1.65 mol L$^{-1}$ (Tab.IV.6.5) and its effect on semi-IPN was determined. The data showed an increase in percentage conversion. This may be attributed to increased crosslinking on increasing the crosslinking agent resulting in increase in percentage yield. Percentage swelling in DMF and $\bar{M}_c$ of IPN are inverse function of [DVB]. This again pointed to increased crosslinking.

Fourier Transform Infrared Spectroscopy:

The FTIR spectrum (Fig.IV.6.1) shows the following bands:

3428 cm$^{-1}$ – due to amine group
3016 cm$^{-1}$ – aromatic C-H stretching
2922 cm$^{-1}$ – aliphatic C-H stretching
1732 cm$^{-1}$ – $\geq$C=O stretching in amide
1698 cm$^{-1}$ – $\geq$C=O stretching in acrylate group
1590-1620 cm$^{-1}$ – N-H def in amide
1450-1600 cm$^{-1}$ – $\geq$C=C stretching in aromatic rings.

Differential Scanning Calorimetry:

The DSC curve of the IPN (Fig.IV.6.2) shows two glass transition temperatures ($T_g$) at 85°C and 136°C.

Scanning Electron Microscopy:

The SEM study revealed that IPNs exhibit dual phase morphology (Fig.IV.6.3-6.5) at a magnification of 500 X, 1.50 KX and 2.50 KX, indicating the presence of two components.

Conclusions:

Triphenylbismuthonium ylide initiated synthesis of SIPN of poly (MA-co-Sty) with acrylamide show that $\bar{M}_c$ is a direct function of the concentration of polymer and initiator whereas it is an inverse function of the concentration of monomer and crosslinker.
TABLE – IV.6.1

Percentage Swelling of various IPN samples in different solvents and percentage extractable material in DMF

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Percentage swelling in solvents</th>
<th>Percentage extractable material</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DMF</td>
<td>Dioxan</td>
</tr>
<tr>
<td>IPN-1</td>
<td>25</td>
<td>19</td>
</tr>
<tr>
<td>IPN-2</td>
<td>50</td>
<td>33</td>
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<td>IPN-3</td>
<td>65</td>
<td>49</td>
</tr>
<tr>
<td>IPN-4</td>
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</tr>
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</tr>
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<td>IPN-10</td>
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<td>IPN-11</td>
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<tr>
<td>IPN-12</td>
<td>50</td>
<td>41</td>
</tr>
<tr>
<td>IPN-13</td>
<td>43</td>
<td>29</td>
</tr>
<tr>
<td>IPN-14</td>
<td>82</td>
<td>70</td>
</tr>
<tr>
<td>IPN-15</td>
<td>74</td>
<td>58</td>
</tr>
<tr>
<td>IPN-16</td>
<td>56</td>
<td>40</td>
</tr>
<tr>
<td>IPN-17</td>
<td>49</td>
<td>29</td>
</tr>
</tbody>
</table>
TABLE – IV.6.2

Effect of [Initiator] on the IPN properties

<table>
<thead>
<tr>
<th>S.No.</th>
<th>[Ylide] $\times 10^5$ (mol L$^{-1}$)</th>
<th>Yield (%)</th>
<th>Swelling in DMF (%)</th>
<th>$\overline{M_c}$</th>
<th>Young’s modulus $\times 10^{-5}$ (dynes cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPN-1</td>
<td>0.41</td>
<td>11.45</td>
<td>25</td>
<td>85</td>
<td>1.59</td>
</tr>
<tr>
<td>IPN-2</td>
<td>1.24</td>
<td>13.00</td>
<td>50</td>
<td>208</td>
<td>3.59</td>
</tr>
<tr>
<td>IPN-3</td>
<td>2.06</td>
<td>14.78</td>
<td>65</td>
<td>286</td>
<td>4.83</td>
</tr>
<tr>
<td>IPN-4</td>
<td>2.88</td>
<td>15.14</td>
<td>73</td>
<td>333</td>
<td>5.48</td>
</tr>
<tr>
<td>IPN-5</td>
<td>3.77</td>
<td>16.22</td>
<td>81</td>
<td>400</td>
<td>6.51</td>
</tr>
</tbody>
</table>

$\text{poly(MA-co-Sty)}_{\text{base}} = 4.74 \times 10^{-5}$ mol L$^{-1}$,
$[\text{DVB}] = 1.18$ mol L$^{-1}$,
$[\text{AAm}] = 4.20 \times 10^{-2}$ mol L$^{-1}$,
Temp = 80 ± 0.2°C,
Solvent = Dioxan,
Time = 1 hr.
TABLE – IV.6.3
Effect of [poly (MA-co-Sty)] on the IPN properties

<table>
<thead>
<tr>
<th>S.No.</th>
<th>poly(MA-co-Sty)\text{baseM} x 10^5 (mol L^{-1})</th>
<th>Yield (%)</th>
<th>Swelling in DMF (%)</th>
<th>$\overline{M_c}$</th>
<th>Young’s modulus x 10^{-5} (dynes cm^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPN-6</td>
<td>2.36</td>
<td>12.06</td>
<td>34</td>
<td>85</td>
<td>1.57</td>
</tr>
<tr>
<td>IPN-7</td>
<td>3.68</td>
<td>13.11</td>
<td>47</td>
<td>159</td>
<td>2.81</td>
</tr>
<tr>
<td>IPN-3</td>
<td>4.74</td>
<td>14.78</td>
<td>65</td>
<td>286</td>
<td>4.83</td>
</tr>
<tr>
<td>IPN-8</td>
<td>5.79</td>
<td>16.78</td>
<td>70</td>
<td>322</td>
<td>5.37</td>
</tr>
<tr>
<td>IPN-9</td>
<td>6.84</td>
<td>18.22</td>
<td>76</td>
<td>385</td>
<td>6.30</td>
</tr>
</tbody>
</table>

[Ylide] = 2.06 x 10^{-5} mol L^{-1}, [AAm] = 4.20 x 10^{-2} mol L^{-1}, [DVB] = 1.18 mol L^{-1}, Temp = 80 ± 0.2°C, Time = 1 hr., Solvent = Dioxan
TABLE – IV.6.4

Effect of [acrylamide] on the IPN properties

<table>
<thead>
<tr>
<th>S.No.</th>
<th>[AAm] x 10^2 (mol L^-1)</th>
<th>Yield (%)</th>
<th>Swelling in DMF (%)</th>
<th>$\overline{M_c}$</th>
<th>Young’s modulus x 10^{-5} (dynes cm^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPN-10</td>
<td>2.31</td>
<td>11.35</td>
<td>78</td>
<td>416</td>
<td>6.77</td>
</tr>
<tr>
<td>IPN-11</td>
<td>3.29</td>
<td>12.00</td>
<td>69</td>
<td>313</td>
<td>5.23</td>
</tr>
<tr>
<td>IPN-3</td>
<td>4.20</td>
<td>14.78</td>
<td>65</td>
<td>286</td>
<td>4.83</td>
</tr>
<tr>
<td>IPN-12</td>
<td>5.22</td>
<td>21.14</td>
<td>50</td>
<td>175</td>
<td>3.07</td>
</tr>
<tr>
<td>IPN-13</td>
<td>6.08</td>
<td>30.40</td>
<td>43</td>
<td>142</td>
<td>2.54</td>
</tr>
</tbody>
</table>

[Ylide] = 2.06 x 10^{-5} mol L^{-1},

[poly(MA-co-Sty)]_{base}M = 4.74 x 10^{-5} mol L^{-1},

[DVB] = 1.18 mol L^{-1},

Temp = 80 ± 0.2°C,

Time = 1 hr.,

Solvent = Dioxan
TABLE – IV.6.5
Effect of [divinylbenzene] on the IPN properties

<table>
<thead>
<tr>
<th>S.No.</th>
<th>[DVB] (mol L⁻¹)</th>
<th>Yield (%)</th>
<th>Swelling in DMF (%)</th>
<th>$\overline{M_c}$</th>
<th>Young's modulus x 10⁻⁵ (dynes cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPN-14</td>
<td>0.71</td>
<td>9.56</td>
<td>82</td>
<td>370</td>
<td>5.98</td>
</tr>
<tr>
<td>IPN-15</td>
<td>0.94</td>
<td>12.89</td>
<td>74</td>
<td>358</td>
<td>5.90</td>
</tr>
<tr>
<td>IPN-3</td>
<td>1.18</td>
<td>14.78</td>
<td>65</td>
<td>286</td>
<td>4.83</td>
</tr>
<tr>
<td>IPN-16</td>
<td>1.41</td>
<td>17.72</td>
<td>56</td>
<td>227</td>
<td>3.91</td>
</tr>
<tr>
<td>IPN-17</td>
<td>1.65</td>
<td>24.45</td>
<td>49</td>
<td>161</td>
<td>2.85</td>
</tr>
</tbody>
</table>

$[\text{Ylide}] = 2.06 \times 10^{-5} \text{ mol L}^{-1}, \quad \text{poly(MA-co-Sty)}_{\text{baseM}} = 4.74 \times 10^{-5} \text{ mol L}^{-1},$

$[\text{AAm}] = 4.20 \times 10^{-2} \text{ mol L}^{-1}, \quad \text{Temp} = 80 \pm 0.2^\circ \text{C},$

Time = 1 hr., \quad \text{Solvent} = \text{Dioxan}$
Fig. IV.6.1: FTIR spectrum of IPN of poly(MA-co-Sty) with acrylamide
Fig. IV.6.2: DSC curve of IPN of poly(MA-co-Sty) with acrylamide
Fig. IV.6.3: SEM picture of IPN of poly(MA-co-Sty) with acrylamide at 500 X magnification

Fig. IV.6.4: SEM picture of IPN of poly(MA-co-Sty) with acrylamide at 1.50 KX magnification
Fig.IV.6.5 : SEM picture of IPN of poly(MA-co-Sty) with acrylamide at 2.50 KX magnification
IV.7: Synthesis and characterization of copolymer of N-vinyl pyrrolidone with n-butyl methacrylate initiated by triphenylbismuthonium ylide.*

Research on the application of copolymer of N-vinyl pyrrolidone with n-butyl methacrylate copolymer has shown its utility in medical field. A publication reported the clinical application of the poly(N-VP-co-BMA) to eliminate mandibular bone defect. The implants were indicated to ensure reliable fixation and promoted the formation of valuable osseous that regenerate due to their capacity to self resolve and osteoconductivity, thus widening the scope of reconstructive surgery. Hydrogel for contact lenses was also reported to be synthesized by the copolymerization of N-VP with BMA. The results showed that dehydration rate increased with N-VP in the copolymer. The copolymers of BMA and N-VP were also found useful as coating filters to remove leukocytes. The coated filters effectively improved platelet permeation through the filters, with an increase in the permeation ratio of leukocytes. N-VP-co-BMA copolymers also find applications in the photography, adhesive and pharmaceutical industries.

The present sub-chapter highlights the synthesis, kinetics and mechanism of copolymerization N-VP with n-BMA using triphenylbismuthonium 1,2,3,4 tetraphenylcyclopentadienylide as the initiator.

**Kinetics of copolymerization**

The copolymerization reactions were carried out in inert atmosphere using dilatometer at 60 ± 0.1°C for 1hr. The polymers were precipitated with diethyl ether and dried under vacuum. The copolymers were refluxed with methanol and acetone to remove the homopolymers of N-VP and n-BMA respectively. The induction period was determined to be 2 min.

The experimental data of the copolymerization reactions are summarized in Fig.IV.7.1-7.3.

*A part of this work is under communication to International Journal.
Effect of Initiator Concentration

The effect of triphenylbismuthonium 1,2,3,4-tetraphenylycyclopentadienylide on the copolymerization of N-VP with n-BMA was observed by varying the [Ylide] concentration from $4.12 \times 10^{-6}$–$12.36 \times 10^{-6}$ mol L$^{-1}$ (Tab.IV.7.1). An increase in the rate of polymerization was noticed upon increasing the concentration of ylide. The order with respect to ylide was calculated from the slope of log $R_p$ vs log [Ylide] (Fig.IV.7.4). The initiator exponent value obtained from the graph is 0.5, which is in agreement with the ideal kinetics. The intrinsic viscosity decreased on increasing the ylide concentration.

Effect of Monomer(s) Concentration (N-vinyl pyrrolidone and n-butyl methacrylate)

The influence of N-vinyl pyrrolidone on the copolymerization was investigated by varying the [N-VP] concentration from 0.94–2.82 mol L$^{-1}$ (Tab.IV.7.2). The $R_p$ increased with increase in [N-VP] concentration. The monomer exponent value with respect to [N-VP], calculated from the slope of log $R_p$ vs log [N-VP] (Fig.IV.7.5), is unity indicating ideal kinetics.

The effect of n-butyl methacrylate was studied by varying the [n-BMA] concentration from 0.63–1.89 mol L$^{-1}$ (Tab.IV.7.2). The $R_p$ increased on increasing the [n-BMA] concentration. The order with respect to [n-BMA], calculated from the slope of log $R_p$ vs log [n-BMA] (Fig.IV.7.6), is unity suggesting ideal kinetics. The $\eta_{int}$ value showed a regular increase with increase in [N-VP] and [n-BMA] concentration.

Effect of temperature

The polymerization runs were also carried out at 55$^\circ$, 65$^\circ$ C to obtain the energy of activation. The activation energy calculated from the Arrhenius plot of log $R_p$ vs $1/T$ (Fig.IV.7.7) is 32 kJ mol$^{-1}$.

Characterization of copolymer

(i) Fourier Transform Infrared Spectroscopy

The FTIR spectrum of poly(N-VP-co-n-BMA) (Fig.IV.7.8) show the following bands:
2958 cm\(^{-1}\) – aliphatic C-H stretching
2874 cm\(^{-1}\) – C-H stretching in C-O-CH\(_2\) group of BMA
1772 cm\(^{-1}\) – \(>\)C=O stretching in BMA
1664 cm\(^{-1}\) – \(>\)C=O stretching in NVP
1462 cm\(^{-1}\) – C-H def. in -CH\(_2\) group
1427 cm\(^{-1}\) – C-H def. in -CH\(_3\) group of BMA
1176 cm\(^{-1}\) – C-O stretching in C-O-C group.

(ii) \(^1\)H Nuclear Magnetic Resonance

The \(^1\)HNMR spectrum of copolymer of N-VP with n-BMA (Fig.IV.7.9) show the peak in the range of 3.4-3.8 \(\delta\) ppm for -OCH\(_2\) group in butyl methacrylate and 6-8 \(\delta\) ppm for protons of N-VP. The peak in the region of 0.9-2.5 \(\delta\) ppm are caused due to -CH\(_2\) and -CH in the copolymer.

(iii) \(^13\)C Nuclear Magnetic Resonance

The \(^13\)CNMR spectrum of poly(N-VP-co-n-BMA) (Fig IV.7.10) gave the following signals:
14 \(\delta\) ppm – -CH\(_3\) (C\(_a\))
20 \(\delta\) ppm – -CH\(_3\) (C\(_b\))
63 \(\delta\) ppm – -OCH\(_3\) (C\(_c\))
171 \(\delta\) ppm – \(>\)C=O of BMA (C\(_d\))
192 \(\delta\) ppm – \(>\)C=O of NVP (C\(_e\))

(iv) Differential Scanning Calorimetry

The DSC curve (Fig.IV.7.11) of poly (N-VP-co-n-BMA) shows glass transition temperature of 39°C. The \(T_g\) value for poly n-butyl methacrylate\(^{382}\) and poly N-vinyl pyrrolidone\(^{335}\) are 14°C and 54°C respectively.

Copolymer Composition

The mole fraction of n-butyl methacrylate was calculated from the peak area due to -OCH\(_2\) protons obtained from \(^1\)HNMR spectra and the mole fraction of N-vinyl pyrrolidone was obtained from the nitrogen elemental analysis data (Tab.IV.7.3). The copolymer composition (Tab.IV.7.4) was calculated using Kelen–Tüdos method.
The reactivity ratios $r_1$ and $r_2$ (Fig.IV.7.12), calculated from Kelen-Tüdos method are 0.01 and 0.09 for N-VP and n-BMA respectively. Although the product of $r_1$ and $r_2$ are approaching zero but the mole fraction of n-BMA and N-VP are not equal, therefore, the copolymer has the tendency towards alternating nature.

**Mechanism**

As discussed earlier in the previous sub-chapters, the ylide dissociates to form phenyl radical that brings about polymerization. This is also confirmed from the ESR spectrum (Fig.IV.7.13). The mechanism is as follows:

**Initiation:**

\[
\begin{align*}
\begin{array}{c}
\text{Initiating N-vinyl pyrrolidone radical} \\
\text{Initiating butyl methacrylate radical}
\end{array}
\end{align*}
\]

**Propagation:**

(Pr type 11)

(Pr type 12)
Termination:
By coupling:

By disproportionation

Conclusions

Triphenylbismuthonium 1,2,3,4-tetraphenylcyclopentadienylide initiated copolymerization of N-vinyl pyrrolidone with n-butyl methacrylate results in nearly alternating copolymer and the system obeys ideal kinetics.
TABLE – IV.7.1

Effect of [Initiator] on the rate of copolymerization of N-vinyl pyrrolidone and n-butyl methacrylate

<table>
<thead>
<tr>
<th>S.No.</th>
<th>[Ylide] x 10^6 (mol L(^{-1}))</th>
<th>Conversion (%)</th>
<th>(R_p) x 10^6 (mol L(^{-1}) s(^{-1}))</th>
<th>(\eta_{\text{int}}) (dL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>4.12</td>
<td>15.01</td>
<td>10.48</td>
<td>0.27</td>
</tr>
<tr>
<td>2.</td>
<td>7.00</td>
<td>17.10</td>
<td>10.66</td>
<td>0.24</td>
</tr>
<tr>
<td>3.</td>
<td>9.48</td>
<td>18.93</td>
<td>14.00</td>
<td>0.16</td>
</tr>
<tr>
<td>4.</td>
<td>12.36</td>
<td>22.19</td>
<td>15.72</td>
<td>0.09</td>
</tr>
</tbody>
</table>

Temp = 60 ± 0.2°C, Time = 1 hr., [n-BMA] = 1.05 mol L\(^{-1}\), [N-VP] = 1.57 mol L\(^{-1}\), Solvent = Dioxan
TABLE – IV.7.2
Effect of [Monomer(s)] on the rate of copolymerization of
N-vinyl pyrrolidone and butyl methacrylate

<table>
<thead>
<tr>
<th>S.No.</th>
<th>[n-BMA] (mol L(^{-1}))</th>
<th>[N-VP] (mol L(^{-1}))</th>
<th>Conversion (%)</th>
<th>(R_p \times 10^6) (mol L(^{-1}) s(^{-1}))</th>
<th>(\eta_{int}) (dL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>1.05</td>
<td>0.94</td>
<td>13.67</td>
<td>7.62</td>
<td>0.16</td>
</tr>
<tr>
<td>2.</td>
<td>1.05</td>
<td>1.57</td>
<td>17.10</td>
<td>10.66</td>
<td>0.24</td>
</tr>
<tr>
<td>3.</td>
<td>1.05</td>
<td>2.19</td>
<td>20.98</td>
<td>18.00</td>
<td>0.38</td>
</tr>
<tr>
<td>4.</td>
<td>1.05</td>
<td>2.82</td>
<td>25.61</td>
<td>27.10</td>
<td>0.56</td>
</tr>
<tr>
<td>5.</td>
<td>0.63</td>
<td>1.57</td>
<td>13.94</td>
<td>9.10</td>
<td>0.11</td>
</tr>
<tr>
<td>6.</td>
<td>1.47</td>
<td>1.57</td>
<td>19.37</td>
<td>18.24</td>
<td>0.28</td>
</tr>
<tr>
<td>7.</td>
<td>1.89</td>
<td>1.57</td>
<td>21.23</td>
<td>23.07</td>
<td>0.43</td>
</tr>
</tbody>
</table>

Temp = 60 ± 0.1°C, Time = 1 hr.,
[Ylide] = 7.00 \times 10^6\text{ mol L}^{-1}, Solvent = Dioxan
### TABLE – IV.7.3
Elemental Analysis Data*

<table>
<thead>
<tr>
<th>S.No.</th>
<th>n-BMA (mol L⁻¹)</th>
<th>N-VP (mol L⁻¹)</th>
<th>Nitrogen (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.21</td>
<td>1.57</td>
<td>5.71</td>
</tr>
<tr>
<td>2.</td>
<td>1.89</td>
<td>1.57</td>
<td>6.22</td>
</tr>
<tr>
<td>3.</td>
<td>1.05</td>
<td>0.31</td>
<td>2.53</td>
</tr>
<tr>
<td>4.</td>
<td>1.05</td>
<td>2.82</td>
<td>5.79</td>
</tr>
</tbody>
</table>

*Elementar Vario EL III Carlo Erba 1108
### TABLE - IV.7.4

Copolymer composition

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Monomer feed [N-VP/n-BMA]</th>
<th>Mole fraction in the copolymer</th>
<th>Ratio of mole fraction in the copolymer [N-VP/n-BMA]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>N-VP</td>
<td>n-BMA</td>
</tr>
<tr>
<td>1.</td>
<td>7.48</td>
<td>0.36</td>
<td>0.64</td>
</tr>
<tr>
<td>2.</td>
<td>0.83</td>
<td>0.37</td>
<td>0.63</td>
</tr>
<tr>
<td>3.</td>
<td>2.69</td>
<td>0.33</td>
<td>0.67</td>
</tr>
<tr>
<td>4.</td>
<td>0.30</td>
<td>0.32</td>
<td>0.68</td>
</tr>
</tbody>
</table>

Temp = 60 ± 0.1°C, Time = 1 hr., [Ylide] = 7.00 x 10⁻⁶ mol L⁻¹, Solvent = Dioxan
Fig. IV.7.1: Percentage conversion vs time plot for the copolymerization of N-VP with n-BMA.

\[ [\text{N-VP}] = 1.57 \text{ mol L}^{-1}, \quad [\text{n-BMA}] = 1.05 \text{ mol L}^{-1}, \]

Temp = 60 ± 0.1°C, Time = 60 min.
Fig. IV.7.2: Percentage conversion vs time plot for the copolymerization of N-VP with n-BMA.

\[ \text{[Ylide]} = 7.00 \times 10^{-6} \text{ mol L}^{-1}, \quad \text{[n-BMA]} = 1.05 \text{ mol L}^{-1} \]

Temp = 60 ± 0.1°C, Time = 60 min.
Fig. IV.7.3: Percentage conversion vs time plot for the copolymerization of N-VP with n-BMA.

\[ [\text{Ylide}] = 7.00 \times 10^{-6} \text{ mol L}^{-1}, \quad [\text{N-VP}] = 1.57 \text{ mol L}^{-1} \]

Temp = 60 ± 0.1°C, \quad Time = 60 min.
**Fig.IV.7.4**: Relationship between $\log R_p$ vs $\log [\text{Ylide}]$ for the copolymerization of N-VP with n-BMA.

- $[\text{N-VP}] = 1.57 \text{ mol L}^{-1}$,
- $[\text{n-BMA}] = 1.05 \text{ mol L}^{-1}$
- $\text{Temp} = 60 \pm 0.1 ^\circ \text{C}$,
- $\text{Time} = 60 \text{ min}$.

**Fig.IV.7.5**: Relationship between $\log R_p$ vs $\log [\text{N-VP}]$ for the copolymerization of N-VP with n-BMA.

- $[\text{Ylide}] = 7.00 \times 10^{-6} \text{ mol L}^{-1}$,
- $[\text{n-BMA}] = 1.05 \text{ mol L}^{-1}$
- $\text{Temp} = 60 \pm 0.1 ^\circ \text{C}$,
- $\text{Time} = 60 \text{ min}$.
Fig.IV.7.6: Relationship between log $R_p$ vs log [n-BMA] for the copolymerization of N-VP with n-BMA.

\[ \text{[Ylide]} = 7.00 \times 10^{-6} \text{ mol L}^{-1}, \quad \text{[N-VP]} = 1.57 \text{ mol L}^{-1} \]

Temp = 60 ± 0.1°C, Time = 60 min.

Fig.IV.7.7: Arrhenius plot of log $R_p$ vs $1/T$ for the copolymerization of N-VP with n-BMA.

\[ \text{[N-VP]} = 1.57 \text{ mol L}^{-1}, \quad \text{[n-BMA]} = 1.05 \text{ mol L}^{-1} \]

\[ \text{[Ylide]} = 7.00 \times 10^{-6} \text{ mol L}^{-1}, \quad \text{Temp} = 60 \pm 0.1^\circ\text{C} \]

Time = 60 min.
Fig. IV.7.8: FTIR spectrum of copolymer of n-BMA with N-VP.
Fig. IV.7.9: $^1$HNMR spectrum of copolymer of n-BMA with N-VP.

Fig. IV.7.10: $^{13}$CNMR spectrum of copolymer of n-BMA with N-VP.
Fig. IV.7.11: DSC curve of copolymer of n-BMA with N-VP.
Fig.IV.7.12: Kelen–Tüdos plot of copolymer of N-vinyl pyrrolidone and n-butyl methacrylate
Fig. IV.7.13: ESR spectrum of copolymer of n-BMA with N-VP.
IV.8: Synthesis and characterization of copolymer of N-vinyl pyrrolidone with n-butyl methacrylate initiated by triphenylbismuthonium 1,2,3,4-tetraphenylcyclopentadienylide – mercuric chloride complex. *

Poly(BMA-co-N-VP) has been widely copolymerized due to its increased applications as discussed in the previous sub-chapter. Literature survey shows that the kinetic features of radical copolymerization of N,N-dimethyl-N,N-diallyl ammonium chloride (DMDAAC) was studied by Topchiev et al. It was found that the rate of copolymerization decreased significantly as the concentration of DMDAAC was increased. Kaneyoshi and Matyjaszewski examined the radical copolymerization of vinylchloroacetate and N-VP mediated by bis (acetylacetonate) cobalt derivatives. The literature is further enriched with the studies on copolymerization of N-vinyl pyrrolidone with vinyl acetate, methyl acrylate, methacrylic acid, styrene etc. In continuation to the previous sub-chapter, where copolymerization of N-VP with BMA was carried out in the presence of triphenylbismuthonium ylide, the present sub-chapter focuses on the synthesis and characterization of poly(n-BMA-co-N-VP) using triphenylbismuthonium 1,2,3,4-tetraphenylcyclopentadienylylide–mercuric chloride complex.

**Kinetic of copolymerization**

The copolymerization reactions were carried out in nitrogen blanket using dilatometer technique at 60 ± 0.1°C for 1hr. The decline in meniscus level was observed through cathetometer. The polymers were precipitated with diethyl ether and vacuum dried to constant weight. The copolymer(s) were further refluxed with methanol and acetone for removal of the traces of homopolymers of N-VP and n-BMA and finally vacuum dried. The maximum induction period was determined from the percent conversion vs time graph as 3 min. The kinetic data of the copolymerization reactions are summarized in Fig.IV.8.1-8.3.

* A part of this work is under communication to International Journal

222
Effect of Initiator Concentration

The influence of triphenylbismuthonium 1,2,3,4-tetraphenylcyclopentadienylide-mercuric chloride complex on the copolymerization of N-VP with n-BMA was investigated by varying the [Complex] concentration from $3.09 \times 10^{-6}$ to $9.26 \times 10^{-6}$ mol L$^{-1}$ (Tab.IV.8.1). Rate of polymerization was found to be the direct function of [Complex] concentration. The initiator exponent value determined from the slope of log $R_p$ vs log [Complex] (Fig.IV.8.4) is 0.5, which is in agreement with the ideal kinetics. The $\eta_{int}$ decreased on increasing the ylide concentration.

Effect of Monomer(s) Concentration (N-vinyl pyrrolidone and butyl methacrylate)

The effect of N-vinyl pyrrolidone on the copolymerization was examined by varying the [N-VP] concentration from 0.31-2.82 mol L$^{-1}$ (Tab.IV.8.2). The $R_p$ increased on increasing the [N-VP] concentration. The order with respect to [N-VP], calculated from the slope of log $R_p$ vs log [N-VP] (Fig.IV.8.5), is unity.

The effect of n-butyl methacrylate was studied by varying the [n-BMA] concentration from 0.63-1.89 mol L$^{-1}$ (Tab.IV.8.2). The $R_p$ is a direct function of [n-BMA]. The order with respect to [n-BMA], calculated from the slope of log $R_p$ vs log [n-BMA] (Fig.IV.8.6), is unity. The order of reaction with respect to complex and monomer(s) suggest that the system follows ideal kinetics. An increase in the intrinsic viscosity ($\eta_{int}$) was observed with increase in [N-VP] and [n-BMA] concentration.

Effect of temperature

The polymerization runs were also performed at 55°, 65°C to calculate energy of activation. The activation energy determined from the Arrhenius plot of log $R_p$ vs 1/T (Fig.IV.8.7), is 38 kJ mol$^{-1}$. 

223
Characterization of copolymer

(i) Fourier Transform Infrared Spectroscopy

The FTIR spectrum of poly(N-VP-co-n-BMA) (Fig IV.8.8) shows the following bands:
2958 cm\(^{-1}\) – aliphatic C-H stretching
2873 cm\(^{-1}\) – C-H stretching in C-O-CH\(_2\) group of n-BMA
1724 cm\(^{-1}\) – >C=O stretching in n-BMA
1664 cm\(^{-1}\) – >C=O stretching in N-VP
1461 cm\(^{-1}\) – C-H def. in -CH\(_2\) group
1426 cm\(^{-1}\) – C-H def. in -CH\(_3\) group of n-BMA
1152 cm\(^{-1}\) – C-O stretching in C-O-C group.

(ii) \(^1\)H Nuclear Magnetic Resonance

The \(^1\)HNMR spectrum of poly(N-VP-co-n-BMA) (Fig IV.8.9) gives the peak for -OCH\(_2\) group in the range of 3.4-3.8 \(\delta\) ppm and protons of N-VP in the range of 6-7 \(\delta\) ppm. The peaks in the region between 0.9-2.5 \(\delta\) ppm are due to the -CH\(_2\) and -CH in the copolymer.

(iii) \(^{13}\)C Nuclear Magnetic Resonance

The \(^{13}\)CNMR spectrum of poly(N-VP-co-n-BMA) (Fig IV.8.10) give the following signals:
16 \(\delta\) ppm – -CH\(_3\) (C\(_{a}\))
17 \(\delta\) ppm – -CH\(_3\) (C\(_{b}\))
66 \(\delta\) ppm – -OCH\(_2\) (C\(_{c}\))
171 \(\delta\) ppm – >C=O of n-BMA (C\(_{d}\))
193 \(\delta\) ppm – >C=O of N-VP (C\(_{e}\))

(iv) Differential Scanning Calorimetry

The \(T_g\) value obtained from the DSC (Fig IV.8.11) of the copolymer synthesized using triphenylbismuthonium 1,2,3,4-tetraphenylcyclopentadienyli-
mercuric chloride complex is 43°C. The glass transition temperature determined for copolymerization with triphenylbismuth ylide is 39°C which is slightly less than the value reported with the complex.

**Copolymer Composition**

The mole fraction of N-vinyl pyrrolidone was calculated from the data obtained through the elemental analysis of nitrogen (Tab.IV.8.3). The mole fraction (Tab.IV.8.4) of n-butyl methacrylate was calculated from the peak area due to -OCH₂ protons obtained from ¹H NMR spectra.

The reactivity ratios r₁ and r₂ (Fig.IV.8.12), calculated from Kelen - Tüdos method are 0.038 and 0.10 for N-VP and n-BMA respectively. Although the mole fraction of n-BMA and N-VP are not equal, but the product of r₁ and r₂ are approaching zero and hence the copolymer formed has tendency towards alternating nature.

**Mechanism**

Since bismuth shows variable valency by formation of complex like Bi₂O₃, Bi₂O₄ and Bi₂O₅, therefore, the probable site of complex formation is the Bi centre of the ylide. The structure of complex is likely to be-

![Complex Structure Diagram]

The free radical mode of polymerization was confirmed by ESR spectrum (Fig.IV.8.13) which shows absorption at 3350 gauss. The gyromagnetic ratio (g) calculated from the ESR spectrum is 1.97, which is close to the value given for H atom (2.0036 ± 0.03).

There are 4 possible ways by which hydrogen atom is produced from the dissociation of metal-ylide complex. The radical formed through route 1 is least
stable as it has no hydrogen atom attached to carbon while the radical formed through route 4 is most stable owing to hyperconjugation while the stability of the radicals formed through route 3 and 4 is intermediate between those formed by route 1 and 4. Therefore, route 4 is the most preferred route for formation of the hydrogen radical. The initiation step is as follows:

**Initiation:**

![Chemical Diagram]
The propagation and termination steps proceed in the similar way as proposed in the previous sub-chapter.

**Conclusions:**

Triphenylbismuthonium 1,2,3,4-tetraphenylcyclopentadienylide–mercuric chloride complex initiated copolymerization of N-vinyl pyrrolidone with n-butyl methacrylate results in nearly alternating copolymer and the system follows ideal kinetics.
<table>
<thead>
<tr>
<th>S.No.</th>
<th>[Complex] x $10^6$ (mol L$^{-1}$)</th>
<th>Conversion (%)</th>
<th>$R_p$ x $10^6$ (mol L$^{-1}$ s$^{-1}$)</th>
<th>$\eta_{int}$ (dL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>3.09</td>
<td>16.42</td>
<td>12.00</td>
<td>0.50</td>
</tr>
<tr>
<td>2.</td>
<td>5.25</td>
<td>21.21</td>
<td>15.72</td>
<td>0.36</td>
</tr>
<tr>
<td>3.</td>
<td>7.00</td>
<td>23.22</td>
<td>17.47</td>
<td>0.25</td>
</tr>
<tr>
<td>4.</td>
<td>9.26</td>
<td>26.49</td>
<td>19.65</td>
<td>0.13</td>
</tr>
</tbody>
</table>

Temp = 60 ± 0.1°C, Time = 1 hr., [n-BMA] = 1.05 mol L$^{-1}$, [N-VP] = 1.57 mol L$^{-1}$, Solvent = Dioxan
TABLE – IV.8.2
Effect of [Monomer(s)] on the rate of copolymerization of
N-vinyl pyrrolidone and n-butyl methacrylate

<table>
<thead>
<tr>
<th>S.No.</th>
<th>[n-BMA] (mol L(^{-1}))</th>
<th>[N-VP] (mol L(^{-1}))</th>
<th>Conversion (%)</th>
<th>(R_p \times 10^6) (mol L(^{-1}) s(^{-1}))</th>
<th>(\eta_{int}) (dL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>1.05</td>
<td>0.31</td>
<td>9.75</td>
<td>4.08</td>
<td>0.11</td>
</tr>
<tr>
<td>2.</td>
<td>1.05</td>
<td>0.94</td>
<td>18.13</td>
<td>10.60</td>
<td>0.19</td>
</tr>
<tr>
<td>3.</td>
<td>1.05</td>
<td>1.57</td>
<td>21.21</td>
<td>15.72</td>
<td>0.36</td>
</tr>
<tr>
<td>4.</td>
<td>1.05</td>
<td>2.19</td>
<td>26.60</td>
<td>24.30</td>
<td>0.40</td>
</tr>
<tr>
<td>5.</td>
<td>1.05</td>
<td>2.82</td>
<td>32.00</td>
<td>33.88</td>
<td>0.83</td>
</tr>
<tr>
<td>6.</td>
<td>0.63</td>
<td>1.57</td>
<td>18.00</td>
<td>11.00</td>
<td>0.12</td>
</tr>
<tr>
<td>7.</td>
<td>1.47</td>
<td>1.57</td>
<td>26.04</td>
<td>22.80</td>
<td>0.29</td>
</tr>
<tr>
<td>8.</td>
<td>1.89</td>
<td>1.57</td>
<td>27.88</td>
<td>28.1</td>
<td>0.46</td>
</tr>
</tbody>
</table>

Temp = 60 ± 0.1°C,
[Complex] = 5.25 x 10\(^{-6}\) mol L\(^{-1}\),
Solvent = Dioxan

Time = 1 hr.,
TABLE – IV.8.3
Elemental Analysis Data*

<table>
<thead>
<tr>
<th>S.No.</th>
<th>n-BMA (mol L(^{-1}))</th>
<th>N-VP (mol L(^{-1}))</th>
<th>Nitrogen (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.21</td>
<td>1.57</td>
<td>15.02</td>
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<tr>
<td>2.</td>
<td>1.89</td>
<td>1.57</td>
<td>5.66</td>
</tr>
<tr>
<td>3.</td>
<td>1.05</td>
<td>0.31</td>
<td>3.38</td>
</tr>
<tr>
<td>4.</td>
<td>1.05</td>
<td>2.82</td>
<td>7.84</td>
</tr>
</tbody>
</table>

*Elementar Vario EL III Carlo Erba 1108
TABLE – IV.8.4

Copolymer composition

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Monomer feed [N-VP/n-BMA]</th>
<th>Mole fraction in the copolymer</th>
<th>Ratio of Mole fraction in the copolymer [N-VP/n-BMA]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>N-VP</td>
<td>n-BMA</td>
</tr>
<tr>
<td>1.</td>
<td>0.61</td>
<td>0.38</td>
<td>0.62</td>
</tr>
<tr>
<td>2.</td>
<td>0.45</td>
<td>0.31</td>
<td>0.69</td>
</tr>
<tr>
<td>3.</td>
<td>0.89</td>
<td>0.47</td>
<td>0.53</td>
</tr>
<tr>
<td>4.</td>
<td>0.79</td>
<td>0.44</td>
<td>0.56</td>
</tr>
</tbody>
</table>

Temp = 60 ± 0.1°C, Time = 1 hr.,
[Complex] = 5.25 x 10⁻⁶ mol L⁻¹, Solvent = Dioxan
\[ [\text{TPB 1,2,3,4-TPCPDY-HgCl}_2] \times 10^6 \text{ mol L}^{-1} \]

\[ @3.09 \]

\[ \bullet 5.25 \]

\[ \bigcirc 7.00 \]

\[ \sqcap 9.26 \]

**Fig. IV.8.1**: Percentage conversion vs time plot for the copolymerization of N-VP with n-BMA.

\[[\text{N-VP}] = 1.57 \text{ mol L}^{-1}, \quad [\text{n-BMA}] = 1.05 \text{ mol L}^{-1}\]

Temp = 60 ± 0.1°C, Time = 60 min.
Fig.IV.8.2 : Percentage conversion vs time plot for the copolymerization of N-VP with n-BMA.

[Complex] = 5.25 x 10^{-6} \text{ mol L}^{-1}, \quad [\text{n-BMA}] = 1.05 \text{ mol L}^{-1},

Temp = 60 \pm 0.1^\circ\text{C}, \quad \text{Time} = 60 \text{ min.}
Fig.IV.8.3: Percentage conversion vs time plot for the copolymerization of N-VP with n-BMA.

[Complex] = 5.25 x 10^{-6} \text{ mol L}^{-1}, \quad [\text{N-VP}] = 1.57 \text{ mol L}^{-1},

Temp = 60 \pm 0.1^\circ\text{C}, \quad \text{Time} = 60 \text{ min.}
Fig.IV.8.4 : Relationship between log $R_p$ vs log [Complex] for the copolymerization of N-VP with n-BMA.

\[
\begin{align*}
[N-VP] &= 1.57 \text{ mol L}^{-1}, \\
n-BMA &= 1.05 \text{ mol L}^{-1}, \\
\text{Temp} &= 60 \pm 0.1°C, \\
\text{Time} &= 60 \text{ min}.
\end{align*}
\]

Fig.IV.8.5 : Relationship between log $R_p$ vs log [N-VP] for the copolymerization of N-VP with n-BMA.

\[
\begin{align*}
[\text{Complex}] &= 5.25 \times 10^{-6} \text{ mol L}^{-1}, \\
n-BMA &= 1.05 \text{ mol L}^{-1}, \\
\text{Temp} &= 60 \pm 0.1°C, \\
\text{Time} &= 60 \text{ min}.
\end{align*}
\]
Fig.IV.8.6: Relationship between $\log R_p$ vs $\log [n\text{-BMA}]$ for the copolymerization of N-VP with n-BMA.

[Complex] = $5.25 \times 10^{-6}$ mol L$^{-1}$, [n-BMA] = 1.57 mol L$^{-1}$,
Temp = 60 ± 0.1°C, Time = 60 min.

Fig.IV.8.7: Arrhenius plot of $\log R_p$ vs $1/T$ for the copolymerization of N-VP with n-BMA.

[N-VP] = 1.57 mol L$^{-1}$, [n-BMA] = 1.05 mol L$^{-1}$,
[Complex] = $5.25 \times 10^{-6}$ mol L$^{-1}$, Temp = 60 ± 0.1°C
Time = 60 min.
Fig. IV.8.8: FTIR spectrum of copolymer of N-VP with n-BMA.
Fig.IV.8.9 : $^1$HNMR spectrum of copolymer of N-VP with n-BMA.

Fig.IV.8.10 : $^{13}$CNMR spectrum of copolymer of N-VP with n-BMA.
Fig. IV.8.11: DSC curve of copolymer of N-VP with n-BMA.
Fig.IV.8.12 : Kelen–Tüdos plot for the copolymer of N-VP and n-BMA
Fig.IV.8.13 : ESR spectrum for the copolymer of N-VP with n-BMA.