# COPOLYMERIZATION OF 2-(*N*-PHTHALIMIDO)-2-METHYLPROPYL ACRYLATE WITH METHYL METHACRYLATE

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## ABSTRACT

The acrylic monomer, 2-(*N*-phthalimido)-2-methylpropyl acrylate was pre-
pared by reacting 2-(*N*-phthalimido)-2-methylpropan-1-ol dissolved in 2-buta-
none with acryloyl chloride in the presence of triethylamine. Copolymers of 2-
(*N*-phthalimido)-2-methylpropyl acrylate with methyl methacrylate having
various feed compositions in 2-butanone solution were synthesized using ben-
zoyl peroxide as a free radical initiator at 70°C. The monomer and the copoly-
mers were characterized by infrared and proton nuclear magnetic resonance
(^{1}H-NMR) spectroscopic techniques. The copolymer compositions were cal-
culated by ^{1}H-NMR technique. The monomer reactivity ratios were deter-
mined by the application of conventional linearization methods suggested by
Fineman-Ross and Kelen-Tüdös. The number and weight average molecular
weights ($M_n$ and $M_w$) of the polymers were determined by gel permeation
chromatography. The thermal stability of the polymers was measured by ther-
mogravimetric analysis in air. The solubility of the polymers was tested.

*Key Words:* 2-(N-Phthalimido)-2-methylpropyl acrylate; MMA; ^{1}H-NMR;
Copolymers; Reactivity ratio.

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## INTRODUCTION

Recently, polymers with reactive functional groups are synthesized because of their specific end applications (1). Copolymers of acrylic monomers with methyl methacrylate have been used as primers for automotive finishes, clean lacquers for polishing metals, and enamels for household appliances (2). Acrylic copolymers are widely used as binders in protective coatings because of their durability and transparency (3). *N*-Substituted phthalimido group containing copolymers have been used as activated drug-binding materials (4) and optical brightening agents (5). The determination of copolymer composition and reactivity ratios of the monomers are important in evaluating the specific end applications of copolymers (6). Proton nuclear magnetic resonance ($^1$H-NMR) spectroscopic analysis has been established as a powerful tool for the estimation of copolymer composition because of simplicity and sensitivity (7–9). The present article discusses the copolymerization behavior of phthalimido group containing acrylic monomer, 2-(*N*-phthalimido)-2-methylpropyl acrylate (NPMPA) with methyl methacrylate (MMA) in solution, characterization of the copolymers and determination of the monomer reactivity ratios.

## EXPERIMENTAL

The preparation of 2-(*N*-phthalimido)-2-methylpropan-1-ol was reported elsewhere (10). MMA was freed from inhibitor by washing with 5% aqueous sodium hydroxide solution followed by distilled water and dried over anhydrous sodium sulphate and distilled under reduced pressure. Acryloyl chloride was synthesized using the procedure described by Stampel *et al.,* (11). Benzoyl peroxide (BPO) was recrystallized from a chloroform-methanol (1:1) mixture. The solvents were purified by distillation.

### Preparation

NPMPA

In a 500-mL three-necked flask, 2-(*N*-phthalimido)-2-methylpropan-1-ol (24.6 g, 0.12 mol) and triethylamine (15.8 mL, 0.12 mol) were dissolved in 150 mL of 2-butanone and cooled to –5 to –0°C. Acryloyl chloride (9.2 mL, 0.12 mol) in 30 mL of 2-butanone was then added dropwise with constant stirring and cooling at –5 to –0°C. After stirring at room temperature for 2 h, the precipitated quaternary ammonium salt was filtered off. Approximately 0.5 g of hydroquinone was added to the filtrate and the solvent was removed using a rotary evaporator. The residue was dissolved in ether, washed successively with 5% aqueous sodium hydroxide solution, and distilled water, dried over anhydrous sodium sulphate, and the solvent was evaporated. The crude monomer, NPMPA was purified by reduced
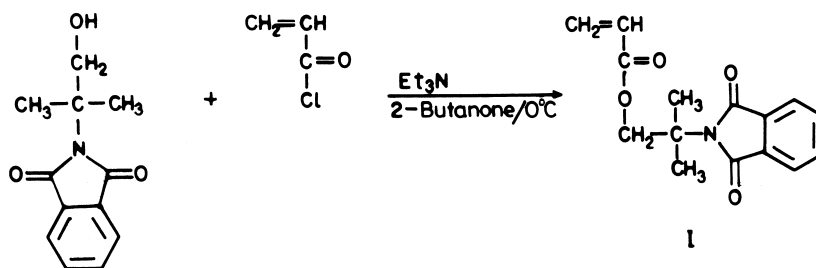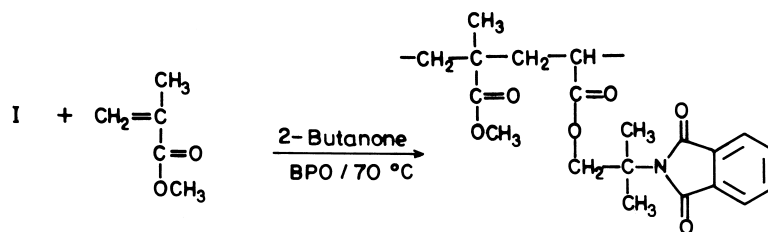
*Scheme 1.*

pressure distillation and the liquid boiling at 80°C and 10 mm pressure was collected. The reaction for the synthesis of NPMPA is shown in Scheme 1. The infrared (IR) and $^1$H-NMR spectra of the compound are consistent with the assigned structure.

IR (KBr, cm$^{-1}$): 3080 (aromatic C-H stretching), 2930 and 2860 (asymmetric and symmetric C-H stretch due to CH$_3$ and CH$_2$ groups), 1740 (C=0 stretching due to the ester group), 1725 (C=0 stretching due to phthalimido group), 1640 (aliphatic C=C stretch, 1600 and 1440 (aromatic C=C stretch) 1380 and 1370 (>CMe$_2$), 1210 (C-0 stretch), 655 (C-H out of plane bending).

$^1$H-NMR (DMSO d$_6$, ppm): 7.81-7.73 (4H) (aromatic), 6.54 and 6.03 (2H) (=CH$_2$), 6.31 (1H) (=CH-), 4.50 (2H) (-CH$_2$O) and 1.02-0.85 (6H) (>CMe$_2$).

Copolymerization of NPMPA with MMA

Copolymers having different composition of NPMPA and MMA were synthesized by free radical solution polymerization using BPO as a free radical initiator in 2-butanone solution (Sch. 2). Appropriate quantities of NPMPA and MMA with 2-butanone and BPO (0.25 wt% with respect to monomer) were mixed in a reaction tube and flushed with N$_2$ for 30 min. The tube was tightly sealed and kept in a thermostatic water bath at 70 ± 1°C. After the desired time (~4–5 h), the reaction mixture was added to excess methanol. The product was washed with methanol, purified by reprecipitation by methanol from the solution of the polymer in chloroform, and finally dried in vacuum at 50°C.



*Scheme 2.*

## Analytic Measurements

IR spectra were obtained with a Hitachi 270-50 spectrophotometer using KBr pellets for solid samples and NaCl flats for liquid samples. ^{1}H-NMR spectra were obtained with a Bruker 270 MHz FT NMR spectrometer with tetramethylsilane (TMS) as an internal reference in (DMSO d$_6$) solution. The number- and weight-average molecular weights ($\bar{M}_n$ and $\bar{M}_w$) and polydispersity index values of the polymers were determined with a Waters 501 gel permeation chromatograph equipped with three ultrastyragel columns and a differential refractive index (RI-401) detector. The molecular weights of the polymers were calibrated against polystyrene standards using tetrahydrofuran as mobile phase. Thermogravimetric analysis were performed with a Mettler TA 3000 thermal analyzer in an air atmosphere at a heating rate of 10°C/min. The solubility of the polymers were tested using various organic solvents at room temperature.

## RESULTS AND DISCUSSION

Copolymerization of NPMPA with MMA in a 2-butanone solution was studied for mole fractions of NPMPA ranging from 0.10 to 0.90 in the monomer feed. The reaction time was initially selected to reach conversions lower than 10 wt% to satisfy the differential copolymerization equation (12). The data of molar compositions of the initial mixtures of comonomers and of the resulting copolymers are presented in Table 1.

***Table 1.*** Composition Data for the Free Radical Polymerization of NPMPA with MMA in 2-butanone at 70°C.

| Feed Composition | Conversion % | Intensities of protons | | $C = \dfrac{I_{Ar}}{I_{OCH_2} + I_{OMe}}$ | Copolymer composition |
|---|---|---|---|---|---|
| $M_1{}^a$ | | $I_{Ar}$ | $I_{OCH_2} + I_{OMe}$ | | $m_1{}^b$ |
| 0.10 | 6.8 | 0.65 | 3.55 | 0.1831 | 0.1313 |
| 0.20 | 7.3 | 1.40 | 3.85 | 0.3636 | 0.2550 |
| 0.35 | 8.9 | 2.10 | 3.35 | 0.6269 | 0.4065 |
| 0.50 | 6.9 | 2.90 | 3.20 | 0.9063 | 0.5542 |
| 0.65 | 7.8 | 3.60 | 2.90 | 1.2413 | 0.7105 |
| 0.80 | 8.1 | 4.20 | 2.85 | 1.4737 | 0.8077 |
| 0.90 | 6.7 | 4.80 | 2.75 | 1.7454 | 0.9114 |

[a] The mole fraction of NPMPA in the feed.

[b] The mole fraction of NPMPA in the copolymer.

## Characterization

Solubility

The solubility of the polymers in various organic solvents was tested in cold conditions. They were easily soluble in polar aprotic solvents, namely dimethyl formamide, *N*-methyl-2-pyrrolidone, dimethyl acetamide, dimethyl sulfoxide, etc., and chlorinated solvents such as chloroform and methylene chloride. They were insoluble in hydrocarbons (eg., benzene, toluene, xylenes), and hydroxy-group containing solvents such as methanol, 2-propanol and water.

IR Spectra

The IR spectrum of the copolymer [0.55:0.45] (Fig. 1) shows the characteristic bands of both monomer units. The peak at 3085 cm$^{-1}$ is due to the aromatic C-H stretching. The absorption bands at 2975 cm$^{-1}$ and 2870 cm$^{-1}$ are due to the aliphatic C-H stretching of methyl and methylene groups. The carbonyl stretchings due to the two ester groups appear at 1765 cm$^{-1}$ and 1785 cm$^{-1}$. The peak at 1725 cm$^{-1}$ corresponds to the C=O stretching of the phthalimido group. The bands at 1600 cm$^{-1}$ and 1450 cm$^{-1}$ are attributed to aromatic C=C stretching. The gem dimethyl group shows signals at 1385 cm$^{-1}$ and 1375 cm$^{-1}$. The absorption peaks at 1210 cm$^{-1}$ and 1185 cm$^{-1}$ are attributed to C-O stretching of the ester groups. The out-of-plane C-H bending vibrations of the ortho disubstituted benzene ring are observed at 675 cm$^{-1}$.
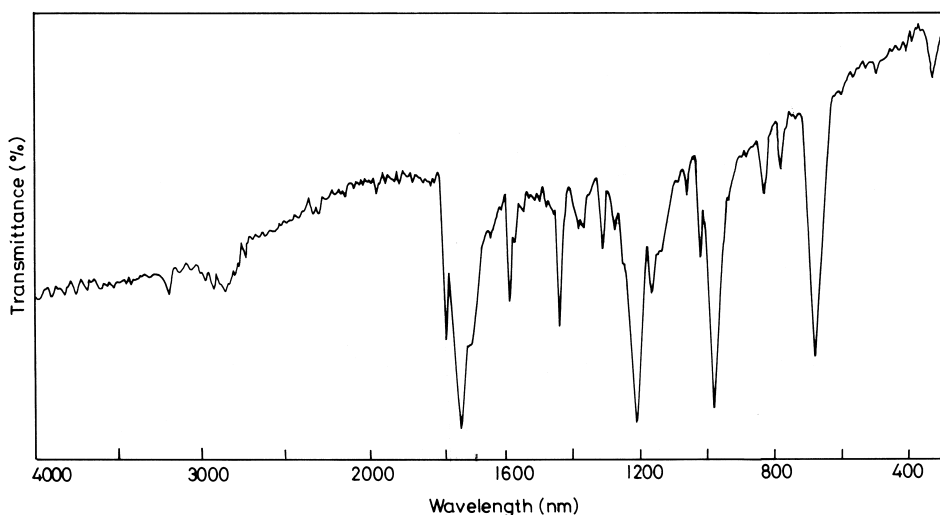


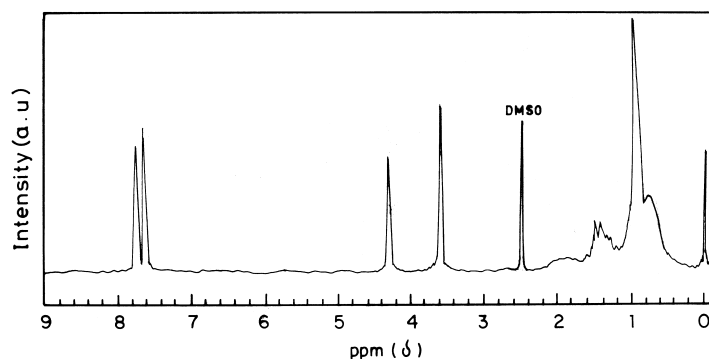***Figure 1.*** IR spectrum of poly(NPMPA-*co*-MMA) [0.55:0.45].

**Figure 2.** $^1$H-NMR spectrum of poly(NPMPA-*co*-MMA) [0.55:0.45].

$^1$H-NMR Spectra

The $^1$H-NMR spectra of poly(NPMPA-*co*-MMA) [0.55:0.45] is shown in Figure 2. The aromatic protons of NPMPA unit appear between 7.80 and 7.73 ppm. The characteristic signal at 4.31 ppm corresponds to the -CH$_2$O- group of the NPMPA unit. A singlet at 3.60 ppm is attributed to the -OCH$_3$ protons of the MMA unit. The broad signal between 2.31 and 1.32 ppm is due to the methyne ($\rightarrow$CH) and methylene (>CH$_2$) protons of the main chain. The methyl protons show signals between 1.00 and 0.85 ppm.

Copolymer Compositions

The $^1$H-NMR technique is a well-established method for the determination of the copolymer composition. The distribution of protons in the two units is an important means of identifying a monomer in the copolymer chains. Thus, the mole fraction of NPMPA in the copolymer chain was determined from the ratio of integrated intensities of aromatic protons of NPMPA unit to that of methoxy and methylenoxy protons of MMA and NPMPA units respectively. Let m$_1$ be the mole fraction of NPMPA and (1-m$_1$) be the mole fraction of MMA. There are 4 aromatic protons and 2 methylenoxy protons in NPMPA. MMA unit contains 3 methoxy protons. Therefore:

$$C = \frac{\text{Intensities of aromatic protons } (I_{Ar})}{\text{Intensities of methylenoxy and methoxy protons } (I_{OCH2} + I_{OMe})}$$

$$C = \frac{4m_1}{2m_1 + 3(1-m_1)} \tag{1}$$

which on simplification gives,

$$m_1 = \frac{3C}{4+C} \tag{2}$$

The composition of the copolymers can be determined by comparing the intensities of aromatic protons with that of total aliphatic protons. To avoid the proton signals due to the solvent DMSO $d_6$, the mole fractions of NPMPA in copolymers were determined by measuring the intensities of aromatic proton signals and methylenoxy and methoxy proton signals from the spectra of copolymer samples using Equation 2. The values of C and the corresponding mole fractions of NPMPA in the copolymers are presented in Table 1. The kinetic behavior was determined by plotting the mole fractions of NPMPA in the feed ($M_1$) vs. that the copolymer ($m_1$) and the curve (Fig. 3) indicates that the composition of NPMPA in the copolymer is always higher than that in the feed.

Copolymerization Reactivity Ratios

The determination of reactivity ratios of the monomers participating in the copolymer will provide the copolymerization behavior of corresponding monomer pair. The reactivity ratios of NPMPA and MMA were determined by the application of the conventional linearization methods suggested by Fineman-Ross (F-R) (13) and Kelen-Tüdös (K-T) (14). The significance of parameters of F-R and K-T methods are presented in Table 2. The reactivity ratios obtained from the F-R plot (Fig. 4) and K-T plot (Fig. 5) are presented in Table 3.

The value of $r_1$ is more than 1 and that of $r_2$ is less than 1, indicates the presence of a higher amount of NPMPA unit in the copolymer than in the feed. The reactivity of growing radicals, as measured by $1/r_1$, shows higher affinity towards NPMPA than MMA. The product of $r_1$ and $r_2$, however, remains less than 1, thus
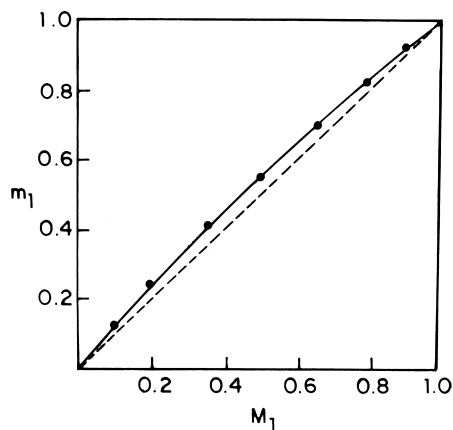


**Figure 3.** Composition diagram of NPMPA-MMA copolymer system.

***Table 2.*** F-R and K-T Parameters for the MPMPA-MMA Copolymer System

| $F = M_1/M_2$ | $f = m_1/m_2$ | $G = F(f-1)/f$ | $H = F^2/f$ | $\eta = G/\alpha + H$ | $\xi = H/\alpha + H$ |
|---|---|---|---|---|---|
| 0.1111 | 0.1511 | -0.6242 | 0.0817 | -0.7063 | 0.0924 |
| 0.2500 | 0.3333 | -0.5001 | 0.1875 | -0.5054 | 0.1895 |
| 0.5385 | 0.6849 | -0.2477 | 0.4234 | -0.2021 | 0.3455 |
| 1.0000 | 1.2432 | 0.1956 | 0.8044 | 0.1218 | 0.5007 |
| 1.8571 | 2.4542 | 1.0040 | 1.4053 | 0.4985 | 0.6366 |
| 4.0000 | 4.2002 | 3.0477 | 3.8093 | 0.6609 | 0.8261 |
| 9.0000 | 10.2867 | 8.1251 | 7.8742 | 0.9365 | 0.9076 |

$\alpha$ is equal to 0.8021.
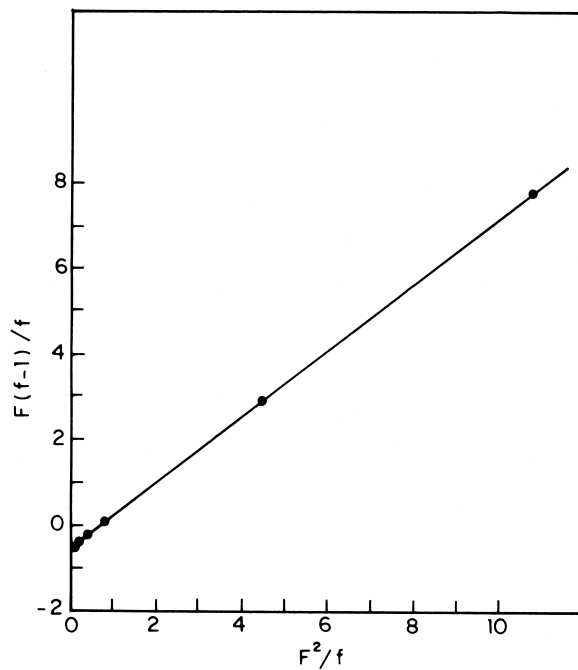


***Figure 4.*** F-R plot for NPMPA-MMA copolymer system.

***Figure 5.*** K-T plot for NPMPA-MMA copolymer system.

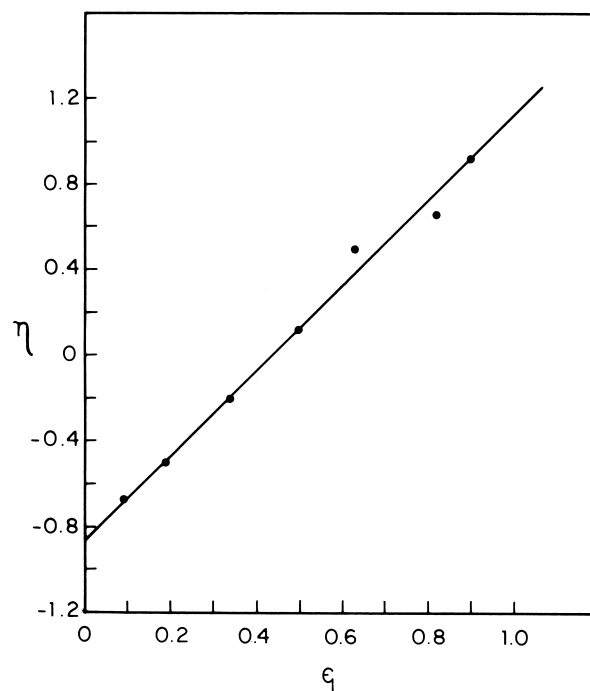indicating that the system follows a random distribution of the monomeric units, as in the case of Schiff base containing acrylate system (15).

## Molecular Weights

The number-average ($\bar{M}_n$), weight-average ($\bar{M}_w$) molecular weights and the polydispersity index ($\bar{M}_w/\bar{M}_n$) of poly(NPMPA), poly(MMA) and seven copolymers determined by gel permeation chromatography (GPC) are presented in Table

***Table 3.*** Copolymerization Parameters for the Free Radical Copolymerization of MPMPA with MMA

| Methods | $r_1{}^a$ | $r_2{}^b$ | $r_1 \times r_2$ | $1/r_1$ | $1/r_2$ |
|---|---|---|---|---|---|
| F-R | 1.12 | 0.71 | 0.79 | 0.89 | 1.41 |
| K-T | 1.14 | 0.69 | 0.78 | 0.87 | 1.45 |
| Average | 1.13 | 0.70 | 0.79 | 0.88 | 1.43 |

[a] The reactivity ratio for NPMPA.

[b] The reactivity ratio for MMA.

*Table 4.* Molecular Weight Data for the Copoloymers of NPMPA with MMA

| Polymers | $m_1{}^a$ | Molecular weights | | |
|---|---|---|---|---|
| | | $\overline{M}_w$ x $10^{-4}$ | $\overline{M}_n$ x $10^{-4}$ | $\overline{M}_w/\overline{M}_n$ |
| Poly(NPMPA) | 1.00 | 3.51 | 2.21 | 1.59 |
| Poly(NPMPA-*co*-MMA) | 0.91 | 3.82 | 2.36 | 1.62 |
| | 0.81 | 3.43 | 2.08 | 1.65 |
| | 0.71 | 3.51 | 2.15 | 1.63 |
| | 0.55 | 3.33 | 1.97 | 1.69 |
| | 0.41 | 3.12 | 1.78 | 1.75 |
| | 0.26 | 3.31 | 1.88 | 1.76 |
| | 0.13 | 2.96 | 1.65 | 1.79 |
| Poly(MMA) | 0.00 | 3.06 | 1.66 | 1.84 |

$^a$ The mole fraction of NPMPA in the copolymer.

4. The theoretical value of $\overline{M}_w/\overline{M}_n$ for polymers produced via radical combination and disproportionation are 1.5 and 2.0, respectively (16). In the homopolymerization of MMA, the tendency for chain termination by disproportionation is more than that for dimerization (17). The polydispersity index value of poly(NPMPA) is close to 1.5 and this suggests that the polymer is obtained mostly by dimerization of the growing chain. When the mole fraction of the NPMPA in the copolymer is 0.41, the tendency for chain termination by dimerization as well as disproportionation are the same. When this value is below 0.41, the tendency for chain termination by disproportionation is more than that for dimerization and when it is above 0.41, the tendency for chain termination by dimerization is more than that for disproportionation.

Thermogravimetric Analysis

The thermal stability of the polymers was measured by thermogravimetric analysis in air. The TG and DTG traces of poly(NPMPA), poly(MMA), and poly(NPMPA-*co*-MMA) [0.55:0.45] are shown in Figure 6. The results of decomposition temperature of the polymers and the weight loss at various stages are given in Table 5. The actual decomposition range depends on the composition of the copolymers. Poly(NPMPA) shows four-stage decomposition, whereas the copolymer shows three-stage decomposition. The decomposition of poly(MMA) occurs in a single stage. The multistage decomposition of the polymers may be attributed to the loss of pendant group and the cleavage of ester group and loss of phthalimido group. The initial decomposition temperature of poly(NPMPA), poly(NPMPA-co-MMA) [0.55:0.45] and poly(MMA) are 151°C, 164°C, and
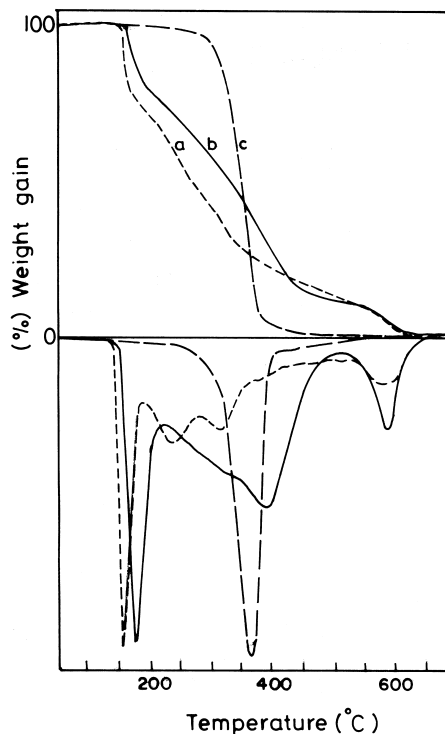
**Figure 6.** TGA-DTG curves in air for: a) Poly(NPMPA); b) Poly(NPMPA-*co*-MMA) [0.55:0.45]; c) Poly(MMA).

**Table 5.** TGA Data of Homo and Copolymers of NPMPA and MMA

| Polymers | $m_1$ [a] | IDT [b] °C | Temperature (°C) of weight loss (%) of polymers | | | | |
|---|---|---|---|---|---|---|---|
| | | | 10% | 30% | 50% | 70% | 90% |
| Poly(NPMPA) | 1.00 | 151 | 160 | 201 | 264 | 337 | 534 |
| Poly(NPMPA-*co*-MMA) | 0.71 | 159 | 172 | 219 | 276 | 351 | 536 |
| | 0.55 | 164 | 213 | 244 | 325 | 394 | 543 |
| | 0.41 | 178 | 237 | 274 | 346 | 412 | 557 |
| Poly(MMA) | 0.00 | 278 | 306 | 338 | 351 | 364 | 370 |

[a] The mole fraction of NPMPA in the copolymer.
[b] Initial decomposition temperature.

278°C, respectively. Because it is an acrylic system, poly(NPMPA) shows a relatively lower initial decomposition temperature. The thermal stability of the copolymers increase with an increase of MMA unit in the copolymer chain.

## CONCLUSION

The acrylic monomer, NPMPA was synthesized and characterized. Poly(NPMPA) and the copolymers of NPMPA and MMA from different feed compositions were synthesized in 2-butanone solution by free radical polymerization. The polymers were easily soluble in polar aprotic solvents and in chlorinated solvents and insoluble in hydrocarbons and hydroxy group containing solvents. IR and $^1$H-NMR spectra confirmed the presence of both monomeric constituents in the copolymers. The copolymer compositions were determined by $^1$H-NMR analysis of the copolymers. The reactivity ratios obtained from F-R and K-T methods are within the experimental error. The fact that the $r_1$ values of both methods are greater than 1 and $r_2$ values are less than 1 indicates that the NPMPA is more reactive than MMA. The product of $r_1$ and $r_2$ is less than 1 indicates the random distribution of monomeric units in the copolymers. The polydispersity index values of the copolymers suggest that the tendency for chain termination by dimerisation is more than disproportionation at high mole fractions of NPMPA in the feed. Thermogravimetric analysis results indicated that poly(MMA) is more stable than poly(NPMPA) and the incorporation of MMA unit in copolymer chain increases the thermal stability of the copolymers.

## ACKNOWLEDGMENT

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