CHAPTER - II
A volumetric literature on different aspects like kinetics & mechanism [214], influence of the reaction medium [215], temperature [216] & solvent [217,218] etc. on copolymerization of methylethacrylate with styrene initiated by conventional radical initiators like $\alpha$-$\alpha'$-azobisisobutyronitrile (AIBN), benzoylperoxide (BPO) etc. is available. However, the data regarding potential applications of ylides in polymer sciences is scarce until a few reports from this laboratory have been published recently. The ylides can be used as new novel initiators because their interaction with vinyl monomers may lead to formation of free radicals via triplet carbene due to presence of $p\pi$ - $d\pi$ bonding. The present article reports the kinetic & mechanism of copolymerization of methylethacrylate with styrene initiated by imidazolium p.chlorophenacylride (ICPY) in DMSO for 120 minutes at 90±1°C. The copolymer has been characterized by elemental analysis, IR , $^1$H-NMR spectroscopy. The thermal stability and chemical resistance (towards different solvents, acids and base) of the copolymer have also been studied.

No polymer was obtained when the polymerization runs were carried out below 80°C for 120 minutes.

* A part of this work is under revision for publication in "Polymer", published by Butler Worth Heineman Ltd. Oxford (U.K.).
However, polymerization occurred at 90±1°C. The volume contraction was converted into percentage conversion by master graph (Fig.IV:2:1). The copolymer, precipitated with acidified methanol and dried to constant weight, was refluxed in soxhlet apparatus with acetonitrile and cyclohexane in order to remove homopolymers of MMA & Sty. respectively.

(I) Effect of [ICPY]:

The effect of [ICPY] on the rate of copolymerization has been studied by varying it's concentration from 0.75x10^{-3} to 15.5x10^{-3} mol l^{-1}, keeping the [monomer(s)] ratio constant ([Sty.] = 1.9 mol l^{-1} & [MMA] = 1.8 mol l^{-1}) It has been noted that 22.6x10^{-3} mol l^{-1} of [ICPY] initiated copolymerization with a maximum conversion of 4.16% at 90±1°C. The copolymerization runs were associated with short induction period of about (2 to 9 minutes) depending upon [ICPY] (Fig.IV:2:2).

(A) On volume concentration, percentage conversion and rate of polymerization:

An examination of Figs.IV:2:2 & IV:2:3 and tables IV:2:1 to IV:2:2 shows that the values of volume concentration ($V_c$), percentage conversion ($P_c$) and rate of polymerization ($R_p$) increase with increasing [ICPY] from 0.75x10^{-3} to 15.5x10^{-3} mol l^{-1}.
FIG. IV:2:1 MASTER GRAPH: COPOLYMERIZATION OF MMA WITH STY. INITIATED BY ICXY
FIG. IV:2:2 TIME-CONVERSION PLOTS FOR THE COPOLYMERIZATION OF STY. WITH MMA INITIATED BY [ICPY]
The order of reaction with respect to [ICPY] evaluated from the least square method (L.S.M.) is 0.18±0.01 (Fig.IV:2:3) upto 15.3x10^-3 mol l^-1. This is low in comparison to 0.5 for ideal radical kinetics i.e. the system follows non-ideal kinetics.

(B) Non-ideality:

Various theories to account for the non-ideality have been proposed but with limited success. The low initiator [ICPY] exponent value suggests that non-ideality may be due to degradative chain-transfer to [ICPY].

The plot of the left side of the Deb & Myerhoff equation, log Rp^2/[Y][M]^2 Vs [I]/[M] (Fig.IV:2.4) has negative slope, indicating degradative initiator transfer.

(C) On average degree of polymerization ($\bar{P}_n$):

It is clear from the table IV:2:3 that the values of $\bar{P}_n$ decrease gradually as the concentration of [ICPY] increases. However, $\bar{P}_n$ remains constant with overall polymerization time although conversion increases. These facts indicate that the system has attained steady state and polymerization proceeds through radical species.

The plot of reciprocal average degree of polymerization against the square root of initiator
FIG. IV:2:3 PLOT OF $\log R_p$ VS. $\log [ICPY]$ FOR THE COPOLYMERIZATION OF STY. WITH MMA INITIATED BY ICPY USING $1.9 \text{ mol} \cdot \text{L}^{-1}$ [STY.], AND $1.8 \text{ mol} \cdot \text{L}^{-1}$ OF [MMA]
FIG. IV:2.4 PLOT OF $\log \frac{R_p^2}{[I][M]^2}$ VS. $R_p/[M]^2$ (NON-IDEAL) FOR THE COPOLYMERIZATION OF STY. WITH MMA INITIATED BY ICPY.
concentration (Fig.IV:2:5) gives straight line passing through the origin, which confirms that ICPY initiated copolymerization is brought about by a radical mechanism with bimolecular termination.

(D) Determination of $k_p^2/k_t$ value:

The absence of an intercept of $1/R_n$ axis is the plot of $1/R_n$ Vs $R_p$ indicated negligible initiator and monomer transfer. Therefore, the value of $k_p^2/k_t$, calculated from slope of linear plot (Fig.IV:2:5) is $1.0 \times 10^{-2} \text{ mol s}^{-1}$.

(II) Determination of energy of activation ($\Delta E$):

The values of $R_p$ at different temperatures have been used to calculate the energy of activation from Arrhenius plot (Fig.IV:2:6) is 26 kJ mol$^{-1}$. The value is low in comparison of conventional free radical initiators like $\alpha,\alpha'$-azobisisobutyronitrile, benzoylperoxide.

(III) Effect of [Monomers]:

The influence of monomer ratio on $R_p$ has been studied by keeping concentration of ICPY ($7.5 \times 10^{-5} \text{ mol l}^{-1}$) constant at $90\pm1^\circ C$ for 120 minutes.

(A) Effect of [Styrene]:

In order to examine the effect of [Sty.], the experiments have been carried out by varying its concentration of styrene from 1.32 to 2.88 mol l$^{-1}$, keeping the
FIG. IV:2.5 PLOT OF $\frac{1}{\bar{P}_n}$ VS. $\frac{R_p}{[M]^2}$ FOR THE COPOLYMERIZATION OF STY. WITH MMA INITIATED BY ICPY
FIG. IV: 2: 6 TIME Vs. CONVERSION PLOTS FOR THE
COPOLYMERIZATION OF STY. WITH MMA
INITIATED BY ICPY USING 7.5 x 10^{-3}
·mol l^{-1} OF [ICPY] AND 1.8 mol l^{-1}
of [MMA]
initiator concentration and methylmethacrylate concentration constant ([ICPY] = 7.5x10^{-5} mol l^{-1} & [MMA] = 1.8 mol l^{-1})

(a) On volume contraction, percentage conversion and rate of copolymerization:

A study of results presented in tables IV:2:4 & IV:2:5 and Fig. IV:2:7 reveals that the values of \( V_c \), \( P_c \) and \( R_p \) increase with [Sty.]. It can be explained on the basis of resonance stabilization of styryl radicals.

The order of reaction with respect to [Sty.], calculated from slope of log \( R_p \) Vs log[Sty.], is unity (Fig.IV:2:8).

(b) Effect of average degree of polymerization (\( \bar{P}_n \)) on [Styrene]:

It is clear from the table IV:2:5 that the values of average degree of polymerization increase gradually as the concentration of styrene increases. However \( \bar{P}_n \) remains constant with overall polymerization time although conversion increases.

(B) Effect of [Methylmethacrylate]:

With a view to obtain informations regarding effect of [MMA] on rate of monomer disappearance, the copolymerization runs have been carried out by varying it's concentration from 1.2 mol l^{-1} to 3.0 mol l^{-1} at 90±1°C for 120 minutes keeping 7.5x10^{-5} mol l^{-1} of [ICPY] and 1.8 mol l^{-1} of [Sty.] constant.
FIG. IV: 2: 7 TIME VS. PERCENTAGE CONVERSION PLOTS FOR THE COPOLYMERIZATION OF STYRENE WITH MMA INITIATED BY ICPY USING 7.5x10^{-3} mol l^{-1} OF [ICPY] AND 1.8 mol l^{-1} OF [MMA]
FIG. IV:2:8 PLOT OF LOG $R_P$ VS [STY.] FOR THE COPOLYMERIZATION OF STY. WITH MMA INITIATED BY ICPY USING $7.5 \times 10^{-3}$ mol l$^{-1}$ OF [ICPY] AND 1.8 mol l$^{-1}$ OF [MMA]
(a) **On volume concentration, percentage conversion and rate of copolymerization:**

A study of results presented in tables IV:2:6 and IV:2:7 and Fig.IV:2:9 reveals that the values of $V_C$, $P_C$ and $R_P$ have increasing trend with increase of [MMA] in the system.

It is attributed to the fact that as [MMA] increase in the system, the [MMA'] also increases, which cause an increase in rate of polymerization.

The order of reaction with respect of [MMA], determined from the slope of the linear plot between $\log R_P$ Vs $\log$[MMA] (Fig.IV:2:10) is computed as unity.

(b) **Effect of average degree of polymerization ($\overline{P_n}$) on [MMA]:**

A study of results presented in the table IV:2:7 that the values of $\overline{P_n}$ of copolymerization increase gradually as the [MMA] increases. However $\overline{P_n}$ remains constant with overall polymerization time although conversion increases.

(IV) **Effect of [Additives] on copolymerization:**

To confirm the radical mode of copolymerization, the effect of hydroquinone on copolymerization was also studied. The copolymerization was retarded in the presence of hydroquinone. An examination of table IV:2:8 further reveals that as we go down the table, rate of
FIG. IV: 2.9 TIME VS. PERCENTAGE CONVERSION PLOTS FOR THE COPOlYMERIZATION OF STY. WITH MMA INITIATED BY ICpy USING 7.5x10^{-3} mol l^{-1} OF [ICPy] AND 1.9 mol l^{-1} OF [STY].
FIG. IV: 2:10 PLOT OF $\log R_p$ VS. $[\text{MMA}]$ FOR THE COPOLYMERIZATION OF STY. WITH MMA INITIATED BY ICPY USING $7.5 \times 10^{-3}$ mol l$^{-1}$ of [ICPY] AND 1.9 mol l$^{-1}$ OF [STY.]
copolymerization increases because polarity of the solvents (toluene, xylene, dioxane) increase which might have favoured the free radical formation from ylide.

(V) **Solubility effect of copolymer film:**

The effect of solubility in the copolymer film of various solvent, acids like HCl, H₂SO₄, HNO₃ and bases like NaOH was examined to check the solubility and chemical resistance of the copolymer film. An examination of table IV:2:9 shows the solubility of copolymer films.

(VI) **Thermogravimetric analysis (T.G.A.) of copolymer:**

Thermal stability of copolymer was studied by thermogravimetric analysis (Fig.IV:2:11). Copolymer is stable upto 70°C and started decomposing after this temperature. The initial weight loss (3.5%) was observed around 90°C and around 150°C, 30 to 35% weight loss was noted (table IV:2:10).

(VII) **Differential scanning calorimetry (D.S.C.) of copolymer:**

The glass transition temperature (Tg) was studied by differential scanning calorimetry (Fig.IV:2:12). The glass transition temperature (Tg) of copolymer is 103°C.
FIG. IV:2:11 T.G.A. THERMOGRAM OF COPOLYMER OF STY.
WITH MMA INITIATED BY ICPY CONTAINING
7.5x10⁻³ mol 1⁻¹ OF [ICPY], 1.9 mol 1⁻¹
OF [MMA]
(VIII) **Spectral studies:**

(A) **Infrared spectrum:**

Fig.IV:2:13 represents the IR spectrum copolymer of MMA with Sty. initiated by ICPY. It consists of following groups of bands:

(i) The appearance of two bands at 3030 and 3075 cm\(^{-1}\) is assigned to aromatic C-H, stretching vibrations.

(ii) The C-H stretching vibrations of methyl, methylene and methyne groups are in the region 2850 to 2940 cm\(^{-1}\).

(iii) The >C=O stretching vibrations of ester carbonyl is in region 1600 cm\(^{-1}\).

(iv) The range of band stretching vibration of phenyl ring shows two bands at 1490 & 1530 cm\(^{-1}\).

(v) C-H deformation appears at 1520 cm\(^{-1}\).

(vi) The C-O-C stretching band appear at 1220 cm\(^{-1}\) as a sharp peak.

(vii) The band at extreme right 730 cm\(^{-1}\) is due to out of phenyl ring deformation.

(B) \(^1\)H-NMR spectrum:

NMR spectrum of copolymer have been used to elucidate the structure, composition, reactivity ratio and stereo chemistry of copolymers.
FIG. IV:2:13 IR SPECTRUM OF STY. MMA COPOLYMER PREPARED BY USING $7.5 \times 10^{-3}$ \text{ mol l}^{-1} \text{ of [ICPY]}, $1.9 \text{ mol l}^{-1} \text{ of [STY.]}$ AND $1.8 \text{ mol l}^{-1} \text{ of [MMA]}$
The NMR spectra of copolymers are shown in Fig.IV:2:14 to IV:2:17, in which the phenyl protons appear at 6.8-7.0 $\delta$ ppm, the methyl protons at 2.0-2.86 $\delta$ ppm, the methoxy protons at 3.0 to 4.0 $\delta$ ppm at 3.4 $\delta$ ppm. The overlapping in region of 1.0 to 2.0 $\delta$ ppm is due to methyne and methyne protons. The appearance of methoxy protons as single peak (3.5 $\delta$ ppm) as mentioned above, shows that the copolymer is random in nature because in case of alternate copolymers, the methoxy protons appear as three splitted peaks. The ratio of aromatic to aliphatic protons is 5:11, which shows that the ylide (ICPY) is not incorporated in the copolymer.

(a) Copolymer composition:

The phenyl protons (Sty.) and methoxy protons (MMA) mol fraction in copolymer, calculated from peak area between 6.8 to 7.5 $\delta$ ppm and 3.2 to 3.6 respectively have been reported in table IV:2:11. The relative peak area due to phenyl and methyl protons has been used to calculate the copolymer composition. Styrene content in the copolymer of styrene occurs.

(b) Reactivity ratios:

The copolymer composition data have also been used to calculate the reactivity ratios (Fig.IV:2:18) using Fineman-Ross method, as 0.066 ($r_1$) and 0.10 ($r_2$) for copolymerization of MMA with styrene respectively. These values match well with those reported for radical
FIG.IV:2:14 $^1H$-NMR SPECTRUM OF MMA-STY. COPOLYMER PREPARED BY USING $7.5 \times 10^{-3}$ mol l$^{-1}$ OF [ICPY], 1.9 mol l$^{-1}$ OF [STY.] AND 1.8 mol l$^{-1}$ OF [MMA]
$\text{H-NMR spectrum of MMA-STY. copolymer prepared by using 7.5:10}^{-3}$

mol \text{1}\text{L}^{-1} \text{of} \text{[ICP]} 1\text{.9 mol}\text{1}\text{L}^{-1} \text{and 1.2 mol}\text{1}\text{L}^{-1} \text{of} \text{[MMA]}$
FIG. IV:2:16 $^1$H-NMR SPECTRUM OF MMA-STY. COPOLYMER PREPARED BY USING $7.5 \times 10^{-3}$ mol l$^{-1}$ OF [ICPY], 1.9 mol l$^{-1}$ OF [STY] AND 3.0 mol l$^{-1}$ OF [MMA]
FIG. IV:2:17 $^1$H-NMR SPECTRUM OF MMA-STY. COPOLYMER PREPARED BY USING 7.5x10^{-3} mol l$^{-1}$ OF [ICPY], 1.32 mol l$^{-1}$ OF [STY.] AND 1.8 mol l$^{-1}$ OF [MMA]
FIG. IV:2:18 PLOT OF $F/f(f-1)$ VS $F^2/f$ OF FINEMAN-ROSS METHOD FOR COPOLYMERIZATION OF STY. WITH MMA INITIATED BY ICPY FROM COPOLYMER COMPOSITION DATA
copolymserization of MMA with Sty. (table IV:2:11).

(c) Stereochemistry:

Theoretically, there are four kinds of trend along a copolymer chain, i.e. MMA, MMS, SMM and SMS where M and S represent MMA and Sty. units respectively. Each triad may be written as consisting of four kinds of configurations, employing the representation of Nishioka et al. [219].

\[
\begin{align*}
\text{MMM} & : \quad \begin{array}{c}
\text{MMM} \\
\text{MMM} \\
\text{MMM}
\end{array} \\
& \quad \begin{array}{c}
\text{M} \\
\text{M}
\end{array} \\
& \quad \begin{array}{c}
\text{M} \\
\text{M}
\end{array} \\
& \quad \begin{array}{c}
\text{M} \\
\text{M}
\end{array}
\end{align*}
\]

(1) (2) (3) (4)

\[
\begin{align*}
\text{MMS} & : \quad \begin{array}{c}
\text{MMS} \\
\text{MMS} \\
\text{MMS}
\end{array} \\
& \quad \begin{array}{c}
\text{M} \\
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& \quad \begin{array}{c}
\text{M} \\
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\end{array} \\
& \quad \begin{array}{c}
\text{M} \\
\text{M}
\end{array}
\end{align*}
\]

(5) (6) (7) (8)

\[
\begin{align*}
\text{SMM} & : \quad \begin{array}{c}
\text{SMM} \\
\text{SMM} \\
\text{SMM}
\end{array} \\
& \quad \begin{array}{c}
\text{S} \\
\text{M}
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& \quad \begin{array}{c}
\text{S} \\
\text{M}
\end{array} \\
& \quad \begin{array}{c}
\text{S} \\
\text{M}
\end{array}
\end{align*}
\]

(9) (10) (11) (12)

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\begin{align*}
\text{SMS} & : \quad \begin{array}{c}
\text{SMS} \\
\text{SMS} \\
\text{SMS}
\end{array} \\
& \quad \begin{array}{c}
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& \quad \begin{array}{c}
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\text{S}
\end{array}
\end{align*}
\]

(13) (14) (15) (16)

The appearance of methoxy protons as single peak in NMR point out that it is possible to distinguish three main
kind of MMA units spectroscopically, as suggested by Bovey [220] for MMA-Sty. copolymer prepared with the help of ICPY. The structure (1), (2), (3), (4), (5), (6), (7) and (10) seems to constitute peak at 3.4-3.6 ppm, giving rise to peak II at the lowest field region of the methoxy resonance because the configurations of the neighbouring S. units in the structure (6), (7) and (10) are opposite to those of the central M units of interest, so that the diamagnetic shielding by such S units may be little enough. Similarly, the triads (11) and (12) are responsible for peak at 2.0-2.86 ppm and triads (5), (8) and (9) are for peak at 2.8 ppm, respectively.

(IX) **Mechanism:**

The value, kinetic data and the inhibitory effect of hydroquinone indicate that copolymerization of MMA with styrene, initiated by (ICPY) ylide, proceeds by a radical mechanism.

The radical generation process can be explained on the basis of the fact that ICPY (ylide) dissociates to a triplet carbene (a) [221] which acts as a source of radicals. The triplet carbene reacts with monomer (MMA) to form a diradical (b) [222, 223] which further decomposes into two radicals (c) and (d).
(A) Radical generated and initiation:

(i) $\text{Cl} - \begin{array}{c} \text{O} \\ \text{N} \\ \text{H} \end{array} - \text{C-CH} - \text{N} \longrightarrow \begin{array}{c} \text{Cl} \\ \text{O} \end{array} - \text{C-CH} + \begin{array}{c} \text{N} \\ \text{H} \end{array}$

triplet corbene (Ia)

$\text{CH}_3$

$\text{CH}_2 = \text{C-COOCH}_3$

(ii) $\text{CH}_2 = \text{C} + \text{H}^* 
\text{COOCH}_3 
\longrightarrow 
\text{CH}_3 - \text{C}^* 
\text{COOCH}_3$

(M_1)

(M_1)

(iii) $\text{CH}_2 = \text{CH} + \text{CH}_3 - \text{C}^* 
\text{COOCH}_3 
\longrightarrow 
\text{CH}_3 - \text{C} - \text{CH}_2 - \text{CH}_3$

(M_2)

(M_1)

(M_2)

(iv) $\text{CH}_3 - \text{C} - \text{CH}_2 - \text{CH} + \text{CH}_2 = \text{C} 
\text{COOCH}_3 
\text{COOCH}_3 
\downarrow 
\text{CH}_3 - \text{C} - \text{CH}_2 - \text{CH}_2 - \text{C}^* 
\text{COOCH}_3 
\text{COOCH}_3$
(B) Propogation:

(I) \[ \text{CH}_3 - \text{C} - \text{CH}_2 - \text{CH}_2 - \text{C}^\cdot + \text{CH}_2 = \text{CH}_2 = \text{C}^\cdot + \text{COOCH}_3 \]

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\[ \text{COOCH}_3 \]

\[ \text{COOCH}_3 \]

\[ \text{COOCH}_3 \]

\[ \text{COOCH}_3 \]

\[ \text{COOCH}_3 \]

\[ \text{COOCH}_3 \]

\[ \text{COOCH}_3 \]

\[ \text{COOCH}_3 \]

\[ \text{COOCH}_3 \]

\[ \text{COOCH}_3 \]

\[ \text{COOCH}_3 \]

\[ \text{COOCH}_3 \]

\[ \text{COOCH}_3 \]

\[ \text{COOCH}_3 \]

\[ \text{COOCH}_3 \]

\[ \text{COOCH}_3 \]

\[ \text{COOCH}_3 \]

\[ \text{COOCH}_3 \]

\[ \text{COOCH}_3 \]

\[ \text{COOCH}_3 \]

\[ \text{COOCH}_3 \]

\[ \text{COOCH}_3 \]

\[ \text{COOCH}_3 \]

\[ \text{COOCH}_3 \]

\[ \text{COOCH}_3 \]

\[ \text{COOCH}_3 \]

\[ \text{COOCH}_3 \]
Conclusion:

On the basis of experimental facts, it is concluded that imidazolium p.chlorophenacylidyde (ICPY) radically initiates the copolymerization of MMA with styrene. The copolymer is random in nature. The system follows non-ideal kinetics due to degradative initiator transfer which is formulated as given below:

\[ R_p \propto [ICPY]^{0.18\pm0.01} [Sty.]^{1.0} [MMA]^{1.0} \]
<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>[ICPY] $\times 10^3$ mol l$^{-1}$</th>
<th>Volume Contraction (Cms)</th>
<th>Polymerization time (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>15</td>
</tr>
<tr>
<td>1</td>
<td>0.75</td>
<td></td>
<td>0.057</td>
</tr>
<tr>
<td>2</td>
<td>1.5</td>
<td></td>
<td>0.061</td>
</tr>
<tr>
<td>3</td>
<td>3.0</td>
<td></td>
<td>0.063</td>
</tr>
<tr>
<td>4</td>
<td>4.5</td>
<td></td>
<td>0.067</td>
</tr>
<tr>
<td>5</td>
<td>7.5</td>
<td></td>
<td>0.078</td>
</tr>
<tr>
<td>6</td>
<td>9.0</td>
<td></td>
<td>0.080</td>
</tr>
<tr>
<td>7</td>
<td>10.5</td>
<td></td>
<td>0.087</td>
</tr>
<tr>
<td>8</td>
<td>13.5</td>
<td></td>
<td>0.098</td>
</tr>
<tr>
<td>9</td>
<td>15.5</td>
<td></td>
<td>0.122</td>
</tr>
</tbody>
</table>

Polymerization conditions:

[Sty.] = 1.9 mol l$^{-1}$

[MMA] = 1.8 mol l$^{-1}$

Solvent = DMSO

Temp. = 90 ±0.1°C
### Table IV:2:2

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>$[\text{ICPY}] \times 10^3$</th>
<th>Initial wt. of copolymer (gm)</th>
<th>Solvent Treatment (Weight loss in gm)</th>
<th>Conversion $^2$</th>
<th>$R_p \times 10^5$</th>
<th>mol l$^{-1}$s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.75</td>
<td>0.0428</td>
<td>0.0419</td>
<td>0.0350</td>
<td>3.08</td>
<td>1.50</td>
</tr>
<tr>
<td>2</td>
<td>1.5</td>
<td>0.0403</td>
<td>0.0378</td>
<td>0.0353</td>
<td>3.11</td>
<td>1.66</td>
</tr>
<tr>
<td>3</td>
<td>3.0</td>
<td>0.0413</td>
<td>0.0381</td>
<td>0.0368</td>
<td>3.24</td>
<td>1.70</td>
</tr>
<tr>
<td>4</td>
<td>4.5</td>
<td>0.0427</td>
<td>0.0408</td>
<td>0.0353</td>
<td>3.27</td>
<td>1.78</td>
</tr>
<tr>
<td>5</td>
<td>7.5</td>
<td>0.0480</td>
<td>0.0468</td>
<td>0.0422</td>
<td>3.64</td>
<td>1.85</td>
</tr>
<tr>
<td>6</td>
<td>9.0</td>
<td>0.0519</td>
<td>0.0473</td>
<td>0.0433</td>
<td>3.86</td>
<td>2.00</td>
</tr>
<tr>
<td>7</td>
<td>10.5</td>
<td>0.0529</td>
<td>0.0481</td>
<td>0.0411</td>
<td>3.91</td>
<td>2.20</td>
</tr>
<tr>
<td>8</td>
<td>13.5</td>
<td>0.0493</td>
<td>0.0483</td>
<td>0.0455</td>
<td>4.01</td>
<td>2.46</td>
</tr>
<tr>
<td>9</td>
<td>15.5</td>
<td>0.0505</td>
<td>0.0489</td>
<td>0.0468</td>
<td>4.16</td>
<td>2.65</td>
</tr>
</tbody>
</table>

Polymerization conditions:

- $[\text{Sty.}] = 1.9$ mol l$^{-1}$
- $[\text{MMA}] = 1.8$ mol l$^{-1}$
- Solvent = DMSO
- Time = 120 minutes
- Temp. = 90 ± 0.1°C

$^*1$ - Used to calculated percentage conversion.

$^*2$ - Used to calculate rate of polymerization.
Table IV:2:3

Effect of [ICPY] on average degree of polymerization for copolymerization of MMA with Sty. initiated by ICPY.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>[ICPY]x10^3 mol l^{-1}</th>
<th>( \bar{P}_n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.75</td>
<td>250</td>
</tr>
<tr>
<td>2</td>
<td>1.5</td>
<td>222</td>
</tr>
<tr>
<td>3</td>
<td>3.0</td>
<td>200</td>
</tr>
<tr>
<td>4</td>
<td>4.5</td>
<td>184</td>
</tr>
<tr>
<td>5</td>
<td>7.5</td>
<td>157</td>
</tr>
<tr>
<td>6</td>
<td>9.0</td>
<td>143</td>
</tr>
<tr>
<td>7</td>
<td>10.5</td>
<td>116</td>
</tr>
<tr>
<td>8</td>
<td>13.5</td>
<td>96</td>
</tr>
<tr>
<td>9</td>
<td>15.5</td>
<td>79</td>
</tr>
</tbody>
</table>

Polymerization conditions:

\[ \text{[Styrene]} = 1.9 \text{ mol l}^{-1} \]
\[ \text{[MMA]} = 1.8 \text{ mol l}^{-1} \]
\[ \text{Solvent} = \text{DMSO} \]
\[ \text{Time} = 120 \text{ minutes} \]
\[ \text{Temp.} = 90 \pm 0.1^\circ\text{C} \]
### Table IV:2:4

Effect of [Styrene] on volume contraction for the copolymerization of Sty. with MMA initiated by ICPY

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>[Styrene] mol l$^{-1}$</th>
<th>Volume Contraction (Cms)</th>
<th>Polymerization time (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>15</td>
</tr>
<tr>
<td>1</td>
<td>1.32</td>
<td></td>
<td>0.063</td>
</tr>
<tr>
<td>2</td>
<td>1.90</td>
<td></td>
<td>0.079</td>
</tr>
<tr>
<td>3</td>
<td>2.40</td>
<td></td>
<td>0.085</td>
</tr>
<tr>
<td>4</td>
<td>2.88</td>
<td></td>
<td>0.089</td>
</tr>
</tbody>
</table>

Polymerization conditions:

- $[ICPY] = 7.5 \times 10^{-3}$ mol l$^{-1}$
- $[MMA] = 1.8$ mol l$^{-1}$
- Solvent = DMSO
- Temp. = $90 \pm 0.1 ^\circ C$
Table IV:2.5

Effect of [Styrene] on the rate of polymerization

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>[Styrene] mol(^{-1})</th>
<th>Initial weight in gm</th>
<th>Solvent Treatment</th>
<th>Weight loss in gm</th>
<th>Polymerization conditions:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cyclo-hexane</td>
<td>Aceto-nitrile</td>
<td></td>
<td>[ICPy] = 7.5 × 10(^{-3}) mol l(^{-1})</td>
</tr>
<tr>
<td>1</td>
<td>1.32</td>
<td>0.0376</td>
<td></td>
<td></td>
<td>[MMA] = 1.8 mol l(^{-1})</td>
</tr>
<tr>
<td>2</td>
<td>1.90</td>
<td>0.0451</td>
<td></td>
<td></td>
<td>Solvent = DMSO</td>
</tr>
<tr>
<td>3</td>
<td>2.40</td>
<td>0.0483</td>
<td></td>
<td></td>
<td>Temp. = 90 ± 0.1°C</td>
</tr>
<tr>
<td>4</td>
<td>2.88</td>
<td>0.0503</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Conversion \(*1\) = \frac{P_{n}}{P_{n}^{1/2}} \times 10\(^5\) mol l\(^{-1}\) s\(^{-1}\)

% Conversion \(*2\) = \frac{P_{n}}{P_{n}^{1/2}} \times 10\(^5\) mol l\(^{-1}\) s\(^{-1}\)

*1 = Used to calculate percentage conversion.
*2 = Used to calculate percentage polymerization.
Table IV.2:6

Effect of [MMA] on volume contraction for the copolymerization of Sty. with MMA initiated by ICPY

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>[MMA] mol l(^{-1})</th>
<th>Volume contraction (Cms)</th>
<th>Polymerization time (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>15</td>
</tr>
<tr>
<td>1</td>
<td>1.2</td>
<td>0.059</td>
<td>0.196</td>
</tr>
<tr>
<td>2</td>
<td>1.8</td>
<td>0.080</td>
<td>0.217</td>
</tr>
<tr>
<td>3</td>
<td>2.4</td>
<td>0.099</td>
<td>0.242</td>
</tr>
<tr>
<td>4</td>
<td>3.10</td>
<td>10.130</td>
<td>0.270</td>
</tr>
</tbody>
</table>

Polymerization conditions:

- [ICPY] = 7.5 \times 10^{-3} \text{ mol l}^{-1}
- [Styrene] = 1.9 \text{ mol l}^{-1}
- Solvent = DMSO
- Temp. = 90 \pm 0.1^\circ C
Table IV:2:7

Effect of [Methylmethacrylate] on the rate of polymerization

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>[MMA] mol l⁻¹</th>
<th>Initial weight in gm</th>
<th>Solvent Treatment (weight loss in gm)</th>
<th>Conversion *¹ (%)</th>
<th>R x 10⁵ mol l⁻¹s⁻¹</th>
<th>Pₙ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cyclohexane</td>
<td>Acetonitrile</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1.2</td>
<td>0.0370</td>
<td>0.0357</td>
<td>0.0350</td>
<td>3.11</td>
<td>1.32</td>
</tr>
<tr>
<td>2</td>
<td>1.8</td>
<td>0.0451</td>
<td>0.0439</td>
<td>0.0422</td>
<td>3.64</td>
<td>1.85</td>
</tr>
<tr>
<td>3</td>
<td>2.4</td>
<td>0.0496</td>
<td>0.0483</td>
<td>0.0460</td>
<td>4.08</td>
<td>2.47</td>
</tr>
<tr>
<td>4</td>
<td>3.0</td>
<td>0.0662</td>
<td>0.0647</td>
<td>0.0636</td>
<td>5.63</td>
<td>3.46</td>
</tr>
</tbody>
</table>

Polymerization conditions:

[ICPY] = 7.5 x 10⁻³ mol l⁻¹

[Styrene] = 1.9 mol l⁻¹

Solvent = DMSO

Temp. = 90 ± 0.5°C

*¹ - Used to calculate percentage conversion.

*² - Used to calculate percentage polymerization
Table IV:28

Effect of [Additives] on copolymerization of methylmethacrylate with Styrene initiated by ICPY

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Additives</th>
<th>[Additives] mol l(^{-1})</th>
<th>Initial wt* in gm</th>
<th>Solvent Treatment (Weight loss in gm)</th>
<th>Conversion *1 (%)</th>
<th>(R_p \times 10^5) mol l(^{-1}) s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Hydroquinone</td>
<td>0.00</td>
<td>0.0480</td>
<td>0.0468</td>
<td>0.0422</td>
<td>3.64</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.06x10(^{-3})</td>
<td>0.0392</td>
<td>0.0378</td>
<td>0.0366</td>
<td>3.24</td>
</tr>
<tr>
<td>2</td>
<td>Toluene</td>
<td>0.62</td>
<td>0.0483</td>
<td>0.0474</td>
<td>0.0463</td>
<td>3.62</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.55</td>
<td>0.0660</td>
<td>0.0643</td>
<td>0.0634</td>
<td>5.63</td>
</tr>
<tr>
<td>3</td>
<td>Xylene</td>
<td>0.54</td>
<td>0.0437</td>
<td>0.0418</td>
<td>0.0356</td>
<td>3.10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.34</td>
<td>0.0520</td>
<td>0.0493</td>
<td>0.0458</td>
<td>4.03</td>
</tr>
<tr>
<td>4</td>
<td>Dioxane</td>
<td>0.75</td>
<td>0.0607</td>
<td>0.0595</td>
<td>0.0578</td>
<td>5.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.52</td>
<td>0.0669</td>
<td>0.0656</td>
<td>0.0647</td>
<td>5.70</td>
</tr>
</tbody>
</table>

Polymerization conditions:

- [ICPY] = 7.5x10\(^{-3}\) mol l\(^{-1}\)
- [Styrene] = 2.1 mol l\(^{-1}\)
- [MMA] = 2.0 mol l\(^{-1}\)
- Solvent = DMSO
- Time = 120 minutes
- Temp. = 90 ± 0.1°C

*1 - Used to calculate percentage conversion.
*2 - Used to calculate percentage polymerization.
Table IV:2:9

Solubility of copolymer film in the presence of ICPY

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Solvent</th>
<th>Copolymer films</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>PF&lt;sub&gt;1&lt;/sub&gt;</td>
</tr>
<tr>
<td>1</td>
<td>HCl (N/10)</td>
<td>++</td>
</tr>
<tr>
<td>2</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt; (N/10)</td>
<td>++</td>
</tr>
<tr>
<td>3</td>
<td>HNO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>--</td>
</tr>
<tr>
<td>4</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;COOH (25%)</td>
<td>--</td>
</tr>
<tr>
<td>5</td>
<td>NaOH (N/20)</td>
<td>--</td>
</tr>
<tr>
<td>6</td>
<td>Benzene</td>
<td>++</td>
</tr>
<tr>
<td>7</td>
<td>Toluene</td>
<td>++</td>
</tr>
<tr>
<td>8</td>
<td>Dioxane</td>
<td>++</td>
</tr>
<tr>
<td>9</td>
<td>DMSO</td>
<td>+-</td>
</tr>
<tr>
<td>10</td>
<td>DMF</td>
<td>+-</td>
</tr>
<tr>
<td>11</td>
<td>Cyclohexane</td>
<td>++</td>
</tr>
<tr>
<td>12</td>
<td>Acetone</td>
<td>++</td>
</tr>
<tr>
<td>13</td>
<td>Methanol</td>
<td>--</td>
</tr>
<tr>
<td>14</td>
<td>Water</td>
<td>++</td>
</tr>
</tbody>
</table>

++ = Soluble at room temperature,
+- = Sparingly soluble at room temperature
-- = Insoluble
++ = Sparingly soluble on heating

PF<sub>1</sub> = [ICPY] = 3.0 x 10<sup>-3</sup> mol l<sup>-1</sup>
PF<sub>2</sub> = [ICPY] = 7.5 x 10<sup>-3</sup> mol l<sup>-1</sup>
PF<sub>3</sub> = [ICPY] = 13.5 x 10<sup>-3</sup> mol l<sup>-1</sup>
[Sty.] = 1.9 mol l<sup>-1</sup>
[MMA] = 1.8 mol l<sup>-1</sup>
Table IV:2:10

Effect of temperature on copolymer of Sty. with MMA initiated by ICPY.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Temperature (°C)</th>
<th>Copolymer weight loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>3.8</td>
</tr>
<tr>
<td>3</td>
<td>150</td>
<td>18.0</td>
</tr>
<tr>
<td>4</td>
<td>200</td>
<td>45.0</td>
</tr>
<tr>
<td>5</td>
<td>300</td>
<td>50.0</td>
</tr>
<tr>
<td>6</td>
<td>400</td>
<td>81.0</td>
</tr>
<tr>
<td>7</td>
<td>500</td>
<td>97.0</td>
</tr>
<tr>
<td>8</td>
<td>600</td>
<td>97.0</td>
</tr>
</tbody>
</table>
### Table IV:2:11

Copolymer composition for the copolymerization of Sty. with MMA initiated by ICPY.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Molar ratio in feed [MMA]/[Sty.]</th>
<th>Mole fraction in copolymer</th>
<th>Mole fraction in copolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>MMA from methyl protons</td>
<td>Sty. from phenyl protons</td>
</tr>
<tr>
<td>1</td>
<td>0.94</td>
<td>0.30</td>
<td>0.69</td>
</tr>
<tr>
<td>2</td>
<td>0.63</td>
<td>0.84</td>
<td>0.15</td>
</tr>
<tr>
<td>3</td>
<td>1.57</td>
<td>0.75</td>
<td>0.24</td>
</tr>
<tr>
<td>4</td>
<td>1.36</td>
<td>0.73</td>
<td>0.26</td>
</tr>
<tr>
<td>5</td>
<td>0.67</td>
<td>0.46</td>
<td>0.53</td>
</tr>
</tbody>
</table>

**Polymerization conditions:**

- \([\text{ICPY}] = 7.5 \times 10^{-3} \text{ mol l}^{-1}\)
- **Solvent** = DMSO
- **Time** = 120 minutes
- **Temp.** = 90 ± 0.1°C