Polymerization of methyl acrylate using a heterocyclic ylide as an initiator and degradative chain transfer agent

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The free radical polymerization of methylacrylate has been investigated at 80 ±1°C for 60 min in 1,4-dioxan using p-bromophenacyl dimethyl sulphonium ylide as initiator and degradative chain transfer agent up to 23% conversion. No gelation occurred due to auto acceleration leading energy and the value of $k_p/k_a$ were calculated as 72 kJ mol$^{-1}$ and $18 \times 10^{-2}$ Ls$^{-1}$, respectively. The radical mode of polymerization was confirmed by ESR and the effect of hydroquinone. A possible mechanism of the system is also proposed.

A substance which decreases the rate of polymerization as well as the average degree of polymerization of the polymers is called a degradative chain transfer agent and the effect is referred to as degradative chain transfer$^1$. It is found that dehydromyocene and isopropylbenzene act as degradative chain transfer agents for the polymerization of vinyl acetate$^2$. Dimethylsulphides and diazoaminobenzene have been used as initiators and degradative chain transfer agents, respectively$^3,4$. It is well-known$^2,5$ that bulk polymerization of methyl acrylate (MA) exhibits a large auto-acceleration of the overall rate of polymerization, referred to as Trommsdorff, or gel effect, with associated increase in the molecular weight of the polymer. The present work shows that the heterocyclic ylide p-bromophenacyl dimethyl sulphonium ylide (p-BPDSY) could be used in low concentration as a radical initiator to carry out polymerization runs up to 23% conversion without gelation due to autoacceleration.

Experimental Procedure
Methyl acrylate (Ranbaxy) and 1,4-dioxan (Qualigen) were purified by standard procedure while p-bromophenacyl dimethyl sulphonium ylide (p-BPDSY) [Br-C$_6$H$_4$-CO-CHS(CH$_3$)$_2$] was prepared by a reported method$^6$.

Polymerization reactions were carried out at 80 ±1°C for 60 min using dilatometric technique. The dilatomer was filled with the required amount of solvent, monomer, initiator and flushed with purified nitrogen gas, stopped and placed in a thermostated bath. The progress of the reaction was monitored with the help of cathetometer. The rate of polymerization ($R_p$) was calculated from the slope of percent conversion vs time plots.

The intrinsic viscosity ($\eta$) of polymethyl acrylate determined in benzene at 30°C with an Ubbelohde viscometer was used to calculate the average viscosity molecular weight ($\bar{M}_v$) using the equation

$$\ln[\eta] = 4.5 \times 10^{-5} \bar{M}_v \quad \ldots \ldots (1)$$

Results and Discussion
The results of kinetic investigations of the polymerization of methyl acrylate at 80 ±1°C initiated by p-BPDSY in 1,4-dioxan for 60 min are summarized in Tables 1-3 and Figs 1-4. The ylide (p-BPDSY) initiates the polymerization in which no gelation occurs up to 23% conversion and the resulting polymers has a high molecular weight.

**Table 1—Effect of [MA] on the polymerization of methyl acrylate initiated by p-BPDSY at 80 ±1°C**

<table>
<thead>
<tr>
<th>[MA], mol L$^{-1}$</th>
<th>Conversion, %</th>
<th>$R_p \times 10^3$, mol L$^{-1}$ s$^{-1}$</th>
<th>$\bar{M}_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.39</td>
<td>7.01</td>
<td>2.64</td>
<td>12,240</td>
</tr>
<tr>
<td>2.09</td>
<td>6.35</td>
<td>7.55</td>
<td>13,880</td>
</tr>
<tr>
<td>2.79</td>
<td>6.62</td>
<td>7.99</td>
<td>15,210</td>
</tr>
<tr>
<td>3.48</td>
<td>10.10</td>
<td>9.66</td>
<td>16,820</td>
</tr>
</tbody>
</table>

*Polymerization condition: [p-BPDSY] = 4.66 x 10$^{-3}$ mol L$^{-1}$; Time = 60 min.

*Author to whom correspondence should be addressed.
Table 2—Effect of concentration on the polymerization of methyl acrylate initiated by p-BPDSY at 80 ± 1°C

<table>
<thead>
<tr>
<th>Additive</th>
<th>Additive, mol L⁻¹</th>
<th>Conversion, %</th>
<th>$R_p \times 10^5$, mol L⁻¹ s⁻¹</th>
<th>$\bar{M}_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>a Benzene</td>
<td>0</td>
<td>2.18</td>
<td>2.02</td>
<td>14,680</td>
</tr>
<tr>
<td>b</td>
<td>0.76</td>
<td>1.85</td>
<td>1.74</td>
<td>14,810</td>
</tr>
<tr>
<td>c</td>
<td>1.53</td>
<td>1.36</td>
<td>1.16</td>
<td>15,800</td>
</tr>
<tr>
<td>a DMSO</td>
<td>0</td>
<td>2.18</td>
<td>2.02</td>
<td>14,680</td>
</tr>
<tr>
<td>b</td>
<td>0.76</td>
<td>4.93</td>
<td>4.64</td>
<td>13,690</td>
</tr>
<tr>
<td>c</td>
<td>1.53</td>
<td>8.12</td>
<td>7.73</td>
<td>12,910</td>
</tr>
<tr>
<td>a Hydroquinone</td>
<td>0</td>
<td>2.18</td>
<td>2.02</td>
<td>14,680</td>
</tr>
<tr>
<td>b</td>
<td>$1.51 \times 10^2$</td>
<td>2.0</td>
<td>1.90</td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>$3.03 \times 10^2$</td>
<td>Inhibited</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Polymerization condition: [MA] = 3.48 mol L⁻¹; [p-BPDSY] = $7.77 \times 10^{-3}$ mol L⁻¹; Time = 60 min.

Fig. 1—Conversion vs time plots, for the polymerization of methyl acrylate at 80°C in [MA] = 3.48 mol L⁻¹ [p-BPDSY] = 0.43 (O), 1.31 (●), 1.74 (△), 2.18 (▲), 2.62 (×), 3.05 (□), 3.93 $\times 10^{-6}$ (■) mol L⁻¹

merization runs were performed at different temperature, i.e., 70, 75, 78 and 80°C using 3.4 mol L⁻¹ of MA and $4.66 \times 10^{-3}$ mol L⁻¹ of (p-BPDSY). $R_p$ increases with polymerization temperature. The overall energy of activation was calculated from the Arrhenius plot (Fig. 3) as $72.0 \text{ kJ mol}^{-1}$. This value also confirms the radical mode of polymerization.

Effect of additives—Table 2 shows the effect of polar and non-polar solvents. It is clear that non-polar solvents like benzene decrease the $R_p$ and polar solvents like DMSO favour the polymer formation. There results can be explained on the basis of the fact that benzene (non-polar) suppresses the decomposition of initiator and DMSO being a polar solvent enhances the decomposition of initiator, thereby, increasing the $R_p$.

Variation of the rate of polymerization with ylide concentration—The results of polymerization of MA in 1,4-dioxan, carried out at 80 ± 1°C varying in (n) (p-BPDSY) from $1.01 \times 10^{-3}$ to $12.43 \times 10^{-3}$ mol L⁻¹ while keeping [MA] constant at $3.48 \text{ mol L}^{-1}$, are presented in Table 3 and Fig. 1. The polymerization was associated with varying induction periods. It is observed that the ylide initiates the radical polymerization of MA and $R_p$ increases when ylide concentration is varied at low concentration (from $1.01 \times 10^{-3}$ to $1.55 \times 10^{-3}$ mol L⁻¹). The order of reaction, calculated from the slope of the plot of log 10 $R_p$ vs log 10 (p-BPDSY), is 0.5, as expected for ideal kinetics. This is further supported by the facts that the line of the plot of $1/\bar{M}_n$ vs p-BPDSY passes through the origin and the hydroquinone inhibits the polymerization reaction at $3.03 \times 10^{-3}$ mol L⁻¹ (Table 2). Besides, the value of $k_p^2/k_i$, calculated from the slope of the plot between $1/\bar{M}_n$ and $R_p/(M)^n$ is $18 \times 10^{-2}$ L mol⁻¹ s⁻¹, which matches well with those reported in literature.


Table 3—Effect of the concentration of p-BPDSY on the polymerization of methyl acrylate initiated by p-BPDSY at 80 ± 1°C

<table>
<thead>
<tr>
<th>[p-BPDSY] × 10^3, mol L⁻¹</th>
<th>Conversion, %</th>
<th>R_p × 10^5, mol L⁻¹ s⁻¹</th>
<th>$\overline{M_n}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.01</td>
<td>21.12</td>
<td>20.30</td>
<td>24340</td>
</tr>
<tr>
<td>1.24</td>
<td>20.92</td>
<td>20.92</td>
<td>22330</td>
</tr>
<tr>
<td>1.39</td>
<td>22.39</td>
<td>22.39</td>
<td>19330</td>
</tr>
<tr>
<td>1.55</td>
<td>23.24</td>
<td>23.20</td>
<td>18540</td>
</tr>
<tr>
<td>3.10</td>
<td>15.36</td>
<td>14.50</td>
<td>—</td>
</tr>
<tr>
<td>4.66</td>
<td>10.10</td>
<td>9.66</td>
<td>16820</td>
</tr>
<tr>
<td>6.21</td>
<td>4.20</td>
<td>4.35</td>
<td>16100</td>
</tr>
<tr>
<td>7.77</td>
<td>2.18</td>
<td>2.02</td>
<td>14680</td>
</tr>
<tr>
<td>9.32</td>
<td>2.07</td>
<td>1.93</td>
<td>—</td>
</tr>
<tr>
<td>12.43</td>
<td>1.55</td>
<td>1.45</td>
<td>—</td>
</tr>
</tbody>
</table>

*Polymerization condition: [MA] = 3.48 mol L⁻¹; Time = 60 min.

However, when kinetic studies were extended at higher [ylide] from $3.1 \times 10^{-3}$ to $12.43 \times 10^{-3}$ mol L⁻¹, $R_p$ is an inverse function of [ylide]. This might be due to mutual anihilation of initiator radicals formed beyond $1.55 \times 10^{-3}$ mol L⁻¹ of [ylide]. The order of reaction was calculated to be 1.6, which shows that the system follows non-ideal kinetics. Table 3 also reveals that $\overline{M_n}$ of the polymers decreases as [ylide] increases. The non-ideality is further confirmed by the fact that the plot of $1/\overline{M_n}$ vs (p-BPDSY) (beyond $1.55 \times 10^{-3}$ mol L⁻¹) does not pass through the origin and some additional mode of termination is operating with usual bimolecular termination.

The additional initiator dependent termination process may be of two kinds as shown below:

(A) Primary radical termination:

$$MA' + H^+ \xrightarrow{k_{pr}} \text{polymer}$$

(B) Termination via degradative transfer, either

(i) With reinitiation:

$$MA' + p\text{-BPDSY} \xrightarrow{k_{ty}} \text{Polymer} + p\text{-BPDSY}$$ (initiator transfer)

$$MA' + p\text{-BPDSY} \xrightarrow{k_{ty}} \text{Polymer}$$ (chain termination)

$$MA + p\text{-BPDSY} \xrightarrow{k_{ty}} MA'$$ (reinitiation)

or
(ii) With little reinitiation:

\[
\text{MA} + p\text{-BPDSY} \xrightarrow{k_p} \text{polymer}
\]

(chain termination) + non-radical or inactive radical byproduct

The equation developed by Deb and Meyerhoff\(^8\) was used to analyse the possibility of additional modes of termination in the following manner:

**Primary radical termination:**

\[
\log_{10} \left( \frac{R_p^2}{(Y)(M)^2} \right) = \log_{10} \left( \frac{k_i \cdot k_d \cdot R_p^2}{k_t} \right) - 0.8684 \frac{k_{pr t} \cdot R_p}{k_i \cdot k_p (M)^2}
\]

\([k_t, k_d, k_p, \text{and} k_i \text{part are rate constant of initiation, initiator decomposition, propagation and termination, respectively, and} Y \text{is the initiator}].\)

The plot of the left hand side of the above equation vs \(R_p/(M)^2\) gave a positive slope, indicating the absence of primary radical termination for the present system.

**Degradative initiation transfer with reinitiation effect**—The equation derived by Deb\(^9\) was used to study the degradative initiator transfer with reinitiation:

\[
\ln \left( \frac{R_p^2}{(Y)(M)^2} \right) = \ln \left( \frac{k_{\text{pr t}} k_p^2}{k_t} \right) - \frac{k_{\text{pr t}} k_{\text{py}}}{k_t} C_y (M)
\]

where \(C_y\) is the initiator transfer constant. The plot of the left hand side of the above equation vs \((Y)(M)\) (Fig. 4) gives a negative slope indicating degradative initiator transfer with reinitiation. The value of \((k_{\text{py}})/(k_{\text{py}} - k_p) \times C_y\) determined from the slope, is \(8.62 \times 10^{-1} \text{ L.s.mol}^{-1}\).

**Degradative initiation transfer with little reinitiation**—This was treated in the following manner:

**Initiation:**

\[
p\text{-BPDSY} \xrightarrow{k_d} \text{H}
\]

\[
\text{MA} + \text{H} \xrightarrow{k_i} \text{MA}_i
\]

**Propagation:**

\[
\text{MA} + n\text{MA} \xrightarrow{k_p} \text{MA}^{(n+1)}
\]

**Termination:**

1. bimolecular \(\text{MA}^+ + \text{MA}^+ \xrightarrow{k_t} \text{polymer}\)

2. by initiator \(\text{MA}^+ + p\text{-BPDSY} \xrightarrow{k_t} \text{polymer}\)

The rates of initiation \((R_i)\), propagation \((R_p)\) and termination \((R_t\) and \(R'_t\)) are given by:

\[
R_i = k_d \times k_i [\text{MA}] [p\text{-BPDSY}]
\]

\[
R_p = k_p [\text{MA}] [\text{MA}^+]
\]

\[
R_t = 2 k'_i [\text{MA}]^2
\]

\[
R'_t = k'_i [\text{MA}][p\text{-BPDSY}]
\]

Assuming steady state conditions:

\[
\frac{R_i}{R_p} = \frac{R_i + R'_t}{R_p} = 2 \cdot k_i [\text{MA}]^2 + k'_i [\text{MA}][p\text{-BPDSY}]
\]

\[
\frac{R_i}{R_p} = \frac{2 \cdot k_i R_p^2}{k_p^2 [\text{MA}]^2} + \frac{k_i R_p [p\text{-BPDSY}]}{k_p [\text{MA}]} R_p
\]

\[
R_i = \frac{2 \cdot k_i R_p^2}{k_p^2 [\text{MA}]^2} + \frac{k_i [p\text{-BPDSY}]}{k_p [\text{MA}]} R_p
\]

The plot of the left hand side of the above equation vs \(R_p/[\text{MA}]^2\) gives a positive slope, \(k'_i/k_p > 0\) \((k'_i) > 0\) which, therefore, excludes the possibility of the above aspect.

**ESR spectrum**—The radical mode of polymerization of the present system is confirmed by the ESR spectrum which shows a characteristic free radical absorption signal at 3,350 gauss. The gyromagnetic ratio \((g)\) is calculated to be \(2.03^{10}\), which confirms the radical mode of polymerization.
NMR spectrum—The NMR spectrum of PMA shows singlet at 3.60 which is due to the ester methoxy group and the methine proton appears at 2.35. The methylene protons appear as triplet at 1.63, 1.88 and 2.15.

It has already been reported\(^\text{11}\) that ylides, in general dissociate to form triplet carbene which combines with acrylates to form diradical and ultimately H'. Although formation of diradical is hypothetical of H' has been confirmed by the ESR spectrum of the system. The H' is responsible for bringing out polymerization. The various steps may be outlined below:

References