Photopolymerization, which uses light energy (photons) to initiate chain reactions to form polymer materials, is the basis for a growing, billion-dollar industry. Light induced polymerization is considered one of the most efficient techniques for rapidly producing polymeric materials with well-defined characteristics. Photopolymerization is often the method of choice for rapid, assembly style, throughput polymerizations.

The results of photopolymerization of vinyl monomers viz. MMA, BA, AN and Sty to prepare homopolymers (Poly-MMA, Poly-Sty, Poly-BA) and copolymers (Poly-(Sty-co-MMA), Poly-(BA-co-MMA), Poly-(Sty-co-BA), Poly-(Sty-co-AN)) have been reported in this chapter. Two new photoinitiators, BrPy and APAS derived from Pyrene have been introduced.

Pyrene, an aromatic hydrocarbon dye, has been reported as photosensitizer in polymerization reactions [Crivello and Lam, 1979 (b); Crivello and Jiang, 2002]. Although it has also been reported as a weak initiator for photopolymerization of vinyl monomers [Capek and Barton, 1979], but it works as better initiator in presence of aliphatic amines and Lewis acids [Encinas et al, 1989; Encinas et al, 1991].
Introduction of chromophoric groups (-COCH3 and phenyl) in pyrene is expected to enhance its efficiency. Moreover, heavy atoms like Br and Cl are also known to cause a significant rise in the photoinitiation ability of the dyes [Pyszka et al, 2003]. Considering these facts into account, the outline of the present work has been framed.

First initiator, BrPy has one additional group as –COCH2Br in Pyrene while second initiator has been prepared by modifying BrPy to its triphenyl arsonium salt.

Following subchapters include the discussion based on the results obtained for the homo and copolymerization of MMA, BA, AN and Sty using the above mentioned new photoinitiators.
4.1 Synthesis, characterization and mode of action of 1-Acetylpyrene triphenylarsonium bromide and 1-(Bromoacetyl)pyrene

4.1.1 Synthesis of 1-Acetylpyrene triphenylarsonium bromide (APAS) from 1-(Bromoacetyl)pyrene

It was prepared by the method of Gosney and Lloyd [Gosney and Lloyd, 1973]. A solution of triphenylarsine (0.5g, 1.63 mmol) and 1-(bromoacetyl)pyrene (0.52g, 1.63 mmol) in benzene was heated under reflux for 10 h. The solid obtained was recrystallized from ethanol-ether to afford 1-Acetylpyrene triphenylarsonium bromide as dark orange colored crystals.
Yield = 75-78 %
m.p. = 102-104°C.
4.1.2. Characterization of APAS

U.V. Spectroscopy
The spectrum of BrPy (3.093 $\times$ 10$^{-5}$ mol/l, DCM) showed $\lambda_{\text{max}}$ at 288 and 366 nm (Fig 4.1.2 (i)) while the spectrum recorded for APAS under identical conditions showed $\lambda_{\text{max}}$ at 278 and 348 nm (Fig 4.1.2 (ii)).

FTIR Spectroscopy
The FTIR spectrum (Figure 4.1.2 (iii)) of BrPy consisted of the following group of bands- C-H str vibrations of methylene group in the region 3000 cm$^{-1}$; $>\text{C}=\text{O}$ str vibrations at 1653 cm$^{-1}$; C-O str bands in the region of 1130-1260 cm$^{-1}$; C=C str bands near 1600 cm$^{-1}$; C-Br str bands in the region 500-600 cm$^{-1}$.

The spectrum of APAS (Fig 4.1.2 (iv)) retained almost all the above bands but the absence of any characteristic peaks in 475 - 600 cm$^{-1}$ region strongly suggests the cleavage of covalent C-Br linkage.

$^1$H NMR Spectroscopy
The spectrum of BrPy (Fig 4.1.2 (v)) gave characteristic peaks at 7.5 - 9.3 $\delta$ due to aromatic H and a peak at 4.5 $\delta$ due to $-\text{CH}_2\text{Br}$ protons. These protons appeared quite upfield i.e. at 2.8 $\delta$ in APAS spectrum (Fig 4.1.2 (vi)) confirming that the electron-withdrawing Br was no more covalently bonded. The aromatic peaks in the spectrum of APAS appeared at almost the same position i.e. between 7.4 - 9 $\delta$. 
E.S.R. Spectroscopy

The spectrum (Fig 4.1.2 (vii)) of BrPy in DMSO (in absence of monomers) by quenching the radicals in liquid nitrogen showed characteristic free radical absorption at 3370 G. Spectrum showed a sharp peak with a ‘g’ value 2.00 which might be conveniently assigned to the Py-CO-CH₂⁻ (A) radical formed by the homolytic cleavage of BrPy. The radical A as given in the scheme 4.1.2 (i) would result into a triplet due to 2 protons, however already simple quantum chemical calculation shows that the spin is delocalized over the whole molecule which is inline with the observed singlet. Remaining peaks may be assigned to the Br⁻ radical formed at the same time assuming that a few peaks have been overlapped by the peak due to radical A. The appearance of these peaks suggests a free radical mechanism for the polymerization.

The spectrum of APAS in DMSO (Figure 4.1.2 (viii)) showed a number of peaks in addition to a sharp peak again at 2.00 ‘g’, which may quite probably be due to triphenyl arsonium cation radical (B). Recent studies on flash photolysis of dialkylphenacyl sulphonium salts [Kawamura et al, 2004] report the formation of phenacyl radicals formed as a result of cleavage of C-S bond. Based on the structural similarity of these salts with APAS, it is proposed that this photoinitiator, APAS, also initiates polymerization free radically by dissociating into radical A and B as depicted in Scheme 4.1.2 (ii).
Result and Discussion

Scheme 4.1.2 (i)

\[ \text{BrPy} \quad \text{hv} \quad \text{Radical A} \]

\[ \text{BrPy} + \text{As} \cdot (\text{Ph})_3 \quad \text{hv} \quad \text{ Radical A} + \text{As} \cdot (\text{Ph})_3 \text{ Br}^\cdot \]

(Radical B)

APAS

Scheme 4.1.2 (ii)
Fig 4.1.2 (i) UV Spectrum of BrPy

Fig 4.1.2 (ii) UV Spectrum of APAS
Fig. 4.1.2 (iii) IR Spectrum of BrPy
Fig 4.1.2 (iv) IR Spectrum of APAS
Fig 4.1.2 (v) $^1$H NMR Spectrum of BrPy

Fig 4.1.2(vi) $^1$H NMR Spectrum of APAS
Fig 4.1.2 (vii) ESR Spectrum of BrPy
Fig 4.1.2 (viii) ESR Spectrum of APAS
Chapter 4

4.2 1-(Bromoacetyl)pyrene as novel photoinitiator for styrene polymerization

The kinetics and mechanism of photopolymerization of Sty in DMSO induced by BrPy (BrPy-Sty system) has been investigated. The results of kinetic investigations of the photopolymerization of Sty at 30°C using varying BrPy concentrations at fixed intensity of light source are presented in Table 4.2 (i). The polymerization time chosen was 4 h in order to limit conversions to low percentage to study kinetics. Since Sty was polymerized to 0.2-0.4% conversions in absence of initiator, the data in Table 4.2 (i) & (ii) present % conversion after having deducted the yield for blank experiments.

The initiator exponent value calculated from the slope of the plot of log \( R_p \) vs. log [BrPy] (Fig 4.2 (i)) was 0.8. The deviation in the exponent value of BrPy and an intercept in the plot of \( 1/\overline{P_n} \) Vs. \( R_p/ [Sty]^2 \) (Fig 4.2 (ii)) suggested that BrPy-Sty system followed non-ideal kinetics. In order to explain this unusual behavior and to ascertain the nature of the transfer reactions involved, plots of \( R_p^2/([\text{BrPy}][\text{Sty}]^2) \) vs. \( R_p/\text{[Sty]}^2 \) (Fig 4.2 (iii)) following the equation of Deb [Deb, 1975] were plotted. The positive slope obtained suggested that degradative solvent transfer is mostly operative in the main termination process instead of degradative initiator transfer or primary radical termination [Sengupta, 1982].
The data obtained to see the effect of monomer concentration on $R_p$ are shown in Table 4.2 (ii). The monomer exponent value, calculated from the slope of the linear plot of $\log R_p$ versus $\log [\text{Sty}]$ was 1.1 (Fig 4.2 (iv)) suggesting that the system follows ideal kinetics with respect to monomer concentration.
<table>
<thead>
<tr>
<th>S. No.</th>
<th>[BrPy] × 10^4 (mol/l)</th>
<th>% Conversion</th>
<th>R_p × 10^5 (mol/l/s)</th>
<th>_Pn</th>
<th>η</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.386</td>
<td>0.92</td>
<td>0.557</td>
<td>384</td>
<td>.33</td>
</tr>
<tr>
<td>2.</td>
<td>0.773</td>
<td>1.73</td>
<td>1.049</td>
<td>322.5</td>
<td>.30</td>
</tr>
<tr>
<td>3.</td>
<td>1.547</td>
<td>2.95</td>
<td>1.782</td>
<td>270</td>
<td>.26</td>
</tr>
<tr>
<td>4.</td>
<td>2.320</td>
<td>3.84</td>
<td>2.322</td>
<td>244</td>
<td>.24</td>
</tr>
<tr>
<td>5.</td>
<td>3.094</td>
<td>4.80</td>
<td>2.904</td>
<td>219.7</td>
<td>.22</td>
</tr>
<tr>
<td>6.</td>
<td>3.860</td>
<td>6.29</td>
<td>3.802</td>
<td>189.3</td>
<td>.20</td>
</tr>
</tbody>
</table>

Table 4.2 (i) Effect of [BrPy] on R_p. [Sty] = 2.18 mol/l; t = 4h; polymn. temp. = 30 ± 0.2°C.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>[Sty] (mol/l)</th>
<th>% Conversion</th>
<th>R_p × 10^5 (mol/l/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>2.18</td>
<td>1.73</td>
<td>1.049</td>
</tr>
<tr>
<td>2.</td>
<td>2.91</td>
<td>2.39</td>
<td>1.445</td>
</tr>
<tr>
<td>3.</td>
<td>3.49</td>
<td>2.93</td>
<td>1.770</td>
</tr>
<tr>
<td>4.</td>
<td>3.97</td>
<td>3.38</td>
<td>2.041</td>
</tr>
<tr>
<td>5.</td>
<td>4.37</td>
<td>3.74</td>
<td>2.264</td>
</tr>
</tbody>
</table>

Table 4.2 (ii) Effect of [Sty] on R_p. [BrPy] = 7.735 × 10^-5 mol/l; t = 4h; polymn. temp. = 30 ± 0.2°C.
**Result and Discussion**

Fig 4.2 (i) Plot of $\log [\text{BrPy}]$ vs. $\log R_p$. $t = 4h$; $[\text{Sty}] = 2.18 \text{ mol/l}$; polymn. temp. = $30 \pm 0.2 \degree C$.

Fig 4.2 (ii) Plot of $1/P_n$ vs. $R_p/[\text{Sty}]^2$. $[\text{Sty}] = 2.18 \text{ mol/l}$; $t = 4h$; polymn. temp. = $30 \pm 0.2 \degree C$. 
Fig 4.2 (iii) Plot of $R_p^2/[\text{Sty}]^2[\text{BrPy}]$ vs. $R_p/[\text{Sty}]^2$.

$[\text{Sty}] = 2.18 \text{ mol/l}; \ t = 4h; \ \text{polymn. temp.} = 30 \pm 0.2 ^\circ \text{C}$.

Fig 4.2 (iv) Plot of $\log [\text{Sty}]$ vs. $\log R_p$.

$[\text{BrPy}] = 7.735 \times 10^{-5} \text{ mol/l}; \ \text{polymn. temp.} = 30 \pm 0.2 ^\circ \text{C}$.
Characterization of polymer

FTIR Spectroscopy

The FTIR spectrum (Fig 4.2 (v)) of polystyrene showed the band at 3010 cm\(^{-1}\) due to C-H stretching of the phenyl group of styrene, 2920 and 2850 cm\(^{-1}\) due to C-H stretching of methine and methylene protons, 1600 cm\(^{-1}\) due to conjugated C=C stretching, 1448 and 1490 cm\(^{-1}\) due to C-H deformations.

![Fig 4.2 (v) IR Spectrum of polystyrene](image)
\textbf{1H-NMR Spectroscopy}

In the \textsuperscript{1}H-NMR spectrum (Fig 4.2 (vi)), the peaks due to the phenyl protons appeared between 6.5-7.1 $\delta$. Both, the methylene and methine protons appeared as broad peak at 1.43 $\delta$ and 1.83 $\delta$, respectively indicating atactic nature of the polymer. The atactic polymer exhibits seemingly poorly resolved multiplets but have a syndiotactic preference, supporting free radical mechanism of polymerization [Allen, 1989, 356].

\begin{center}
\textbf{Fig 4.2 (vi) 1H-NMR spectrum of polystyrene}
\end{center}
\textbf{\textsuperscript{13}C-NMR Spectroscopy}

The spectrum (Fig 4.2 (vii)) showed a series of peak between 125-127 ppm owing to the unsaturated carbons of phenyl rings [Silverstein, 2001]. The methylene and methine carbons resonate at 30 and 40 ppm respectively. A band of resonances between 145-146 ppm is strong evidence in support of the atacticity of the polymer [Allen, 1989, 356]. These bands of resonances are consistent with a syndiotactic bias in free radical propagations. The syndiotactic bias characterizes the free radical polymerization of all vinyl monomers.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{c-nmr_spectrum.png}
\caption{\textsuperscript{13}C-NMR Spectrum of polystyrene}
\end{figure}
Mechanism

The inhibition to polymerization in the presence of a small quantity of hydroquinone, ESR studies and the kinetics suggest a radical mechanism for BrPy-Sty system. ESR studies suggest the formation of Radical A (Scheme 4.2 (i)) and Br on photo cleavage of BrPy, both of which have the possibility of initiating polymerization. On the basis of the above facts, a proposed mechanism is as given in Scheme 4.2 (i).

Initiation

\[
\text{BrPy} \rightarrow \text{Py-CO-CH}_2^- + \text{Br}^- \quad (\text{Radical A})
\]

\[
\text{Br Or Radical A} + \text{Ph} \rightarrow \text{Br-CH}_2^- + \text{A-CH}_2^- \quad \text{Or}
\]

Scheme 4.2(i)

Conclusions

The photopolymerization of styrene with BrPy followed non-ideal kinetics (\(R_p \propto [\text{BrPy}]^{0.8} [\text{Sty}]^{1.1}\)) with respect to initiator concentration. Degradative transfer was thought to be mainly responsible for this unusual kinetic behavior for BrPy-Sty system. The mechanism of polymerization was free radical as evident by inhibiting effect of hydroquinone and ESR studies. IR and NMR spectra showed the atactic nature of polystyrene.

This part of the thesis has been accepted in "Journal of Applied Polymer Science"
4.3 Polymerization of Styrene using 1-Acetylpyrene triphenyl arsionium bromide as Photoinitiator

The arsionium salt of 1-(Bromoacetyl)pyrene is reported as novel free radical photoinitiator for styrene polymerization. The kinetics and mechanism of photopolymerization of Sty in DMSO induced by APAS (APAS-Sty system) has been investigated. All conversions were limited to < 10% to study kinetics. Since Sty alone was polymerized to 0.2-0.4% conversions in absence of initiator, the data in Table 4.3 (i) & (ii) present % conversion after having deducted the yield for blank experiments.

The effect of [APAS] on $R_p$ has been studied by varying its concentration from $0.39 \times 10^{-4}$ mol/l to $1.98 \times 10^{-4}$ mol/l, keeping [Sty] constant at 2.18 mol/l (Table 4.3 (i)). The initiator exponent value calculated from the slope of the plot of log $R_p$ vs. log [APAS] (Fig 4.3 (i)) was 0.48. The plot of reciprocal average degree of polymerization ($\bar{P}_n$) against the square root of the initiator concentration (Fig 4.3 (ii)) gave a straight line passing through the origin, suggesting ideal radical polymerization with bimolecular termination. The value of $k_p^2 / k_t$ obtained from the plot of $1/\bar{P}_n$ Vs. $R_p/ [Sty]^2$ (Fig 4.3 (iii)) was found to be $0.24 \times 10^{-2}$ 1 mol$^{-1}$ s$^{-1}$.

The data obtained to see the effect of monomer concentration on $R_p$ are shown in Table 4.3 (ii). The monomer exponent value, calculated from the slope of the linear plot of log $R_p$ versus log [Sty] was 1.1 (Fig 4.3 (iv))
suggested that the system APAS-Sty followed ideal kinetics with respect to monomer concentration as well.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>[APAS] x 10^4 (mol/l)</th>
<th>% Conversion</th>
<th>Rp x 10^5 (mol/l/s)</th>
<th>( \bar{P}_n )</th>
<th>( \eta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.397</td>
<td>3.27</td>
<td>1.321</td>
<td>909.1</td>
<td>.62</td>
</tr>
<tr>
<td>2.</td>
<td>0.794</td>
<td>4.52</td>
<td>1.823</td>
<td>657.9</td>
<td>.49</td>
</tr>
<tr>
<td>3.</td>
<td>1.190</td>
<td>5.54</td>
<td>2.233</td>
<td>540.5</td>
<td>.42</td>
</tr>
<tr>
<td>4.</td>
<td>1.580</td>
<td>6.31</td>
<td>2.546</td>
<td>467.2</td>
<td>.39</td>
</tr>
<tr>
<td>5.</td>
<td>1.980</td>
<td>7.08</td>
<td>2.857</td>
<td>416.6</td>
<td>.35</td>
</tr>
</tbody>
</table>

Table 4.3 (i) Effect of [APAS] on Rp. [Sty] = 2.18 mol/l; t = 4h; polymn. temp. = 30 ± 0.2 °C.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>[Sty] (mol/l)</th>
<th>% Conversion</th>
<th>Rp x 10^5 (mol/l/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>2.18</td>
<td>3.27</td>
<td>1.321</td>
</tr>
<tr>
<td>2.</td>
<td>2.91</td>
<td>4.53</td>
<td>1.828</td>
</tr>
<tr>
<td>3.</td>
<td>3.49</td>
<td>5.60</td>
<td>2.259</td>
</tr>
<tr>
<td>4.</td>
<td>3.97</td>
<td>9.83</td>
<td>3.962</td>
</tr>
<tr>
<td>5.</td>
<td>4.37</td>
<td>10.83</td>
<td>4.365</td>
</tr>
</tbody>
</table>

Table 4.3 (ii) Effect of [Sty] on Rp. [APAS] = 3.97 x 10^{-5} mol/l; t = 6h; polymn. temp. = 30 ± 0.2 °C.
Fig 4.3 (i) Plot of log [APAS] vs. log $R_p$; $t = 6h$; [Sty] = 2.18 mol/l; polymn. temp. = 30 ± 0.2 °C.

Fig 4.3 (ii) Plot of $1 / \bar{P}_n$ vs. [APAS]$^{0.5}$. [Sty] = 2.18 mol/l; $t = 6h$; polymn. temp. = 30 ± 0.2 °C.
Fig 4.3 (iii) Plot of $1/P_n$ vs. $R_p/[\text{Sty}]^2$. $[\text{Sty}] = 2.18$ mol/l; $t = 6$ h; polymn. temp. = $30 \pm 0.2$°C.

Fig 4.3 (iv) Plot of log $[\text{Sty}]$ vs. log $R_p$. $[\text{APAS}] = 3.97 \times 10^{-5}$ mol/l; $t = 6$; polymn. temp. = $30 \pm 0.2$°C.
Characterization of polymer

FTIR Spectroscopy

The FTIR spectrum (Fig 4.3 (v)) of polystyrene showed bands in proximity of 3000 cm\(^{-1}\) due to C-H stretching of the phenyl group of styrene, 2923 and 2850 cm\(^{-1}\) due to C-H stretching of methine and methylene protons, 1600 cm\(^{-1}\) due to conjugated C=C stretching, 1449 cm\(^{-1}\) due to C-H deformations.

Fig 4.3 (v) IR Spectrum of polystyrene
\textbf{\textsuperscript{1}H-NMR Spectroscopy}

In the \textsuperscript{1}H-NMR spectrum (Fig 4.2 (vi)), the peaks due to the phenyl protons appeared between 6.5-7.1 $\delta$. Both the methylene and methine protons, at 1.4 $\delta$ and 1.83 $\delta$ respectively, appeared as broad peak indicating atactic nature of the polymer.

To compare the photoinitiating ability of APAS with BrPy, two sets of polymerization were carried out. It was observed that in case of APAS-Sty system, the percent conversion was 3.27\% at $0.39 \times 10^{-4}$ mol l$^{-1}$ in 6 hours while BrPy-Sty system under similar conditions gave 6.4\% conversion. The polymer obtained with these photoinitiators was essentially the same as evident through IR and NMR characterization.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig4.3_vii_hnmr_spectroscopy_of_polystyrene}
\caption{\textsuperscript{1}H-NMR spectrum of polystyrene}
\end{figure}
Mechanism
The inhibition to polymerization in the presence of a small quantity of hydroquinone and the kinetics suggest a radical mechanism for APAS-Sty system. The possible radicals generated by this photoinitiator are radical A and B (Scheme 4.3 (i)) as evident by ESR studies. On the basis of these observations, arsonium salt (APAS) may be satisfactorily cleaved homolytically into the above-mentioned radicals. Also, the cation radical (B) formed is probably too reactive to participate in polymerization. Hence, only radical A might be involved in polymerization for the APAS-Sty system. This also justifies the greater polymerization efficiency of BrPy, since both radical A and Br radical propagate in that case. A proposed mechanism is as given in Scheme 4.3 (i).

Initiation

\[
\begin{align*}
\text{Initiation} & \\
\text{APAS} & \rightarrow \text{Py-CO-CH}_2^- + \text{As (Ph}_3\text{)Br} \\
H_2C=CH & \\
\text{Radical A} & + \\
\text{Radical A} & \rightarrow \text{A-CH}_2\text{-CH}_2^- + \text{Ph}
\end{align*}
\]

Scheme 4.3 (i)
Conclusions

The APAS induced photopolymerization of Sty followed ideal kinetics \( (R_p \propto [\text{APAS}]^{0.48} [\text{Sty}]^{1.1}) \). The mechanism of polymerization was free radical as evident by inhibiting effect of hydroquinone, kinetic data and ESR studies. IR and NMR spectra showed the atactic nature of polystyrene. The kinetic data proved that BrPy was more effective and faster initiator than APAS.

This part of the thesis has been accepted in "Journal of Applied Polymer Science"
4.4 Methylmethacrylate Polymerization Photoinitiated by 1-(Bromoacetyl)pyrene

The free radical polymerization of MMA is the predominant industrial mechanism to produce PMMA. Solution polymerizations of MMA are used commercially to produce adhesives, paint resins, and additives [Kine and Novak, 1985; Stickler and Rhein, 1992]. The solution photopolymerization of MMA induced by BrPy in DMSO (BrPy-MMA) has been investigated in detail.

The effect of [BrPy] on $R_p$ has been studied by varying [BrPy] from $1.54 \times 10^{-4}$ mol/l to $6.18 \times 10^{-4}$ mol/l, keeping [MMA] constant at 2.35 mol/l (Table 4.4 (i)). The $R_p$ increased with increasing concentration of BrPy. The initiator exponent calculated from the slope of the plot of log $R_p$ vs. log [BrPy] was 0.5 (Fig 4.4 (i)). The value of the initiator exponent and the observation that the plot of reciprocal average degree of polymerization ($\bar{P}_n$) against the square root of the initiator concentration gave a straight line passing through the origin (Fig 4.4 (ii)), suggesting radical polymerization with bimolecular termination. The dependence of average molecular weight of polymer upon [BrPy] is as expected for radical polymerization.

The effect of monomer concentration on $R_p$ is studied by varying [MMA] from 2.35 mol/l to 5.87 mol/l, keeping [BrPy] constant at $1.54 \times 10^{-4}$ mol/l. The respective data are shown in Table 4.4 (ii). The monomer exponent value, calculated from the slope of the linear plot of log $R_p$ versus log
[MMA] was 0.98 (Fig 4.4 (iii)) suggesting that the system follows ideal kinetics.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>[BrPy] (\times 10^4) (mol/l)</th>
<th>% Conversion</th>
<th>(R_p \times 10^5) (mol/l/s)</th>
<th>(\frac{1}{P_n})</th>
<th>(\eta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>1.54</td>
<td>4.81</td>
<td>2.403</td>
<td>781</td>
<td>.40</td>
</tr>
<tr>
<td>2.</td>
<td>2.32</td>
<td>5.77</td>
<td>2.880</td>
<td>609</td>
<td>.32</td>
</tr>
<tr>
<td>3.</td>
<td>3.09</td>
<td>6.80</td>
<td>3.396</td>
<td>537</td>
<td>.28</td>
</tr>
<tr>
<td>4.</td>
<td>4.64</td>
<td>8.31</td>
<td>4.146</td>
<td>431</td>
<td>.24</td>
</tr>
<tr>
<td>5.</td>
<td>6.18</td>
<td>9.59</td>
<td>4.780</td>
<td>386</td>
<td>.21</td>
</tr>
</tbody>
</table>

Table 4.4 (i) Effect of [BrPy] on \(R_p\). [MMA] = 2.35 mol/l; \(t = 5\)h; polymn. temp. = 30 ± 0.2 °C.

| Sample no. | [MMA] (mol/l) | % Conversion | \(R_p \times 10^5\) (mol/l/s) |
|------------|--------------|-------------|----------------|------|
| 1.         | 2.35         | 4.81        | 2.403          |
| 2.         | 3.52         | 7.11        | 3.548          |
| 3.         | 4.7          | 9.15        | 4.56           |
| 4.         | 5.87         | 12.07       | 6.02           |

Table 4.4 (ii) Effect of [MMA] on \(R_p\). [BrPy]= 1.54 \(\times 10^{-4}\) mol/l; \(t = 5\)h; polymn. temp. = 30 ± 0.2 °C.
Result and Discussion

Fig 4.4 (i) Plot between log [BrPy] vs. log \( R_p \). [MMA] = 2.35 mol/l; 
\( t = 5\)h; polymn. temp. = 30 ± 0.2 °C.

Fig 4.4 (ii) Plot of log [MMA] vs. log \( R_p \). [BrPy] = 1.54 \times 10^{-4} \text{ mol/l}; 
\( t = 5\)h; polymn. temp. = 30 ± 0.2 °C.
Fig 4.4 (iii) Plot of $1/P_n$ vs $[\text{BrPy}]^{0.5}$, $[\text{MMA}]=2.35$ mol/l; $t=5$ h; polymn. temp.$=30 \pm 0.2$ °C.
Characterization of polymer

FTIR Spectroscopy

The FTIR spectrum (Fig 4.4 (iv)) of polymer consisted of the following group of bands- C-H str vibrations of methyl and methylene group at 2951 and 2843 cm\(^{-1}\) respectively; >C=O str vibrations of ester carbonyl at 1731 cm\(^{-1}\); the C-H deformation bands in the region of 1387-1480 cm\(^{-1}\); C-O str bands in the region of 1150-1250 cm\(^{-1}\); characteristic band at 1060, 988, 482 cm\(^{-1}\) are supportive of the atactic nature of the polymer [Hummel, 1966].

![Fig 4.4 (iv) FTIR Spectrum of Polymer](image)
**1H-NMR Spectroscopy**

In the 1H-NMR spectrum (Fig 4.4 (v)), a singlet due to methoxy protons, appeared at 3.6δ. Methyl protons appeared in the region between 0.9-1.02 and methylene protons between 1.62-1.81δ. The methylene protons appear as singlet at 1.83 in syndiotactic PMMA whereas a doublet at 1.62 and 2.33 is observed in isotactic PMMA. In this case neither of these characteristic peaks [Stevens, 1975] were observed, therefore, it was concluded that an atactic PMMA was formed by BrPy-MMA system.

**13C-NMR Spectroscopy**

The spectrum (Fig 4.4 (vi)) showed a series of peaks between 176-178 ppm owing to the ester carbon [Silverstein, 2001], further confirming the atactic nature of polymer. The methoxy carbon appeared at 51 ppm while the peaks at 44 and 16-18 ppm are attributed to methylene and methyl carbons.

**Mechanism**

The inhibition to polymerization in the presence of a small quantity of hydroquinone and kinetics suggest a radical mechanism for BrPy-MMA system. ESR studies suggest the formation of Radical A and Br' (Scheme 4.4 (i)) on photo cleavage of BrPy, both of which have the possibility of initiating polymerization. On the basis of the above facts, a proposed mechanism is as given in Scheme 4.4 (i).
Fig 4.4 (v) $^1$H-NMR Spectrum of Polymer

Fig 4.4 (vi) $^{13}$C-NMR Spectrum of Polymer
Initiation

\[
\begin{align*}
\text{BrPy} & \quad \rightarrow \quad \text{Py-CO-CH}_2^+ + \text{Br}^- \\
\text{(Radical A)}
\end{align*}
\]

\[
\begin{align*}
\text{Br} \quad \text{Or Radical A} & \quad + \\
\end{align*}
\]

\[
\begin{align*}
\text{Br-CH}_2^- \text{C}^+ & \quad \rightarrow \quad \text{A-CH}_2^- \text{C}^+ \\
\text{CO}_2\text{CH}_3 & \quad \text{Or} \\
\text{CO}_2\text{CH}_3
\end{align*}
\]

Scheme 4.4 (i)

Conclusions

A detailed polymerization kinetics and mechanism with 1-(Bromoacetyl)pyrene as photoinitiator suggest a free radical approach for the synthesis of PMMA. The polymerization followed ideal kinetics with respect to both monomer and initiator. IR and NMR spectra showed the atactic nature of polymethylmethacrylate.

This part of the thesis has been published in "Journal of Applied Polymer Science (2006) 99(3), 920-926"
4.5 Polymerization of MMA using 1-Acetylp yrene triphenyl arsonium bromide as Photoinitiator

This sub-chapter discusses the kinetics and mechanism of APAS initiated photopolymerization of MMA (APAS-MMA). All polymerization were limited to low conversions in order to study kinetics. No polymerization was observed in absence of initiator.

The effect of [APAS] on $R_p$ has been studied by varying [BrPy] from $0.39 \times 10^{-4}$ mol/l to $1.98 \times 10^{-4}$ mol/l, keeping [MMA] constant at $2.35$ mol/l (Table 4.5 (i)). $R_p$ increased with increasing concentration of APAS. The initiator exponent calculated from the slope of the plot of log $R_p$ vs. log [APAS] was 0.49 (Fig 4.5 (i)), which suggests ideal kinetics with respect to initiator. The observation that the plot of reciprocal average degree of polymerization ($\bar{P_n}$) against the square root of the initiator concentration gave a straight line passing through the origin (Fig 4.5 (ii)), suggests radical polymerization with bimolecular termination. The average molecular weight of Poly-MMA (PMMA) decreased with increase in [APAS], as expected for radical polymerization.

The effect of monomer concentration on $R_p$ is studied by varying [MMA] from $1.17$ mol/l to $4.7$ mol/l, keeping [APAS] constant at $0.79 \times 10^{-4}$ mol/l. The respective data are shown in Table 4.5 (ii). The monomer exponent value, calculated from the slope of the linear plot of log $R_p$ versus log
[MMA] was 0.98 (Fig 4.5 (iii)) suggesting that the system follows ideal kinetics with respect to monomer as well.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>[APAS] $\times 10^4$ (mol/l)</th>
<th>% Conversion</th>
<th>$R_p \times 10^5$ (mol/l/s)</th>
<th>$\bar{P}_n$</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
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<td>2.4</td>
<td>1.197</td>
<td>884.9</td>
<td>.45</td>
</tr>
<tr>
<td>2.</td>
<td>0.794</td>
<td>3.36</td>
<td>1.676</td>
<td>625</td>
<td>.33</td>
</tr>
<tr>
<td>3.</td>
<td>1.191</td>
<td>4.12</td>
<td>2.055</td>
<td>571.4</td>
<td>.30</td>
</tr>
<tr>
<td>4.</td>
<td>1.589</td>
<td>4.7</td>
<td>2.395</td>
<td>452.5</td>
<td>.25</td>
</tr>
<tr>
<td>5.</td>
<td>1.985</td>
<td>5.25</td>
<td>2.619</td>
<td>395.2</td>
<td>.22</td>
</tr>
</tbody>
</table>

Table 4.5 (i) Effect of [APAS] on $R_p$. [MMA] = 2.35 mol/l; $t = 5h$; polymn. temp. = 30 ± 0.2 °C.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>[MMA] (mol/l)</th>
<th>% Conversion</th>
<th>$R_p \times 10^5$ (mol/l/s)</th>
</tr>
</thead>
<tbody>
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<td>1.7</td>
<td>0.848</td>
</tr>
<tr>
<td>2.</td>
<td>2.35</td>
<td>3.36</td>
<td>1.676</td>
</tr>
<tr>
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<td>5.19</td>
<td>2.589</td>
</tr>
<tr>
<td>4.</td>
<td>4.7</td>
<td>6.56</td>
<td>3.273</td>
</tr>
</tbody>
</table>

Table 4.5 (ii) Effect of [MMA] on $R_p$. [APAS] = 0.79 $\times 10^{-4}$ mol/l; $t = 5h$; polymn. temp. = 30 ± 0.2 °C.
Result and Discussion

Fig 4.5 (i) Plot between log [APAS] vs. log \( R_p \), \( t = 5 \text{h} \);

\[ [\text{MMA}] = 2.35 \text{ mol/l}; \text{ polymn. temp.} = 30 \pm 0.2 \degree \text{C}. \]

Fig 4.5 (ii) Plot of log [MMA] vs. log \( R_p \), \( t = 5 \text{h} \);

\[ [\text{APAS}] = 0.79 \times 10^{-4} \text{ mol/l}; \text{ polymn. temp.} = 30 \pm 0.2 \degree \text{C}. \]
Fig 4.5 (iii) Plot of $1/P_n$ vs [APAS]^{0.5}. [MMA] = 2.35 mol/l; $t = 5h$; polymn. temp. = $30 \pm 0.2$ °C.
Characterization of polymer

FTIR Spectroscopy

The FTIR spectrum (Fig 4.5 (iv)) of polymer showed the following group of bands- C-H str vibrations of methyl and methylene group at 2950 and 2844 cm\(^{-1}\) respectively; >C=O str vibrations of ester carbonyl at 1734 cm\(^{-1}\); the C-H deformation bands in the region of 1380-1480 cm\(^{-1}\); C-O str bands in the region of 1150-1250 cm\(^{-1}\); characteristic band at 1063, 988 are supportive of the atactic nature of the polymer [Hummel, 1966].

Fig 4.4 (iv) FTIR Spectrum of PMMA
\textbf{\textsuperscript{1}H-NMR Spectroscopy}

In the \textsuperscript{1}H-NMR spectrum (Fig 4.5 (v)), a singlet due to methoxy protons, appeared at 3.6$\delta$. Methyl protons appeared in the region between 0.9-1.01 and methylene protons between 1.6-1.9$\delta$. The methylene protons appear as singlet at 1.83 in syndiotactic PMMA whereas a doublet at 1.62 and 2.33 is observed in isotactic PMMA. Since in this case neither of these characteristic peaks [Stevens, 1975] was observed, therefore, it was concluded that an atactic PMMA was formed.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Fig45v.png}
\caption{\textsuperscript{1}H-NMR Spectrum of PMMA}
\end{figure}
Mechanism
The inhibition to polymerization in the presence of a small quantity of hydroquinone and the kinetics suggest a radical mechanism for APAS-MMA system. ESR studies also suggest that APAS may be satisfactorily cleaved homolytically into radical A and B (Scheme 4.5 (i)). Also, the cation radical (B) formed is probably too reactive to participate in polymerization. Hence, only radical A might be involved in polymerization for the APAS-MMA system. On the basis of the above facts, a proposed mechanism is as given in Scheme 4.5 (i).

\[
\text{Initiation} \quad \text{APAS} \quad \rightarrow \quad \text{Py-CO-CH}_2^\cdot + \quad \text{As (Ph}_3\text{) Br}^+ \\
\text{(Radical A)} \quad \text{(Radical B)}
\]

Scheme 4.5 (i)

Conclusions
A detailed polymerization kinetics and mechanism with APAS as photoinitiator suggest a free radical approach for the synthesis of PMMA. The polymerization followed ideal kinetics with respect to both monomer and initiator. IR and NMR spectra showed the atactic nature of PMMA. Kinetics suggests that this photoinitiator APAS is less effective than its precursor BrPy, since percent conversion by the former is less under identical conditions.
4.6 Polymerization of n-Butylacrylate using 1-(Bromoacetyl)pyrene as Photoinitiator

Poly (n-alkyl acrylates) have been of continuing interest due to their physical properties such as the glass transition and melting temperatures, heats of fusion, crystalline structure, mechanical properties, adhesion etc. This subchapter discusses the kinetics and mechanism of polymerization of BA using BrPy as a photoinitiator.

The results of kinetic investigations of the photopolymerization of BA at 25°C using varying concentrations of BA and BrPy (BrPy-BA) at fixed intensity of light source are presented in Table 4.6 (i). No polymerization was observed in absence of initiator. The effect of monomer concentration on $R_p$ was studied by varying [BA] from 1.74 mol/l to 3.48 mol/l, keeping [BrPy] constant at $3.86 \times 10^{-5}$ mol/l. The monomer exponent value, calculated from the slope of the linear plot of log $R_p$ versus log [BA] is 0.98 (Fig 4.6 (i)).

Dependence of $R_p$ on [BrPy] displayed a maximum at [BrPy] = $1.16 \times 10^{-4}$ mol/l (Table 4.6 (i)). Further increase in the concentration of BrPy lead to a decrease in $R_p$, which can be ascribed to the consumption of [BrPy] in a fast chain transfer reaction leading to extremely higher termination rate. The initiator exponent value calculated from the positive slope of the linear plot of log $R_p$ vs. log [BrPy] (Fig 4.6 (ii)) was 0.8. The deviation in the exponent value suggests that the system followed non-ideal kinetics. An initiator exponent in a range of 0.5-1 would be the consequence of the co-occurrence
of normal bimolecular termination due to propagating radical occlusion. The occlusion theory was first developed by Bamford and Jenkins [Bamford, 1959] according to which the growing radical precipitates from the liquid phase before termination occurs and becomes tightly coiled. Although this termination is first order because the radical becomes trapped and inaccessible to the monomer, there seems to be no direct correlation between the extent of occlusion and the initiator exponent [Guyot, 1989]. Degradative solvent transfer also seems to be a probable cause for the kinetic non-ideality. In order to ascertain the nature of the transfer reactions involved, plots of $R_p^2/([\text{BrPy}][\text{BA}]^2)$ vs. $R_p/[\text{BA}]^2$ (Fig 4.6 (iii)), following the equation of Deb [Deb, 1975] were plotted. The positive slope obtained suggests that degradative solvent transfer is mostly operative in the main termination process instead of degradative initiator transfer or primary radical termination [Sengupta, 1982].

The viscosity average molecular weight for poly n-butylacrylate obtained by varying [BrPy] are reported in Table 4.6 (i). As is evident, $M_v$ decreased more rapidly with increase in [BrPy] than expected for an ideal free-radical polymerization. Moreover, the exponent value of 0.8 and the positive slope of Fig 4.6 (iii) ruled out the possibility of chain transfer to initiator [Sengupta, 1982]. Hence, it is assumed that, the greater number of radicals formed with increase in the concentration of BrPy would go into a fast transfer reaction with the solvent resulting into a decrease in $M_v$. Hence, the unusual kinetic behavior for BrPy-BA system can be interpreted in light of degradative transfer and the emergence of occlusion.
<table>
<thead>
<tr>
<th>S. No.</th>
<th>([\text{BrPy}] \times 10^4) (mol/l)</th>
<th>[BA] (mol/l)</th>
<th>% Conversion</th>
<th>(R_p \times 10^5) (mol/l/s)</th>
<th>(M_v)</th>
<th>(\eta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.38</td>
<td>1.74</td>
<td>5.27</td>
<td>3.404</td>
<td>87,321</td>
<td>.35</td>
</tr>
<tr>
<td>2.</td>
<td>0.77</td>
<td>1.74</td>
<td>9.11</td>
<td>5.875</td>
<td>69,798</td>
<td>.29</td>
</tr>
<tr>
<td>3.</td>
<td>1.16</td>
<td>1.74</td>
<td>12.89</td>
<td>8.317</td>
<td>50,504</td>
<td>.23</td>
</tr>
<tr>
<td>4.</td>
<td>1.54</td>
<td>1.74</td>
<td>9.78</td>
<td>6.309</td>
<td>39,195</td>
<td>.19</td>
</tr>
<tr>
<td>5.</td>
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<td>30,389</td>
<td>.16</td>
</tr>
<tr>
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<td>6.95</td>
<td>4.487</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.</td>
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<td>2.79</td>
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<td>5.382</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.</td>
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<td>3.17</td>
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<td>6.137</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9.</td>
<td>0.38</td>
<td>3.48</td>
<td>10.36</td>
<td>6.683</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.6 (i) Effect of [BrPy] and [BA] on \(R_p\), \(t = 3\)h; polymn. temp. = 25 ± 0.2 °C.
**Result and Discussion**

![Graph](image)

Fig 4.6 (i) Plot of log [BA] vs. log $R_p$. [BrPy] = $3.86 \times 10^{-5}$ mol/l; $t = 3h$; polymn. temp. = $25 \pm 0.2$ °C.

Fig 4.6 (ii) Plot of log [BrPy] vs. log $R_p$. [BA] = 1.74 mol/l; $t = 3h$; polymn. temp. = $25 \pm 0.2$ °C.
Fig 4.6 (iii) Plot of $R_p^2 / [BA]^2 [BrPy]$ vs. $R_p/[BA]^2$. $[BA] = 1.74$ mol/l; $t = 3h$; polymn. temp. = 25 ± 0.2°C.

Characterization of polymer

FTIR Spectroscopy

The FTIR spectrum (Fig 4.6 (iv)) of polymer consisted of the following group of bands- C-H str vibrations of methyl and methylene groups in the region 2980-2910 cm$^{-1}$; >C=O str vibrations of ester carbonyl at 1735 cm$^{-1}$; C-O str bands in the region of 1180-1260 cm$^{-1}$.

$^1$H-NMR Spectroscopy

In the $^1$H-NMR spectrum (Fig 4.6 (v)), a singlet due to -OCH$_2$ protons appeared at 3.96 $\delta$. Methyl protons appeared at 0.9, methylene protons between 1.18-1.33 and methine protons at 2.2 $\delta$. 

Mechanism

The inhibition to polymerization in the presence of a small quantity of hydroquinone and kinetics suggest a radical mechanism for BrPy-BA system. ESR studies suggest the formation of Radical A and Br⁻ (Scheme 4.6 (i)) on photo cleavage of BrPy, both of which have the possibility of initiating polymerization. On the basis of the above facts, a proposed mechanism is as given in Scheme 4.6 (i).

Initiation

\[
\begin{align*}
\text{BrPy} & \quad \rightarrow \quad \text{Py-CO-CH}_2^- + \text{Br}^- \\
\text{Br}^- & \quad \text{Or} \quad \rightarrow \quad \text{CO}_2\text{(CH}_2\text{)}_3\text{CH}_3
\end{align*}
\]

(Radical A)

Scheme 4.6 (i)
Fig 4.6 (iv) IR Spectrum of Poly (BA)

Fig 4.6 (v) $^1$H-NMR Spectrum of Poly (BA)
Conclusions

The polymerization of n-Butylacrylate (BA) with BrPy followed non-ideal kinetics \( R_p \propto [\text{BrPy}]^{0.8} [\text{BA}]^{0.98} \) with respect to initiator concentration. This unusual kinetic behavior can be interpreted in light of degradative transfer and the emergence of occlusion. A plausible mechanism for free radical polymerization was suggested on the basis of the data obtained by kinetic investigation and ESR studies.

This part of the thesis is under publication in "Journal of Macromolecular Science Part A: Pure and Applied Chemistry"
Chapter 4

4.7 Polymerization of n-Butylacrylate using 1-Acetylpyrene triphenyl arsonium bromide as Photoinitiator

The kinetics and mechanism of polymerization using APAS as photoinitiator have been investigated in detail. No polymerization was observed in absence of initiator. The polymerization time chosen was 6 h in order to limit conversions to low percentage to study kinetics. The effect of monomer concentration on \( R_p \) was studied by varying \([BA]\) from 1.74 mol/l to 3.48 mol/l, keeping \([APAS]\) constant at \(1.19 \times 10^{-4}\) mol/l. The data obtained to see the effect of monomer concentration on \( R_p \) are shown in Table 4.7 (i). The monomer exponent value, calculated from the slope of the linear plot of log \( R_p \) versus log \([BA]\) was 1.07 as expected for free-radical polymerization (Fig 4.7 (i)).

The effect of \([APAS]\) on \( R_p \) was studied by varying the initiator concentration from \(1.19 \times 10^{-4}\) mol/l to \(2.38 \times 10^{-4}\) mol/l keeping all other parameters constant. No polymerization was observed when concentration of APAS was \(< 1.19 \times 10^{-4}\) mol/l and the time period \(< 5\) h. The initiator exponent value, calculated from the slope of the linear plot of log \( R_p \) versus log \([APAS]\) was 0.49 (Fig 4.7 (ii)) suggesting that the system followed ideal kinetics with respect to both monomer and initiator concentration.
<table>
<thead>
<tr>
<th>S. No.</th>
<th>[APAS] × 10⁴ (mol/l)</th>
<th>[BA] (mol/l)</th>
<th>% Conversion</th>
<th>R_p × 10⁵ (mol/l/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
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<td>1.74</td>
<td>4.29</td>
<td>1.388</td>
</tr>
<tr>
<td>2.</td>
<td>1.58</td>
<td>1.74</td>
<td>4.96</td>
<td>1.603</td>
</tr>
<tr>
<td>3.</td>
<td>1.98</td>
<td>1.74</td>
<td>5.51</td>
<td>1.778</td>
</tr>
<tr>
<td>4.</td>
<td>2.38</td>
<td>1.74</td>
<td>6.05</td>
<td>1.954</td>
</tr>
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<td>1.19</td>
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<td>5.83</td>
<td>1.883</td>
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<tr>
<td>6.</td>
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<td>2.79</td>
<td>7.09</td>
<td>2.291</td>
</tr>
<tr>
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<td>1.19</td>
<td>3.17</td>
<td>8.18</td>
<td>2.642</td>
</tr>
<tr>
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<td>1.19</td>
<td>3.48</td>
<td>9.03</td>
<td>2.917</td>
</tr>
</tbody>
</table>

Table 4.7 (i) Effect of [APAS] and [BA] on R_p, t = 6h; polymn. temp. = 25 ± 0.2 °C.
Fig 4.7 (i) Plot of log [BA] vs. log $R_p$. [APAS] = $1.19 \times 10^{-4}$ mol/l;
polyn. temp. = $25 \pm 0.2$ °C; $t = 3h$.

Fig 4.7 (ii) Plot of log [APAS] vs. log $R_p$. [BA] = $1.74$ mol/l;
polyn. temp. = $25 \pm 0.2$ °C; $t = 3h$. 

Characterization of polymer

FTIR Spectroscopy

The FTIR spectrum (Fig 4.7 (iii)) of polymer consisted of the following group of bands- C-H str vibrations of methyl protons at approximately 2950 cm\(^{-1}\); methylene protons at 2870-2910 cm\(^{-1}\); >C=O str vibrations of ester carbonyl at 1733 cm\(^{-1}\); C-O str bands in the region of 1060-1160 cm\(^{-1}\).

\(^1\)H-NMR Spectroscopy

In the \(^1\)H-NMR spectrum (Fig 4.7 (iv)), a singlet due to -OCH\(_2\) protons appeared at 4.8. Methyl protons appeared at 0.9, methylene protons between 1.3-1.8 and methine protons at 2.38.

Mechanism

The inhibition to polymerization by addition of hydroquinone and kinetic studies suggest radical polymerization. The possible radicals generated by APAS are radical A and B (scheme 4.7 (i)) as evident by ESR studies. Also, the cation radical (B) formed is probably too reactive to participate in polymerization. Hence, only radical A might be involved in polymerization for the APAS-MMA system. On the basis of the above facts, a proposed mechanism is as given in Scheme 4.7 (i).
Initiation

APAS $\rightarrow$ Py-CO-CH$_2$· + $\cdot$ \text{(Radical A)}

(Radical B)

\[ \text{Radical A} + \text{CH}_2=\text{CH}_3 \rightarrow \text{A-CH}_2\text{C}· \text{CO}_2(\text{CH}_2)_3\text{CH}_3 \]

Scheme 4.7 (i)

Conclusions

The polymerization of n-Butylacrylate (BA) with APAS followed ideal kinetics. A plausible mechanism for free radical polymerization was suggested on the basis of the data obtained by kinetic investigation and ESR studies. The kinetic data proved that BrPy was more effective and faster initiator than APAS since the latter required more time to bring about the same percent conversion as BrPy.

This part of the thesis is under publication in "Journal of Macromolecular Science Part A: Pure and Applied Chemistry".
Fig 4.7 (iii) IR Spectrum of Poly (BA)

Fig 4.7 (iv) $^1$H-NMR Spectrum of Poly (BA)
Chapter 4

4.8 1-(Bromoacetyl)pyrene, a novel photoinitiator for the copolymerization of styrene and methylmethacrylate

Free radical copolymerization of styrene and methacrylic acid esters have been studied extensively and described in many publications. This subchapter studies the kinetics and mechanism of copolymerization of Sty with MMA (Sty-co-MMA) using BrPy in detail. A negligible percent 0.4 - 0.6 % polymerization was observed, in absence of initiator, by the light employed, hence, % conversion (Table 4.8 (i) and (ii)) was reported after having deducted the yield for blank experiments. All conversions were limited to <10 % to obtain kinetic data.

The effect of [BrPy] on $R_p$ was studied by varying its concentration from $1.54 \times 10^{-4}$ mol/l to $7.735 \times 10^{-4}$ mol/l for a fixed monomer feed ratio. The $R_p$ increased with increasing [BrPy], keeping [Sty] and [MMA] constant. The initiator exponent calculated from the slope of the plot of log $R_p$ vs. log [BrPy] was 0.71 (Fig 4.8(i)). The deviation in the exponent value and an intercept in the plot of $1 / \widetilde{P_n}$ vs. $R_p/[M]^2$ (Fig 4.8 (ii)) suggested that the system followed non-ideal kinetics. The value of $k_p^2/k_i$ obtained from the slope of this plot was $2.28 \times 10^{-5}$ l mol$^{-1}$ s$^{-1}$.

In order to explain this unusual behavior and to ascertain the nature of the transfer reactions involved, plots of $R_p^2/([BrPy][M]^2)$ vs. $R_p/[M]^2$ (Fig 4.8(iii)), following the equation of Deb [Deb, 1975] were plotted. The positive slope obtained suggests that degradative solvent transfer is mostly
### Table 4.8 (i) Effect of [BrPy] on $R_p$. $[\text{MMA}] = 4.7 \text{ mol/l}$; $[\text{Sty}] = 4.37 \text{ mol/l}$; $t = 5\text{h}$; polymn. temp. = $30 \pm 0.2 \degree\text{C}$.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>$[\text{BrPy}] \times 10^4$ (mol/l)</th>
<th>% Conversion</th>
<th>$R_p \times 10^6$ (mol/l/s)</th>
<th>$\bar{P}_n$</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
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<td>1.54</td>
<td>1.413</td>
<td>3.539</td>
<td>243</td>
<td>.35</td>
</tr>
<tr>
<td>2.</td>
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<td>2.308</td>
<td>5.781</td>
<td>190</td>
<td>.29</td>
</tr>
<tr>
<td>3.</td>
<td>4.641</td>
<td>3.099</td>
<td>7.762</td>
<td>158</td>
<td>.25</td>
</tr>
<tr>
<td>4.</td>
<td>6.18</td>
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<td>9.506</td>
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<td>.21</td>
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Table 4.8 (ii) Effect of $[\text{MMA}]$ and $[\text{Sty}]$ on $R_p$. $[\text{BrPy}] = 1.54 \times 10^{-4}$ mol/l; $t = 5\text{h}$; polymn. temp. = $30 \pm 0.2 \degree\text{C}$.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>$[\text{MMA}]$ (mol/l)</th>
<th>$[\text{Sty}]$ (mol/l)</th>
<th>% Conversion</th>
<th>$R_p \times 10^6$ (mol/l/s)</th>
</tr>
</thead>
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</tr>
<tr>
<td>6</td>
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<td>1.711</td>
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</tr>
<tr>
<td>7</td>
<td>6.26</td>
<td>4.37</td>
<td>1.902</td>
<td>4.764</td>
</tr>
</tbody>
</table>

Table 4.8 (ii) Effect of $[\text{MMA}]$ and $[\text{Sty}]$ on $R_p$. $[\text{BrPy}] = 1.54 \times 10^{-4}$ mol/l; $t = 5\text{h}$; polymn. temp. = $30 \pm 0.2 \degree\text{C}$.
Fig 4.8(i) Plot of log [BrPy] on log $R_p$. [MMA] = 4.7 mol/l; [Sty] = 4.37 mol/l; $t =5h$; polymn. temp. = 30 ± 0.2°C.

Fig 4.8(ii) Plot of $1/\overline{P_n}$ vs $R_p/[M]^2$. [MMA] = 4.7 mol/l; [Sty] = 4.37 mol/l; $t =5h$; polymn. temp. = 30 ± 0.2°C.
operative in the main termination process instead of degradative initiator transfer or primary radical termination [Sengupta, 1982].

**Effect of comonomer concentration**

The effect of MMA concentration on \( R_p \) was studied by varying [MMA] from 3.13 mol/l to 6.26 mol/l, keeping [BrPy] and [Sty] constant. Similarly, the effect of [Sty] on \( R_p \) was studied by varying its concentration from 2.91 mol/l to 5.82 mol/l, keeping [BrPy] and [MMA] constant (Table 4.8(ii)). It was found that \( R_p \) increased as concentration of monomer was increased in both cases. The exponent values, calculated from the slope of the linear plot
of log $R_p$ versus log [MMA] (Fig 4.8(iv)) and log $R_p$ versus log [Sty] (Fig 4.8(v)) were 1.04 and 1, respectively.

Fig 4.8 (iv) Plot of log [MMA] vs. log $R_p$. $t = 5h$; [BrPy] = $1.54 \times 10^{-4}$ mol/l; polymn. temp. = $30 \pm 0.2^\circ C$.

Fig 4.8 (v) Plot of log [Sty] vs. log $R_p$. [BrPy] = $1.54 \times 10^{-4}$ mol/l; $t = 5h$; polymn. temp. = $30 \pm 0.2^\circ C$. 
Characterization of copolymers

Infrared Spectroscopy
The IR spectrum (Fig 4.8 (vi)) of copolymer showed band at 3000 cm\(^{-1}\) due to aromatic C-H str vibrations, 2927 and 2850 cm\(^{-1}\) due to C-H str vibrations of methyl, methylene and methine groups, 1730 cm\(^{-1}\) due to >C=O str vibrations of ester carbonyl, ~1600 cm\(^{-1}\) due to aromatic C=C str vibrations, 1450-1390 cm\(^{-1}\) due to C-H deformation bands, 1160-1120 cm\(^{-1}\) due to C-O-C str vibrations.

NMR Spectroscopy
In the NMR spectrum of copolymer (Fig 4.8 (vii)), phenyl protons appeared at 6.8-7.2 \(\delta\), methylene protons at 1.2-1.5 \(\delta\), methyl protons at 0.8 \(\delta\) and the region of ester methyl protons (2.2-3.6 \(\delta\)) splits into three distinct group of resonances assigned to the different configurational sequences on the basis of phenyl ring current shielding of the methoxy protons by the adjacent styrene units. The resonances appear to be broad, but this is mainly because of a multitude of chemical shifts corresponding to the many possible sequences present in the random copolymer [Bovey, 1989]. Moreover, the presence of the \(^1\)H-NMR signals (despite being poorly resolved) for the MMA---MMA---\(^{syn}\)---Sty triad (\(\delta\) 3.5 ppm) and the MMA---MMA-----MMA triad (\(\delta\) 3.6 ppm) further suggest the random nature of copolymer [Hirai, 1985].
Fig 4.8(vi) IR Spectrum of Sty-co-MMA

Fig 4.8 (vii) NMR Spectrum of Sty-co-MMA. $t = 5\text{h}$;

$[\text{MMA}] = 4.7 \text{ mol/l}$; $[\text{Sty}] = 4.37 \text{ mol/l}$;

$[\text{BrPy}] = 1.54 \times 10^{-4} \text{ mol/l}$; polymn. temp. $= 30 \pm 0.2 ^\circ\text{C}$.
<table>
<thead>
<tr>
<th>S. No.</th>
<th>Molar ratio in monomer feed [MMA]/<a href="X">Sty</a></th>
<th>Molar ratio in copolymer [MMA]/<a href="Y">Sty</a></th>
</tr>
</thead>
<tbody>
<tr>
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</tr>
<tr>
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</tr>
<tr>
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<td>1.678</td>
</tr>
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</table>

**Table 4.8 (iii) Copolymer Composition**

**Copolymer composition and monomer reactivity ratio**

The relative peak areas due to phenyl and methoxy protons (Table 4.8(iii)) have been used to calculate copolymer composition [Morrison, 2003, 609].

The Finemann–Ross (FR) and Kelen-Tudos (KT) plots are given in Fig 4.8(viii) and 4.8 (ix), respectively. The reactivity ratios as calculated by FR and KT methods are $r_1$ (MMA) = 0.48 and $r_2$ (Sty) = 0.52. Since $r_1$ and $r_2$ are both < 1 and $r_1$ nearly equal to $r_2$, at equimolar feed ratio, the copolymer is expected to have equal number of Sty and MMA units, but arranged in a random sequence [Gowarikar, 2000].
Fig 4.8 (viii) Finemann - Ross plot

Fig 4.8 (ix) Kelen-Tudos plot
Mechanism

The inhibition to polymerization in the presence of a small quantity of hydroquinone, ESR studies and the kinetics suggest a radical mechanism for BrPy initiated Sty-co-MMA system. As evidenced by ESR, the possible radicals generated by the initiator, BrPy, are radical A and bromine. In the proposed mechanism for polymerization, both Br and radical A have been considered to initiate the reaction. Although radical A is delocalized and usually delocalized radicals show very little tendency for addition to double bonds but its participation in initiation cannot be ruled out completely. Considering the above facts, a proposed mechanism is as given in Scheme 4.8 (i).

Initiation

\[
\begin{align*}
\text{BrPy} & \quad \rightarrow \quad \text{Py-CO-CH}_2^- + \text{Br}^- \\
& \quad \text{(Radical A)} \\
\text{H}_2\text{C} &= \text{CH} \\
\text{Ph} & \quad \rightarrow \quad \text{Br-CH}_2^- \text{CH}_2^- \\
& \quad \text{Ph} \quad \text{Ph} \\
\text{Or} & \\
\text{Br}^- \quad \text{or radical A} + \quad & \\
\text{Br}^- \quad \text{or radical A} + \\
\text{CO}_2\text{CH}_3 & \quad \rightarrow \quad \text{CO}_2\text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{Or} & \\
\text{AH}_2\text{C} & \quad \rightarrow \quad \text{CO}_2\text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]

Scheme 4.8 (i)
Conclusions

The kinetic data, inhibiting effect of benzoquinone and ESR studies suggested that the polymerization proceeded via a free radical mechanism. The system followed non-ideal kinetics \( R_p \propto [\text{BrPy}]^{0.7}[\text{Sty}]^{1}[\text{MMA}]^{1.04} \) with respect to initiator concentration and degradative solvent transfer reasonably explained these kinetic non-idealities. The co-monomer reactivity ratios calculated by using the Finemann-Ross and Kelen-Tudos models were \( r_1 (\text{MMA}) = 0.48 \) and \( r_2 (\text{Sty}) = 0.52 \). The value of \( k_p^2/k_i \) for the present system was found to be \( 2.28 \times 10^{-5} \text{ mol}^{-1} \text{s}^{-1} \). IR and NMR analysis confirmed the random structure of the copolymer.

This part of the thesis has been accepted in the journal “Radiation Physics and Chemistry”.

4.9 Copolymerization of n-butylacrylate with methylethacrylate by a novel photoinitiator, 1-(Bromoacetyl)pyrene

The kinetics and mechanism of copolymerization of BA with MMA (MMA-co-BA), at 30°C, using BrPy as photoinitiator have been studied in detail. No polymerization was observed, in absence of initiator, by the light employed. All conversions were limited to <10 % to obtain kinetic data.

The effect of [BrPy] on $R_p$ was studied by varying its concentration from $0.618 \times 10^{-4}$ mol/l to $3.712 \times 10^{-4}$ mol/l for a fixed monomer feed ratio (Table 4.9 (i)). $R_p$ increased with increasing [BrPy], keeping [BA] and [MMA] constant. The initiator exponent calculated from the slope of the plot of log $R_p$ vs. log [BrPy] is 0.67 (Fig 4.9 (i)). The deviation in the exponent value suggests that the system followed non-ideal kinetics. In order to explain this unusual behavior and to ascertain the nature of the transfer reactions involved, plots of $R_p^2/([\text{BrPy}][\text{M}]^2)$ vs. $R_p/[\text{M}]^2$ (Fig 4.9 (ii)), following the equation of Deb [Deb, 1975] were plotted. The positive slope obtained suggests that degradative solvent transfer is mostly operative in the main termination process instead of degradative initiator transfer or primary radical termination [Sengupta, 1982].
Effect of comonomer concentration

The effect of MMA concentration on $R_p$ was studied by varying [MMA] from 0.65 mol/l to 1.88 mol/l, keeping [BrPy] and [BA] constant. Similarly, the effect of [BA] on $R_p$ was studied by varying its concentration from 0.48 mol/l to 1.39 mol/l, keeping [BrPy] and [MMA] constant (Table 4.9 (ii)). It was observed that $R_p$ increased with increase in monomer concentration in both the cases. The exponent values, calculated from the slope of the linear plot of log $R_p$ versus log [MMA] (Fig 4.9 (iii)) and log $R_p$ vs. log [BA] (Fig 4.9 (iv)) were 0.98 and 1, respectively.
**Result and Discussion**

<table>
<thead>
<tr>
<th>S. No.</th>
<th>[BrPy] $\times 10^4$ (mol/l)</th>
<th>Conversion</th>
<th>$R_p \times 10^6$ (mol/l/s)</th>
</tr>
</thead>
<tbody>
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</tr>
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</table>

**Table 4.9 (i) Effect of [BrPy] on $R_p$.** [BA] = 1.39 mol/l; $t$ = 7 h; [MMA] = 1.88 mol/l; polymn. temp. = 30 ± 0.2°C.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>[MMA] (mol/l)</th>
<th>[BA] (mol/l)</th>
<th>Conversion</th>
<th>$R_p \times 10^6$ (mol/l/s)</th>
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</thead>
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<td>1.590</td>
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<td>7.</td>
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<td>1.395</td>
<td>2.317</td>
<td>3.698</td>
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</table>

**Table 4.9 (ii) Effect of [MMA] and [BA] on $R_p$.** [BrPy] = 3.71 $\times 10^{-4}$ mol/l; $t$ = 7 h; polymn. temp. = 30 ± 0.2°C.
Fig 4.9 (i) Plot of log [BrPy] vs. log $R_p$. $[BA] = 1.39$ mol/l; 
$t = 7h; [MMA] = 1.88$ mol/l; polymn. temp. = $30 \pm 0.2$ °C.

Fig 4.9 (ii) Plot of $R_p^2/[M]^2[BrPy]$ vs. $R_p/[M]^2$. $[BA] = 1.39$ mol/l; 
$t = 7h; [MMA] = 1.88$ mol/l; polymn. temp. = $30 \pm 0.2$ °C.
Result and Discussion

Fig 4.9 (iii) Plot of $\log [\text{MMA}]$ vs. $\log R_p$. $[\text{BA}] = 1.39 \text{ mol/l}$; $t = 7h$; $[\text{BrPy}] = 3.71 \times 10^{-4} \text{ mol/l}$; polymn. temp. = 30 ± 0.2°C.

Fig 4.9 (iv) Plot of $\log [\text{BA}]$ vs. $\log R_p$. $[\text{MMA}] = 1.88 \text{ mol/l}$. $t = 7h$; $[\text{BrPy}] = 3.71 \times 10^{-4} \text{ mol/l}$; polymn. temp. = 30 ± 0.2°C.
Characterization of copolymers

Infrared Spectroscopy
The IR spectrum (Fig 4.9 (v)) of copolymer showed band at 2953 cm\(^{-1}\) due to C-H str vibrations of methyl, methylene and methine groups, 1731 cm\(^{-1}\) due to >C=O str vibrations of ester carbonyl, 1450-1385 cm\(^{-1}\) due to C-H deformation bands, 1240-1150 cm\(^{-1}\) due to C-O-C str vibrations.

NMR Spectroscopy
In the NMR spectrum of copolymer (Fig 4.9 (vi)), -OCH\(_2\) protons of BA unit appeared at 4.2 \(\delta\), -OCH\(_3\) protons of MMA unit at 3.8 \(\delta\), methyl and methylene protons of both units between 0.8-1.1 \(\delta\) and 1.4-1.8 \(\delta\), respectively.

Copolymer composition and monomer reactivity ratios (MRR)
For calculating the copolymer compositions (F\(_M\)), the relative areas of the proton resonances of -OCH\(_3\) of the MMA unit and -OCH\(_2\) of the n-BA unit in the \(^1\)H-NMR spectra were used (Table 4.9 (iii)). The Finemann–Ross (FR) and Kelen-Tudos (KT) plots are given in Fig 4.9 (vii) and Fig 4.9 (viii), respectively. The reactivity ratios as calculated by FR and KT methods were \(r_1\) (MMA)= 2.17 and \(r_2\) (BA) =0.44. The MRR of MMA is much higher than that of BA. It is ideal copolymerization, from the fact that \(r_1r_2\) value is near one, and clearly MMA is more reactive than BA. The relative reactivity of monomers and their corresponding radicals can be obtained from an analysis of the MRRs [Walling, 1957]. The random copolymers so obtained, contain a high concentration of alternating
sequences, as anticipated by the five times higher value of $r_1$ than $r_2$ [Patnaik et al, 1970].

Fig 4.9 (v) IR Spectrum of MMA-co-BA
Fig 4.9 (vi) NMR Spectrum of MMA-co-BA. \([\text{BA}] = 1.39 \text{ mol/l};\)
\([\text{MMA}] = 1.88 \text{ mol/l};\) \([\text{BrPy}] = 0.618 \times 10^{-4} \text{ mol/l};\) \(t = 7\text{h};\)
\(\text{polymn. temp.} = 30 \pm 0.2 \degree\text{C}.\)

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Molar ratio in monomer feed ([\text{MMA}]/[\text{BA}]) ((X))</th>
<th>Molar ratio in copolymer ([\text{MMA}]/[\text{BA}]) ((Y))</th>
</tr>
</thead>
<tbody>
<tr>
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</tr>
<tr>
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</tr>
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</tr>
<tr>
<td>5.</td>
<td>2.703</td>
<td>5.896</td>
</tr>
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</table>

Table 4.9 (iii) Copolymer Composition
Mechanism

The inhibition to polymerization in the presence of a small quantity of hydroquinone, ESR studies and the kinetics suggest a radical mechanism for BrPy initiated BA-co-MMA system. As evidenced by ESR, the possible radicals generated by the initiator, BrPy, are radical A and bromine. Considering the above facts, a proposed mechanism is as given in Scheme 4.9 (i).

**Initiation**

\[
\text{BrPy} \rightarrow \text{Py-CO-CH}_2^\cdot + \text{Br}^-
\]

(Radical A)

\[
\text{Br or radical A} + \text{CH}_2\text{=CH}_2 \rightarrow \text{ACH}_2\text{CH}_2\text{CO}_2(\text{CH}_2)_3\text{CH}_3 \quad \text{Or}
\]

\[
\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CO}_2(\text{CH}_2)_3\text{CH}_3
\]

\[
\text{Br or radical A} + \text{H}_3\text{C}((\text{CH}_2)_3\text{O}_2\text{C} \rightarrow \text{BrH}_2\text{C}\text{CH}_2\text{CO}_2(\text{CH}_2)_3\text{CH}_3 \quad \text{Or}
\]

**Scheme 4.9 (i)**
Chapter 4

Fig 4.9 (vii) Finemann –Ross plot

Fig 4.9 (viii) Kelen-Tudos plot
Conclusion

The system followed non-ideal kinetics \( R_p \propto [\text{BrPy}]^{0.67}[\text{BA}]^{1}[\text{MMA}]^{0.98} \) and degradative solvent transfer reasonably explained these kinetic non-idealities. The values of \( r_1(\text{MMA}) \) and \( r_2(\text{BA}) \) were found to be 2.17 and 0.44, respectively, which suggested the high concentration of alternating sequences in the random copolymers obtained.

This part of the thesis has been communicated for publication to the journal "Polymer Bulletin".
4.10 Copolymerization of n-butylacrylate with styrene by a novel photoinitiator, 1-(Bromoacetyl) pyrene

Multicomponent polymers based on styrene / acrylate formulations are a basis for many important applications such as paints, adhesives and coatings. This has stimulated the considerable body of study on copolymerizations of styrene with various acrylate monomers. The kinetics and mechanism of copolymerization of BA with Sty using BrPy as photoinitiator have been studied in detail. No polymerization was observed, in absence of initiator, by the light employed. All conversions were limited to <10 % to obtain kinetic data.

The effect of [BrPy] on $R_p$ was studied by varying its concentration from $0.618 \times 10^{-4}$ mol/l to $3.712 \times 10^{-4}$ mol/l for a fixed monomer feed ratio (Table 4.10 (i)). Dependence of $R_p$ on [BrPy], keeping [BA] and [MMA] constant, displayed a maximum at [BrPy] = $2.475 \times 10^{-4}$ mol/l (Table 4.10 (i)). The upward trend of the curve of log $R_p$ Vs. log [BrPy] was greatly reduced at high concentrations of [BrPy], which can be ascribed to the consumption of [BrPy] in a fast chain transfer reaction. The initiator exponent calculated from the slope of the plot of log $R_p$ vs. log [BrPy] was 0.34 (Fig 4.10 (i)). The deviation in the exponent value of initiator from 0.5 suggests that the present system follows non-ideal kinetics, which can be explained on the basis of primary radical termination and degradative chain transfer.
To analyze the effect of primary radical termination, the following expression given by Deb and Meyerhoff [Deb and Meyerhoff, 1974; Deb, 1975] has been used

\[
\log \frac{R_p^2}{[I][M]^2} = \log 2f_k k_d k_p^2 / k_t - 0.8684 k_{prn} R_p / k_t k_p [M]^2
\]

Where, \( f_k \) represents the fraction of free radical to initiate chain growth; \( k_d \) is the initiator decomposition rate constant; \( k_p \) is the propagation rate constant; \( k_{prn} \) is the primary, radical termination constant; and \([I]\) and \([M]\) are initiator and monomer concentrations, respectively. In the present study, a plot on the left hand side of the above equation versus \( R_p/[M]^2 \) gave a linear negative slope (Fig 4.10 (ii)), indicating significant primary radical termination along with simultaneous bimolecular termination. The following equation has frequently been used to examine degradative chain transfer

\[
\log \frac{R_p^2}{[I][M]^2} = \log 2f_k k_d k_p / k_t - 0.434k_p^2 k_{itl} c_i[I] / k_t k_{il} k_p [M]
\]

Where, \( C_i \) is the initiator transfer constant; \( k_{itl} \) is the rate constant for degradative chain transfer to initiator; and \( k_{il} \) is the initiator rate constant. A plot on the left-hand side of the above equation versus \([I]/[M]\) gave a linear negative slope (Fig 4.10 (iii)), suggesting measurable degradative initiator transfer [Ghosh and Mitra, 1977]. The non-ideality in the present system is attributed to both primary radical termination and degradative initiator transfer.
Effect of comonomer concentration

The effect of BA concentration on \( R_p \) was studied by varying [BA] from 0.48 mol/l to 1.39 mol/l, keeping [BrPy] and [Sty] constant. Similarly, the effect of [Sty] on \( R_p \) was studied by varying its concentration from 0.61 mol/l to 1.74 mol/l, keeping [BrPy] and [BA] constant (Table 4.10 (ii)). It was observed that \( R_p \) increased with increase in monomer concentration in both the cases. The exponent values, calculated from the slope of the linear plot of log \( R_p \) versus log [Sty] (Fig 4.10 (iv)) and log \( R_p \) versus log [BA] (Fig 4.10 (v)) were 0.97 and 1.07, respectively.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>[BrPy] ( \times 10^4 ) (mol/l)</th>
<th>% Conversion</th>
<th>( R_p ) ( \times 10^6 ) (mol/l/s)</th>
</tr>
</thead>
<tbody>
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<td>3.439</td>
</tr>
<tr>
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<td>1.237</td>
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<td>3.20</td>
<td>5.753</td>
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<tr>
<td>4.</td>
<td>2.475</td>
<td>3.63</td>
<td>6.526</td>
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<tr>
<td>5.</td>
<td>3.094</td>
<td>3.41</td>
<td>6.137</td>
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<tr>
<td>6.</td>
<td>3.712</td>
<td>3.23</td>
<td>5.807</td>
</tr>
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</table>

Table 4.10 (i) Effect of [BrPy] on \( R_p \). [BA] = 1.39 mol/l; [Sty] = 1.748 mol/l; \( t = 6h \); polymn.temp. = 30 ± 0.2°C.
Table 4.10 (ii) Effect of [Sty] and [BA] on $R_p$. [BrPy] = $6.18 \times 10^{-5}$ mol/l; 
$t = 6h$; polymn. temp. = $30 \pm 0.2^\circ C$.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>[Sty] (mol/l)</th>
<th>[BA] (mol/l)</th>
<th>% Conversion</th>
<th>$R_p \times 10^6$ (mol/l/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>1.748</td>
<td>0.488</td>
<td>0.69</td>
<td>1.240</td>
</tr>
<tr>
<td>2.</td>
<td>1.748</td>
<td>0.697</td>
<td>0.98</td>
<td>1.762</td>
</tr>
<tr>
<td>3.</td>
<td>1.748</td>
<td>1.046</td>
<td>1.44</td>
<td>2.589</td>
</tr>
<tr>
<td>4.</td>
<td>1.748</td>
<td>1.395</td>
<td>1.91</td>
<td>3.439</td>
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<td>5.</td>
<td>0.611</td>
<td>1.395</td>
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<td>1.114</td>
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<tr>
<td>6.</td>
<td>0.874</td>
<td>1.395</td>
<td>0.92</td>
<td>1.654</td>
</tr>
<tr>
<td>7.</td>
<td>1.311</td>
<td>1.395</td>
<td>1.42</td>
<td>2.553</td>
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</table>

Fig 4.10 (i) Plot of log [BrPy] vs. log $R_p$. [BA] = 1.39 mol/l; 
[Sty] = 1.748 mol/l; $t = 6h$; polymn. temp. = $30 \pm 0.2^\circ C$. 
Fig 4.10 (ii) Plot of $R_p^2/[BA]^2[BrPy]$ vs. $R_p/[BA]$. $[BA] = 1.39$ mol/l; $[Sty] = 1.748$ mol/l; $t = 6$ h; polymer. temp. = 30 ± 0.2°C.

Fig 4.10 (iii) Plot of $R_p^2/[BA]^2[BrPy]$ vs. $[BrPy]/[BA]$. $[BA] = 1.39$ mol/l; $[Sty] = 1.748$ mol/l; $t = 6$ h; polymer. temp. = 30 ± 0.2°C.
Fig 4.10 (iv) Plot of log [Sty] vs. log R_p. [BA] = 1.39 mol/l; [BrPy] = 6.18 \times 10^{-5} \text{ mol/l}; t = 6h; polymn. temp. = 30 \pm 0.2^{\circ}\text{C}.

Fig 4.10 (v) Plot of log [BA] vs. log R_p. [Sty] = 1.748 \text{ mol/l}; [BrPy] = 6.18 \times 10^{-5} \text{ mol/l}; t = 6h; polymn. temp. = 30 \pm 0.2^{\circ}\text{C}.
Characterization of copolymers

**Infrared Spectroscopy**

The IR spectrum (Fig 4.10 (vi)) of copolymer showed band at 3059-2928 cm\(^{-1}\) due to C-H str vibrations of methyl, methylene and methine groups, 1732 cm\(^{-1}\) due to >C=O str vibrations of ester carbonyl, 1492-1451 cm\(^{-1}\) due to C-H deformation bands, 1155-1028 cm\(^{-1}\) due to C-O-C str vibrations.

**NMR Spectroscopy**

In the NMR spectrum of copolymer (Fig 4.10 (vii)), the signals at 3.5-3.8 \(\delta\) were assigned to -OCH\(_2\) protons of BA unit, the signals at 6.6-7.1 \(\delta\) to aromatic protons of Sty, 0.9 \(\delta\) to methyl protons of BA unit, 1-2.1 \(\delta\) to methine and methylene protons of both units. It is believed that the range of chemical shifts, observed for the –OCH\(_2\) signal, stems from different triad and tacticities possible for the copolymer.

**Copolymer composition and monomer reactivity ratios (MRR)**

For calculating the copolymer compositions (\(F_M\)), the relative areas of the proton resonances of –C\(_6\)H\(_5\) of the Sty unit and –OCH\(_2\) of the BA unit in the \(^1\)H-NMR spectrum were used (Table 4.10 (iii)). The Finemann–Ross (FR) and Kelen-Tudos (KT) plots are given in Fig 4.10 (viii) and Fig 4.11 (ix), respectively. The reactivity ratios as calculated by FR and KT methods are \(r_1\) (Sty)= 0.78 and \(r_2\) (BA) =0.25. The MRR of Sty is much higher than that of BA showing its more reactivity than BA. The random copolymers so obtained, contain a high concentration of alternating sequences, as anticipated by the three times higher value of \(r_1\) than \(r_2\) [Patnaik et al, 1970].
Fig 4.10 (vi) IR Spectrum of copolymer
Fig 4.10 (vii) NMR Spectrum of copolymer [BA] = 1.39 mol/l; 
t = 6 h; [Sty] = 1.748 mol/l; [BrPy] = 6.18 \times 10^{-5} \text{ mol/l}; 
polymn. temp. = 30 \pm 0.2^\circ \text{C.}

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Molar ratio in monomer feed [Sty]/<a href="X">BA</a></th>
<th>Molar ratio in copolymer [Sty]/<a href="Y">BA</a></th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.628</td>
<td>1.079</td>
</tr>
<tr>
<td>2.</td>
<td>0.943</td>
<td>1.381</td>
</tr>
<tr>
<td>3.</td>
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<td>1.659</td>
</tr>
<tr>
<td>4.</td>
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<td>2.012</td>
</tr>
<tr>
<td>5.</td>
<td>2.506</td>
<td>2.690</td>
</tr>
</tbody>
</table>

Table 4.10 (iii) Copolymer Composition
Mechanism

The inhibition to polymerization in the presence of a small quantity of hydroquinone, ESR studies and the kinetics suggest a radical mechanism for BrPy- (BA-co-Sty) system. As evidenced by ESR, the possible radicals generated by the initiator, BrPy, are radical A and bromine. Considering the above facts, a proposed mechanism is as given in Scheme 4.10 (i)

**Initiation**

\[ \text{BrPy} \rightarrow \text{Py-CO-CH}_2^\cdot + \text{Br}^- \]  
(Radical A)

**Scheme 4.10 (i)**
Fig 4.10 (viii) Finemann - Ross plot

Fig 4.10 (ix) Kelen-Tudos plot
Conclusions

The system followed non-ideal kinetics ($R_p \propto [\text{BrPy}]^{0.34}[\text{BA}]^{1.07}[\text{Sty}]^{0.97}$). The non-ideality was attributed to both primary radical termination and degradative initiator transfer. The values of $r_1$ (Sty) and $r_2$ (BA) were found to be 0.78 and 0.25, respectively, which suggested the high concentration of alternating sequences in the random copolymers obtained.

This part of the thesis has been accepted in “Journal of Applied Polymer Science”
4.11 1-(Bromoacetyl)pyrene, a novel photoinitiator for the copolymerization of styrene and acrylonitrile

Sty-AN copolymer is a system of practical interest and has been studied extensively. This sub-chapter discusses the kinetics and mechanism of copolymerization of Sty with AN (Sty-co-AN) using BrPy as photoinitiator. No polymerization was observed, in absence of initiator, by the light employed. The reaction time was selected to give conversions of less than 10% to satisfy the differential copolymerization equation.

The effect of [BrPy] on \( R_p \) was studied by varying its concentration from \( 0.618 \times 10^{-4} \) mol/l to \( 3.09 \times 10^{-4} \) mol/l for a fixed monomer feed ratio (Table 4.11 (i)). \( R_p \) increased with increasing [BrPy], keeping [Sty] and [AN] constant. The initiator exponent calculated from the slope of the plot of log \( R_p \) vs. log [BrPy] was 0.71 (Fig 4.11 (i)). The deviation in the exponent value from 0.5 suggests that the system followed non-ideal kinetics. In order to explain this unusual behavior and to ascertain the nature of the transfer reactions involved, plots of \( R_p^2 / ([BrPy][M]^2) \) vs. \( R_p/[M]^2 \) (Fig 4.11 (ii)), following the equation of Deb [Deb, 1975] were plotted. The positive slope obtained suggested that degradative solvent transfer was mostly operative in the main termination process instead of degradative initiator transfer or primary radical termination [Sengupta, 1982].
Effect of comonomer composition
The effect of Sty concentration on $R_p$ was studied by varying [Sty] from 0.61 mol/l to 1.74 mol/l, keeping [BrPy] and [AN] constant. Similarly, the effect of [AN] on $R_p$ was studied by varying its concentration from 1.06 mol/l to 3.03 mol/l, keeping [BrPy] and [Sty] constant (Table 4.11 (ii)). It was found that $R_p$ increased as concentration of monomer was increased in both cases. The exponent values, calculated from the slope of the linear plot of log $R_p$ versus log [Sty] (Fig 4.11 (iii)) and log $R_p$ versus log [AN] (Fig 4.11 (iv)) were 1.09 and 1.01, respectively.

Characterization of copolymers
Infrared Spectroscopy
The IR spectrum (Fig 4.11 (v)) of copolymer showed band at 3028 cm$^{-1}$ due to aromatic C-H str vibrations, 2926 and 2856 cm$^{-1}$ due to C-H str vibrations of methylene and methine groups, 2238 cm$^{-1}$ due to C=O str vibrations, 1600 cm$^{-1}$ due to aromatic C=C str vibrations, 1450-1390 cm$^{-1}$ due to C-H deformation bands and C-N str vibrations. The characteristic nitrile peaks provide sufficient evidence for the formation of the copolymer.

NMR Spectroscopy
The $^1$H-NMR spectrum of Sty-co-AN (Fig 4.11 (vi)) showed broad peaks at 6.5-7.5 $\delta$ (phenyl ring protons), 2.7-2.9 $\delta$ (-CHCN-), 1.4 -2.6 $\delta$ (-CH$_2$-CH-). The main evidence of the polymer formation is certainly the vanishing of two singlets at 6.3 and 5.8 $\delta$ of the vinyl protons and the appearance of the
broad signal at 2.5-1.7 δ, which is assigned to an aliphatic –CH₂– group [Ilter et al, 2003].

<table>
<thead>
<tr>
<th>S. No.</th>
<th>[BrPy] × 10⁴ (mol/l)</th>
<th>% Conversion</th>
<th>Rp × 10⁶ (mol/l/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.618</td>
<td>2.342</td>
<td>5.070</td>
</tr>
<tr>
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<td>1.236</td>
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</tr>
<tr>
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</tr>
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<td>4.</td>
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<td>6.230</td>
<td>13.488</td>
</tr>
<tr>
<td>5.</td>
<td>3.090</td>
<td>7.422</td>
<td>16.068</td>
</tr>
</tbody>
</table>

Table 4.11 (i) Effect of [BrPy] on Rp. [Sty]= 1.748 mol/l; t =7h;
[AN] = 3.034 mol/l; polymn. temp. = 30 ± 0.2°C.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>[Sty] (mol/l)</th>
<th>[AN] (mol/l)</th>
<th>% Conversion</th>
<th>Rp × 10⁶ (mol/l/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.611</td>
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<td>0.75</td>
<td>1.623</td>
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<tr>
<td>2.</td>
<td>0.874</td>
<td>3.034</td>
<td>1.09</td>
<td>2.359</td>
</tr>
<tr>
<td>3.</td>
<td>1.311</td>
<td>3.034</td>
<td>1.72</td>
<td>3.724</td>
</tr>
<tr>
<td>4.</td>
<td>1.748</td>
<td>3.034</td>
<td>2.34</td>
<td>5.070</td>
</tr>
<tr>
<td>5.</td>
<td>1.748</td>
<td>1.062</td>
<td>3.23</td>
<td>6.999</td>
</tr>
<tr>
<td>6.</td>
<td>1.748</td>
<td>1.517</td>
<td>4.83</td>
<td>10.469</td>
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<tr>
<td>7.</td>
<td>1.748</td>
<td>2.275</td>
<td>6.83</td>
<td>14.789</td>
</tr>
</tbody>
</table>

Table 4.11 (ii) Effect of [Sty] and [AN] on Rp. [BrPy]= 6.18 × 10⁻⁵ mol/l;
t=7h; polymn. temp. = 30 ± 0.2 °C.
Result and Discussion

Fig 4.11 (i) Plot of $\log \text{[BrPy]}$ vs. $\log R_p$. $[\text{Sty}]=1.748 \text{ mol/l}$; $t=7h$; $[\text{AN}]=3.034 \text{ mol/l}$; polynm. temp. $=30 \pm 0.2 ^\circ \text{C}$.

Fig 4.11 (ii) Plot of $R_p^2/[M]^2[\text{BrPy}]$ vs. $R_p/[M]^2$. $[\text{Sty}]=1.748 \text{ mol/l}$; $t=7h$; $[\text{AN}]=3.034 \text{ mol/l}$; polynm. temp. $=30 \pm 0.2 ^\circ \text{C}$.
Fig 4.11 (iii) Plot of log [Sty] vs. log \( R_p \). \( t = 7h; \)
\([\text{BrPy}] = 6.18 \times 10^{-5} \text{ mol/l}; \) polyln. temp. = 30 ± 0.2 °C.

Fig 4.11 (iv) Plot of log [AN] vs. log \( R_p \). \( t = 7h; \)
\([\text{BrPy}] = 6.18 \times 10^{-5} \text{ mol/l}; \) polyln. temp. = 30 ± 0.2 °C.
Result and Discussion

Fig 4.11 (v) IR Spectrum of Sty-co-AN

Fig 4.11 (vi) NMR Spectrum of Sty-co-AN. [Sty] = 1.748 mol/l; [AN] = 3.034 mol/l; [BrPy] = 6.18 x 10^{-5} mol/l; t = 7h; polymn. temp. = 30 ± 0.2°C.
Copolymer composition and monomer reactivity ratio

$^1$H NMR spectra have not been used for the determination of the monomer content in the copolymers since signals from different monomeric units overlap with each other. Elemental analysis was considered to be an accurate method for the determination of copolymer composition. Hence, the copolymer composition was calculated from the percentage of nitrogen in the copolymers (Table 4.11 (iii)).

The Finemann–Ross (FR) and Kelen-Tudos (KT) plots are given in Fig 4.11 (vii) and Fig 4.7 (viii), respectively. The reactivity ratios as calculated by FR method are $r_1$ (Sty) = 0.39 and $r_2$ (AN) =0.05 while the reactivity ratios as calculated by KT method are $r_1$ (Sty) = 0.38 and $r_2$ (AN) =0.05 [Gowarikar, 2000]. Since the product of $r_1$ and $r_2$ is approximately zero, the two monomers enter in almost alternating arrangement along the copolymer chain [Odián, 2002, 461].

Mechanism

The inhibition to polymerization in the presence of a small quantity of hydroquinone, ESR studies and the kinetics suggest a radical mechanism for Sty-co-AN system. As evidenced by ESR, the possible radicals generated by the initiator, BrPy, are radical A and bromine. Both Br and radical A have the probability of initiating the polymerization reaction. Considering the above facts, a proposed mechanism is as given in Scheme 4.11 (i).
## Result and Discussion

### Table 4.11 (iii) Copolymer Composition

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Mol fraction of AN in feed (M₂)</th>
<th>N(%)</th>
<th>Mol fraction of AN in copolymer (m₂)</th>
<th>Molar ratio in monomer feed [Sty]/<a href="X">AN</a></th>
<th>Molar ratio in copolymer [Sty]/<a href="Y">AN</a></th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.465</td>
<td>7.11</td>
<td>0.419</td>
<td>1.150</td>
<td>1.386</td>
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<td>2.</td>
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<td>7.82</td>
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<td>1.217</td>
</tr>
<tr>
<td>3.</td>
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<td>8.25</td>
<td>0.471</td>
<td>0.574</td>
<td>1.123</td>
</tr>
<tr>
<td>4.</td>
<td>0.699</td>
<td>8.68</td>
<td>0.489</td>
<td>0.4306</td>
<td>1.045</td>
</tr>
<tr>
<td>5.</td>
<td>0.777</td>
<td>9.26</td>
<td>0.514</td>
<td>0.287</td>
<td>0.945</td>
</tr>
</tbody>
</table>

**Fig 4.11 (vii) Finemann –Ross plot**
Fig 4.11 (viii) Kelen-Tudos plot

**Initiation**

\[
\text{BrPy} \rightarrow \text{Py-CO-CH}_2^+ + \text{Br}^- \\
\text{(Radical A)}
\]

\[
\begin{align*}
\text{Br}^- \text{ Or radical A } + \\
\text{CN} & \rightarrow \text{CN} \\
\end{align*}
\]

\[
\begin{align*}
\text{Br}^- \text{ Or radical A } + \\
\text{Ph} & \rightarrow \text{Ph} \\
\end{align*}
\]

**Scheme 4.11 (i)**
Conclusion
The kinetic data, inhibiting effect of benzoquinone and ESR studies suggest that the polymerization proceeds via a free radical mechanism. The system follows non-ideal kinetics ($R_p \alpha [\text{BrPy}]^{0.7}[\text{Sty}]^{1.09}[\text{AN}]^{1.01}$) and degradative solvent transfer reasonably explains these kinetic non-idealities. The co-monomer reactivity ratios calculated by using the Finemann-Ross and Kelen-Tudos models were $r_1 (\text{Sty}) = 0.39$ and $r_2 (\text{AN}) = 0.05$. The reactivity ratios strongly indicate that the two monomers enter in almost alternating arrangement along the copolymer chain.

This part of the thesis has been communicated for publication to “Journal of Applied Polymer Science”.