Synthesis, characterization and reactivity ratios of co-polymers derived from 4-nitrophenyl methacrylate and butyl methacrylate

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Poly (NPNA) has been synthesized from 4-nitrophenylmethacrylate (NPMA) in 2-butanone using BPO as a free radical initiator. Copolymers of NPMA and BMA [poly(NPMA-co-BMA)] have also likewise been obtained. The polymers have been characterized by IR, $^1$H NMR and $^{13}$C NMR spectral studies. The weight average molecular weights of the polymers lie in the range (4.1-5.2) x $10^4$ while the number average molecular weights are found to be in the range (2-2.8) x $10^4$. The monomer reactivity ratios for NPMA-BMA copolymers and Q-e values for NPMA have been determined. TG and DSC studies indicate a random arrangement for the copolymers with thermal decomposition occurring in two stages.

The synthesis of and studies on several acrylates, and methacrylates have been undertaken as they find extensive applications in different fields$^{8,9}$. The use of polymers containing 2-hydroxyethyl methacrylate (HEMA) as adhesives, sealants and coatings has been reported$^7$. The graft copolymerization of MMA and HEMA with cotton and silk fabric has considerably enhanced their strength properties$^{9,10}$. The present study aims at the synthesis and characterization of poly (nitrophenyl methacrylate) (NPMA), as well as its copolymers with butyl methacrylate (BMA). The reactivity ratios of these copolymers have been calculated by Fineman-Ross$^{10}$, Kelen-Tudós$^{11}$ and extended Kelen-Tudós$^{12}$ methods while the Q-e values of NPMA are evaluated by Alfrey-Price method$^{13}$. Their molecular weights and thermal properties have also been investigated.

Experimental
Butyl methacrylate (BMA) (Aldrich) was purified by repeated washing with 5% NaOH and water and finally distilled in vacuo. 2-Butanone, chloroform and petroleum ether were distilled before use. Benzoyl peroxide (BPO) was used as such without further purification.

Methacryloyl chloride was synthesized from methacrylic acid and benzoyl chloride according to the reported procedure$^{8}$. 

Synthesis of 4-nitrophenylmethacrylate (NPMA)

4-Nitrophenol (20 g, 0.15 mol) and triethylamine (20.0 ml, 17 mol) were taken in a three-necked round bottom flask fitted with a stirrer, dropping funnel and a thermometer. The solvent, 2-butanone, (200 ml) was added to the flask and the contents were cooled to below 0°C. Methacryloyl chloride (14.0 ml, 0.13 mol) dissolved in 50 ml of CHCl₃ was taken in the dropping funnel and added slowly to nitrophenol. The temperature of the reaction mixture was maintained in the range 0°-5°C during the addition. The reaction mixture was stirred for 2h and then transferred to a separating funnel and extracted with water. The unreacted nitrophenol was removed by repeatedly washing the reaction mixture with 10% NaOH solution and water. The solution was dried over anhydrous MgSO₄. The solvent was distilled off and the crude product was recrystallized from petroleum ether to get pale yellow crystals [Yield: 64%; mp: 80-82°C; Req'd. for C₁₆H₁₂N₂O₄: C=57.97%; H=4.35%; N=6.76%; Found: C=57.90%; H=4.39%; N=6.80%].

Synthesis of poly (4-nitrophenylmethacrylate) [Poly(NPMA)]

The monomer, NPMA, (4 M) and the initiator BPO(=1% wt of the monomer) along with 2-butanol (20 ml) were taken in polymerization tubes and deaerated by passing nitrogen through the solution for 10 min. The temperature of the reaction mixture was maintained at 65°C by keeping the tubes in a thermostatic bath. Methanol was added to the reaction mixture and the precipitated polymer was dissolved in CHCl₃ and reprecipitated using methanol. The last step was repeated twice and the product dried in air (Yield: 52%).

Synthesis of copolymer [Poly(NPMA-co-BMA)]

The monomers, NPMA (1) and BMA (2), were taken in different mole ratios in 2-butanol along with 1% BPO in polymerization tubes and N₂ was
passed through the solution for 20 min. The reaction was carried out at 65°C for 6-8 h and methanol was added in excess to precipitate the copolymer from the solution. The solid which separated out was dissolved in CHCl₃, precipitated from methanol and finally dried at 45°C in vacuo.

The ¹H NMR spectra of the polymers were recorded on a Jeol 400 MHz spectrometer using CDCl₃ as solvent and TMS as internal reference. The IR spectra of the samples were recorded on a Hitachi 270-50 infrared spectrophotometer using KBr pellets. Thermograms of the polymers were recorded using Mettler 3000 TA thermal analyser. About 10 mg of the sample was used for thermal analysis and the heating rate was maintained at 20°C/min. The molecular weights of the samples were determined using a gel permeation chromatograph (Waters 501) equipped with a RI detector. The instrument was calibrated using polystyrene standard. Tetrahydrofuran (THF) was used as an eluent and the flow was maintained at 10 ml/min.

Results and discussion

The free radical polymerization of the monomers, NPMA and BMA, in different molar ratios gave the copolymers, which were freely soluble in CHCl₃ and were precipitated on addition of excess methanol. BPO was used as a free radical initiator since in some systems like poly(styrene-benzyl methacrylate), it was found to be more effective than 2,2'-azobis(isobutironitrile)²⁰.

In the IR spectra of the polymers synthesized in the present study the frequency due to ester carbonyl appears as a strong band at 1760 cm⁻¹. The bands observed at 1350 cm⁻¹ and 1500 cm⁻¹ indicate the presence of >C–N group in the system¹⁶,¹⁷. The bands due to methyl and methylene groups in both the monomer units are observed in the 2800-3000 cm⁻¹ region. In the present systems, the aromatic >C=C< frequencies are observed in the range 1440-1600 cm⁻¹, similar to that reported in other polymeric compounds²⁸.

In the NMR spectra, the aromatic protons of NPMA unit exhibit two doublets, one at δ 7.32 ppm and the other at δ 8.24 ppm. The signal observed at δ 4.00 ppm is attributed to methyleneoxy protons, while those appearing at δ 2.35 ppm (2H) and δ 1.03 ppm (3H) are due to methylene and methyl protons of the backbone respectively (Table 1).

The proton decoupled ¹³C NMR spectrum of the copolymer recorded as CDCl₃ solution exhibits resonances corresponding to different carbon atoms present in both NPMA and BMA. The chemical shift values for the copolymer do not vary much from those of the homopolymers. The ester carbonyl resonance of both the monomeric units appears at 178.23 ppm. The pendant group, comprising ¹C, ³C, ⁵C and ¹⁰C carbon atoms of the BMA unit, exhibits peaks at δ 64.64, 31.04, 19.63 and 14.02 ppm, respectively. The aromatic carbons in the NPMA unit exhibit resonances at δ 152.2, 120.9 and 129.4 ppm which are attributed to ¹C, ²C/C and ¹C/C respectively. The carbon (¹⁰C) attached to the nitro group exhibits signal at δ 135.4 ppm. The marked shifts observed in the case of ¹C and ³C from the rest of the aromatic carbons are attributed to the substitution at these positions. The shift in the case of ¹C is more pronounced when compared to that in the case of ⁵C due to the greater electronegativity of oxygen when compared to that of nitrogen.

The content of each kind of monomeric unit incorporated into copolymer chain [poly(NPMA-co-BMA)] can be calculated from the data obtained from ¹H NMR spectral studies. The mole fraction of NPMA in the copolymer was determined from the ratio of the integrated intensities of aromatic protons of NPMA and methyleneoxy protons of BMA.

Let m₁ and m₂ be the mole fractions of NPMA and BMA units in the copolymer. Then the term C corresponds to the ratio between the intensities of aromatic protons to those of methyleneoxy protons. This can be represented by the following equation (Eq. 1).

<table>
<thead>
<tr>
<th>System</th>
<th>¹H NMR (ppm)</th>
<th>¹³C NMR (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Aromatic protons</td>
<td>O–CH₂</td>
</tr>
<tr>
<td>NPMA</td>
<td>8.8-8.2 (s, 2H)</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>7.7-7.42 (s, 2H)</td>
<td>(s, 2H)</td>
</tr>
<tr>
<td>poly(NPMA)</td>
<td>8.05-8.2 (s, 2H)</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>7.2-7.4 (s, 2H)</td>
<td>(s, 2H)</td>
</tr>
</tbody>
</table>
\[
C = \frac{\text{Intensities of aromatic protons (Ia)}}{\text{Intensities of methyleneoxy protons (Im)}} \quad \text{... (i)}
\]

Substituting the values of Ia and Im in Eq. (i), we get
\[
C = \frac{4m_1}{2m_2} \quad \text{... (ii)}
\]

Simplification of (ii) gives
\[
m_1 = \frac{C}{C + 2} \quad \text{... (iii)}
\]

The mole fraction values of NPMA obtained for different compositions are provided in Table 2. A plot of NPMA monomer feed composition vs copolymer is shown in Fig. 1.

**Molecular weight**

The molecular weights of the copolymer systems, viz., poly (NPMA-co-BMA), have been determined by taking three different compositions of the monomers. Gel permeation chromatography was employed in the determination of both number and weight average molecular weights. The copolymer compositions chosen for the molecular weight determination were 0.20:0.80, 0.50:0.50 and 0.80:0.20. The corresponding weight average molecular weights \((M_w)\) are 4.17×10^4, 4.49×10^4 and 5.19×10^4, respectively. The number average molecular weights \((M_n)\) of these systems were found to be 2.05×10^4, 2.28×10^4 and 2.81×10^4, respectively. The ratio \((M_w / M_n)\) lies in the range 1.85-2.03.

**Reactivity ratios**

The reactivity ratios of NPMA \((r_1)\) and BMA \((r_2)\) were calculated from the monomer feed ratios and the copolymer compositions using three different methods, viz., Fineman-Ross\(^{10}\), Kelen-Tiédós\(^{11}\) and extended Kelen-Tiédós\(^{12}\).

The reactivity ratios obtained from all the three methods are very close to each other and the present system is an example of the case where \(r_1 < r_2\) and the product of \(r_1 r_2\) ranges between zero and one \((0 < r_1, r_2 < 1)\). The product of the reactivity ratios observed is close to 1 and hence a significant deviation from the ideal behaviour is expected. The compositional drift in this case is quite pronounced as there is a considerable difference between \(r_1\) and \(r_2\). The \(r_2\) values range from 0.50 to 0.53 while \(r_1\) values lie between 1.41 and 1.44. The product \(r_1 r_2\) is around 0.250 and this clearly suggests that the arrangement of monomers NPMA and BMA in the polymeric chain is less random when compared to the systems with \(r_1 r_2\) values close to zero. Tanaka et al.\(^{18}\) have reported that in the case of copolymers synthesized from 2-nitrobutyl acrylate and MMA, the reactivity ratios are found to be 0.22 \((r_1)\) and 1.60 \((r_2)\), respectively. The temperature, at which the copolymerization is carried out, is

![Fig. 1 — Composition curve of NPMA-BMA copolymer system](image)

**Table 2 — Copolymerization of NPMA-BMA system**

<table>
<thead>
<tr>
<th>Sl No.</th>
<th>Feed composition</th>
<th>Conversion (%)</th>
<th>Intensity of aromatic protons (I_a)</th>
<th>Intensity of methyleneoxy protons (I_m)</th>
<th>(C = I_a / I_m)</th>
<th>Copolymer composition (M_w \times 10^4)</th>
<th>(M_n \times 10^4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.10 0.90</td>
<td>7.38</td>
<td>1.20</td>
<td>2.90</td>
<td>0.4138</td>
<td>0.170</td>
<td>0.831</td>
</tr>
<tr>
<td>2</td>
<td>0.20 0.80</td>
<td>6.71</td>
<td>2.00</td>
<td>2.25</td>
<td>0.8889</td>
<td>0.308</td>
<td>0.692</td>
</tr>
<tr>
<td>3</td>
<td>0.35 0.65</td>
<td>9.74</td>
<td>3.10</td>
<td>1.70</td>
<td>1.8235</td>
<td>0.477</td>
<td>0.323</td>
</tr>
<tr>
<td>4</td>
<td>0.50 0.50</td>
<td>8.61</td>
<td>4.70</td>
<td>1.50</td>
<td>3.1333</td>
<td>0.610</td>
<td>0.390</td>
</tr>
<tr>
<td>5</td>
<td>0.65 0.35</td>
<td>8.78</td>
<td>6.20</td>
<td>1.10</td>
<td>5.6364</td>
<td>0.738</td>
<td>0.262</td>
</tr>
<tr>
<td>6</td>
<td>0.80 0.20</td>
<td>7.91</td>
<td>7.20</td>
<td>0.55</td>
<td>13.0909</td>
<td>0.857</td>
<td>0.143</td>
</tr>
<tr>
<td>7</td>
<td>0.90 0.10</td>
<td>9.03</td>
<td>10.40</td>
<td>0.40</td>
<td>26.0000</td>
<td>0.929</td>
<td>0.071</td>
</tr>
</tbody>
</table>
out, also plays an important role in the determination of reactivity ratios. The activity ratios obtained in the present study from the extended Kelen-Tudós method was used in the determination of Q and e values for the monomer by Alfrey-Price method. The values of e_2=0.28 and Q_2=0.82 for BMA were taken from the literature and these values have been substituted in the following equations for the calculations of e_1 and Q_1 for NPMA, which are found to be 0.834 and 1.845 respectively.

\[ e_1 = e_2 + ((\ln r_1) e_2)^{1/2} \]  \(\cdots\) (iv)

\[ Q_1 = Q_2 / r_2 \exp[(e_2(e_1-e_2))] \]  \(\cdots\) (v)

The Alfrey-Price Q-e scheme is based on the assumption that steric factors can be neglected. The Q-e values for methyl acrylate and methyl methacrylate were reported to be 0.42/0.60 and 0.74/0.40 respectively. In the case of acrylonitrile-tert-butyl methacrylate copolymers, acrylonitrile has a positive e-value due to its electron accepting nature. tert-Butoxy radical also has a positive e-value because of its electron accepting property.

**Thermal studies**

Thermal properties of five different copolymer systems obtained from NPMA and BMA have been studied (Table 3). The decomposition of the copolymers occurs in two stages except in the case of copolymer 5. The first stage of decomposition occurs in the temperature range 175°C-456°C while the second stage is observed between 350°C-565°C. The initial decomposition temperature (IDT) is minimum (175°C) for 1 and maximum (263°C) for 4. The IDT of other members are 205°C, 242°C and 225°C when the BMA mole ratios are 0.692, 0.390 and 1.0 respectively.

The maximum temperature for complete decomposition (565°C) is exhibited by copolymer 4 which is closely followed by copolymer 1 (535°C) in the second stage of decomposition. The temperature vs percentage weight loss data show that there is a gradual increase in the temperature when m_1 is increased from 0 to 1. The behaviour of copolymer 4 is totally different from that of others. Tamplinini et al. indicated that the degree of imidization of PMMA can be followed by ¹H NMR which in turn can be correlated to T_g and polymeric structure.

The glass transition temperature (T_g) of poly(NPMA-co-BMA) obtained in the present study with a molar composition of 0.48:0.52 is found to be 103.6°C. This value is quite low when compared to that of the homopolymer poly(NPMA) (T_g=127°C). The glass transition temperature of poly(butyl methacrylate) is reported to be 20°C if it is atactic and -24°C if the polymer is isotactic. The T_g of copolymers obtained from NPMA and BMA are expected to show values which are intermediate between the values exhibited by the individual homopolymers. Thus above 103.6°C, the copolymer would have acquired sufficient thermal energy for rotational motion to occur about the majority of the bonds in the backbone. The T_g of the polymer synthesized in the present case very closely follows the trend observed in related systems wherein the NPMA based polymers exhibit a higher T_g when compared to that of nitrophenyl acrylate (NPA) polymers.

**Acknowledgement**

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**References**
