4-Nitrophenyl Methacrylate—Glycidyl Methacrylate Copolymers
Synthesis, Characterization and Reactivity Ratios

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ABSTRACT

4-Nitrophenyl methacrylate is prepared, characterized by IR and NMR spectroscopic techniques and polymerized in methyl ethyl ketone using benzoyl peroxide as initiator. Copolymers of 4-nitrophenyl methacrylate with glycidyl methacrylate are prepared in methyl ethyl ketone at 65°C using benzoyl peroxide as initiator. The homopolymer and the copolymers are characterized by IR, 1H and 13C NMR. Their compositions are determined by 1H NMR analysis. The monomer reactivity ratios are determined by the application of conventional linearization methods of Finmann–Ross and Kelen–Tudos. The molecular weights are determined by gel permeation chromatography. The thermal behaviour of the polymers are studied by TGA.

Key Words: 4-nitrophenyl methacrylate, glycidyl methacrylate, reactivity ratios, characterization, NMR spectroscopy

INTRODUCTION

The incorporation of active groups in polyphenyl methacrylate is known to enhance the thermal stability of polymers [1]. Such activated methacrylates are used in peptide synthesis and also as electroactive polymers [2,3]. Copolymers of these monomers have been employed to study the kinetic aspects of macromolecular reactions [4]. Similarly, copolymers based on glycidyl methacrylates (GMA) have versatile applications due to the presence of an epoxy group [5,6], particularly in the immobilization of enzymes, DNA and other catalysts and also in chromatography [7–9]. Compositions of copolymers based on methacrylates and acrylates are usually determined by NMR techniques [10–13]. Recently, we have synthesized some phenyl reactive copolymers and polymer metal chelates to study their reactivities. The present work has been undertaken with the objective of enhancing the thermal stability and flame retardancy of phenyl methacrylate by introducing an active nitro-group in the phenyl ring. The synthesis, characterization and copolymerization behaviour of 4-nitrophenyl methacrylate (NPMA) and GMA in solutions are discussed and their reactivity ratios determined by 1H NMR spectroscopy.

EXPERIMENTAL

Materials

4-Nitrophenol was recrystallized from ethanol. Benzoyl peroxide (BPO) was recrystallized from chloroform/methanol mixtures. Glycidyl methac-
4-tiitmphtnyl Methacrylate-Glyddyl Maduuylate Copolymer was distilled under reduced pressure before use. All other chemicals used were of the purest possible grade.

Synthesis of 4-Nitrophenyl Methacrylate
Methacryloyl chloride was prepared by reacting methacrylic acid with benzoyl chloride [14]. NPMA was synthesized by reacting 4-nitrophenol (1 mole) with methacryloyl chloride (1 mole) in the presence of triethylamine in 2-butaneon solution. The reaction mixture was washed first with 5% sodium hydroxide solution to remove unreacted phenol, then with water and dried over anhydrous sodium sulphate. The solvent was evaporated in a rotating evaporator, and the resulting solid was recrystallized in petroleum ether (60–80 °C) with 63% yield and melting point of 54–56 °C.

The IR and 'H NMR spectra of the compound as well as the result of elemental analysis were consistent with the assigned structure.

<table>
<thead>
<tr>
<th>Analysis</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Found</td>
<td>56.04</td>
<td>4.61</td>
<td>7.23</td>
</tr>
<tr>
<td>Calculated</td>
<td>55.39</td>
<td>4.65</td>
<td>7.18</td>
</tr>
</tbody>
</table>

Copolymerization
Copolymers of NPMA and GMA of various compositions were prepared in 2-butaneon solution at 65 °C in the presence of benzoyl peroxide. In all cases, the initial total concentration of the monomers was 1 mol/L and BPO as initiator was 1% by wt. based on the monomers. Predetermined amounts of monomers, BPO and solvents were mixed in a polymerization tube, purged with nitrogen gas for 20 minutes and kept at 65 °C in a thermostat. Copolymers were precipitated in excess methanol, purified by at least two reprecipitation by methanol from chloroform solution, any impurity of monomers and low molecular weight homopolymers were effectively removed and dried in vacuum at 40 °C. Poly(NPMA) was prepared similarly and its yield after 3 hours corresponded to 21% by wt.

RESULTS AND DISCUSSION
4-Nitrophenyl methacrylate was prepared according to the following scheme.

\[
\text{OH} + \text{CH}_2=\text{C}(-\text{CH}_3)\xrightarrow{0 \degree \text{C}} \text{O}=\text{C}(-\text{Cl}) \quad \xrightarrow{(\text{C}_6\text{H}_5)_3\text{N}} \quad \text{CH}_2=\text{C}(-\text{CH}_3)
\]

The copolymerization of NPMA with GMA in 2-butaneon solution was studied for varying molar fractions of NPMA from 0.1 to 0.9 in the feed. The reaction time was selected to give conversions < 10% by wt. in order to satisfy the copolymerization equation. The compositions of feed and copolymers are presented in Table 1.

The copolymers were soluble in DMF, THF, DMSO and chloroform but were insoluble in non-polar and hydroxylic solvents (benzene, toluene, methanol, ethanol, water, etc.).

IR Spectroscopy
The IR spectra of the copolymer apparently show more predominant absorption bands than homo-
Table 1. Copolymerization of 4-nitrophenyl methacrylate and glycidyl methacrylate.

<table>
<thead>
<tr>
<th>Feed composition in mole fraction</th>
<th>%Conversion</th>
<th>Intensity of aromatic protons</th>
<th>Intensity of total aliphatic protons</th>
<th>Copolymer composition in mole fraction</th>
<th>$M_n \times 10^4$</th>
<th>$M_w \times 10^4$</th>
<th>$M_n / M_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPMA (M$_1$) GMA (M$_2$)</td>
<td></td>
<td></td>
<td></td>
<td>NPMA (m$_1$) GMA (m$_2$)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.10 0.90</td>
<td>7.16</td>
<td>0.60</td>
<td>7.60</td>
<td>0.1739 0.8204</td>
<td>3.82</td>
<td>8.92</td>
<td>2.34</td>
</tr>
<tr>
<td>0.20 0.80</td>
<td>6.62</td>
<td>1.20</td>
<td>7.20</td>
<td>0.3448 0.6551</td>
<td>4.21</td>
<td>9.28</td>
<td>2.20</td>
</tr>
<tr>
<td>0.35 0.65</td>
<td>8.02</td>
<td>1.73</td>
<td>6.35</td>
<td>0.5124 0.4816</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.50 0.50</td>
<td>7.14</td>
<td>2.45</td>
<td>6.00</td>
<td>0.6758 0.3242</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.65 0.35</td>
<td>6.83</td>
<td>2.75</td>
<td>5.40</td>
<td>0.7766 0.2238</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.80 0.20</td>
<td>9.45</td>
<td>3.10</td>
<td>4.95</td>
<td>0.8782 0.1218</td>
<td>4.76</td>
<td>9.73</td>
<td>2.04</td>
</tr>
<tr>
<td>0.90 0.10</td>
<td>8.26</td>
<td>3.25</td>
<td>4.55</td>
<td>0.9434 0.0966</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Temperature: 65°C; solvent: MEK initiator: BPO.

polymers of GMA and NPMA. The IR spectrum (Figure 1) of poly (NPMA-co-GMA) (50/50 mol%) has the same characteristic absorption bands as that of the homopolymer units. The broad bands at 3020 and 1590 cm$^{-1}$ due to aromatic stretching vibrations confirm the incorporation of an NPMA unit in the copolymer chain. The strong absorption at 1760 cm$^{-1}$ was due to the carbonyl (>C=O) stretchings of both acrylates. The peak at 915 cm$^{-1}$ confirms the incorporation of a GMA unit in the copolymer and also confirms the participation of the double bond in copolymerization. The strong absorption bands at 1520 and 1365 cm$^{-1}$ are due to asymmetric and symmetric vibrations of C-N. The medium intense band at 1200 cm$^{-1}$ corresponds to the ester of NPMA.

$^1$H NMR Spectroscopy
The $^1$H NMR spectrum of poly(NPMA) shows signals at 8.02 and 7.89 ppm due to aromatic protons. A group of multiplets at 1.35–2.32 ppm may be due to the backbone CH$_2$ and CH protons. The signals at 0.90–1.2 ppm may be assigned to -methyl protons (-CH$_3$).

The $^1$H NMR spectrum (Figure 2) of poly (NPMA-co-GMA) shows signals at 7.98 and 8.2 ppm due to aromatic protons of NPMA. The signals at 3.8 and 4.2 ppm are due to -OCH$_2$ protons in GMA; the epoxy group protons of GMA shows signals at 3.2 ppm due to -CH and at 2.6–2.8 ppm due to -CH$_2$ protons. The backbone methylene protons of the two monomer units gave signals at 1.9–2.3 ppm. The two methyl (responsible for tacticity) protons in NPMA and GMA gave signals at 0.89–1.3 ppm.

$^{13}$C NMR Spectroscopy
The proton decoupled $^{13}$C NMR spectrum (Figure 3) of the copolymer has the same characteristic peaks as that of the homopolymer. The presence of two monomers was confirmed by their carbon chemical shifts. The carboxyl group of the two esters in the monomeric unit exhibited peaks at 175.6 to 172.8 ppm, respectively. The peaks at 16.1

![IR spectrum of poly(NPMA-co-GMA) 50:50.](image)
9-Nitrophenyl Methacrylate—Oligodiyl Methacrylate Copolymers

Figure 2. 1H NMR spectrum of poly(NPMA-co-GMA).

to 19.5 ppm were due to the α-methyl group in the two monomers. The peak at 133.4 ppm was due to the C-4 atom. The peak at 129.1 ppm was due to the C-3 and C-5 atoms, while the sharp peak at 121.05 ppm being due to C-2 and C-6 atoms. These chemical shifts indicate the presence of NPMA in the copolymer. The sharp peak at 65.5 ppm was due to the -OCH2 group. The epoxy carbons of the GMA unit gave peaks at 52.5 and 54.3 ppm, respectively. The backbone of NPMA and GMA units appeared at 48.3 and 54.3 ppm, respectively.

Copolymer Compositions
The constituted monomeric units of the copolymers are represented in Figure 3.

The average composition of copolymer samples was determined from the corresponding 1H NMR spectra. The resonance peaks help in the determination of the content of both kinds of monomeric units in the copolymer. Hence, the mole fraction of NPMA in the copolymer chains was determined from the integrated intensities of aromatic protons of NPMA to that of the aliphatic protons present in the copolymer. The following expression holds for a copolymer system:

\[ C = \frac{I_A}{I_a} = \frac{\text{Intensities of aromatic protons}}{\text{Intensities of aliphatic protons}} \]

leading to:

\[ m_1 = \frac{10I_A}{5I_a + 4I_a} \]

Figure 3. Proton decoupled 13C NMR spectrum of poly(NPMA-co-GMA).
where \( m_1 \) is the mole fraction of NPMA and \((1-m_1)\) is that of GMA. These equations are based on the fact that there are four aromatic protons and five aliphatic protons in NPMA and ten aliphatic protons in GMA.

The distribution of protons in the two units is an important means of distinguishing monomeric units in the copolymer chain. The aromatic protons of the NPMA unit appear at higher field while the backbone methylene and methine protons overlap with the aliphatic protons of GMA-co-units. Table 1 gives the values of \( C \) and the corresponding mole fractions of NPMA in the copolymers. The reactivity ratios and copolymer compositions of NPMA and GMA were determined by the Kelen–Tüdos (K–T) [15] and Fineman–Ross (F–R) [16] methods.

The Finemann–Ross proposed a method for determining reactivity ratios by graphical representation. Let \( M_1/M_2=F; \) and \( m_1/m_2=f. \)

By substituting these values in copolymer equation,

\[
f = F(r_1F + 1)/(r_2 + F)
\]

and re-arranging the equation and dividing by \( F, \) the equation becomes:

\[
G = Hr_1-r_2,
\]

hence:

\[
G = F(f-1)/f \text{ and } H = F^2/f
\]

A plot of \( G \) as ordinate and \( H \) as abscissa is a straight line whose slope is \( r_1 \) and intercept is \(-r_2\). Kelen–Tüdos derived a simple graphically measureable linear method for the determination of the monomer reactivity ratios of \( r_1 \) and \( r_2 \) in copolymerization:

\[
\frac{G}{\alpha+H} = \frac{r_1 + \frac{r_2}{\alpha}H}{\alpha+H} - \frac{r_2}{\alpha}
\]

where \( \alpha = \sqrt{\text{H_{min} H_{max}}} \) which is an arbitrary constant. By introducing \( \eta = G/(\alpha+H) \) and \( \xi = H/(\alpha+H), \) this method provides an accurate value of \( r_1 \) and \( r_2. \)

The values would be between 0 and 1. A plot of \( \eta \) against \( \xi \) gives a straight line having the values of \( r_1 \) as the intercept at \( \xi =1 \) and the value of \(-r_2/\alpha \) as the intercept at \( \xi =0. \)

The values of K–T plot (Figure 4) and F–R plot (Figure 5) are represented in Tables 2 and 3. The product of \( r_N r_0 < 1 \) indicates that this system copolymerizes randomly. The higher concentrations of NPMA in the copolymer system clearly explain the greater probability of NPMA entering into the copolymer chain than GMA.

The number-average and weight-average molecular weights of poly(NPMA) and the copolymers were determined by gel permeation chromatography as represented in Table 1. The polydispersity index of poly(NPMA) is close to 2. The values of \( M_w/M_n \) of these polymers strongly suggest a tendency for chain termination by disproportionation. In the homopolymerization of NPMA, the number-average molecular weight is 46.
Figure 5. F–R plot for NPMA-GMA copolymer system.

radicals undergo termination by disproportionation [17].

Table 2. Finemann–Ross and Kelen–Tudos parameters.

<table>
<thead>
<tr>
<th>$M_1/M_2$</th>
<th>$m_1/m_2$</th>
<th>Finemann–Ross</th>
<th>Kelen–Tudos</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$f$</td>
<td>$(f-1)F/f$</td>
<td>$F^2/f$</td>
</tr>
<tr>
<td>0.1111</td>
<td>0.2189</td>
<td>-0.3965</td>
<td>0.0564</td>
</tr>
<tr>
<td>0.2500</td>
<td>0.5385</td>
<td>0.2250</td>
<td>0.1188</td>
</tr>
<tr>
<td>0.5385</td>
<td>1.0509</td>
<td>0.0261</td>
<td>0.2760</td>
</tr>
<tr>
<td>1.1000</td>
<td>2.0846</td>
<td>0.5203</td>
<td>0.4797</td>
</tr>
<tr>
<td>1.8371</td>
<td>3.5032</td>
<td>1.3271</td>
<td>0.9846</td>
</tr>
<tr>
<td>4.0000</td>
<td>7.2102</td>
<td>3.4452</td>
<td>2.2191</td>
</tr>
<tr>
<td>9.0000</td>
<td>16.6677</td>
<td>8.4600</td>
<td>4.8597</td>
</tr>
</tbody>
</table>

$\alpha = \sqrt{\frac{H_{\min}}{H_{\max}}} = 0.5235$
The copolymers vary between those of the poly-(GMA) on the high temperature side and poly-(NPMA) on the low temperature side (Figure 6).

CONCLUSION

The NPMA-GMA copolymer system is found to obey Finemann-Ross and Kelen-Tudos equations and their reactivity ratios calculation indicated the formation of random copolymers. An increase in GMA content of the copolymer is found to enhance the thermal stability.

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REFERENCES

4-Nitophenyl Methacrylate–Glycidyl Methacrylate Copolymers