

# Copolymers of 2-(3-mesityl-3-methylcyclobutyl)-2-ketoethyl Methacrylate with Acrylonitrile and Styrene: Synthesis, Characterization, and Monomer Reactivity Ratios

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## Abstract

The copolymerization of 2-(3-mesityl-3-methylcyclobutyl)-2-ketoethyl methacrylate monomer with acrylonitrile and styrene were carried out in 1,4-dioxane solution at 60 °C using AIBN as an initiator. The copolymers were characterized by Fourier transform infrared, <sup>1</sup>H-NMR, and <sup>13</sup>C-NMR spectroscopic techniques. Thermal properties of the polymers were also studied by thermogravimetric analysis and differential scanning calorimetry. The copolymer compositions were determined by elemental analysis and <sup>1</sup>H-NMR technique. The monomer reactivity ratios were calculated by the application of conventional linearization methods as a result of Fineman–Ross and Kelen–Tüdös to less than 1 for both monomers.

## Introduction

Many polymers with reactive functional groups are now being synthesized, tested, and used not only for their macromolecular properties but also for the properties of functional groups. In polymer science the improvement of the mechanical properties has been the center of interest for many years, but today special electrical and optical properties of polymers receive an increasing interest. Functional groups give the polymer structure special character, substantially different from the inherent properties of the basic polymer chain [1–3].

Polymers containing the cyclobutane ring, which is a small, strained carbon ring are generally decomposed by irradiation with deep ultraviolet light [4, 5]. However, polymethacrylates with keto side chains are readily transformed into other derivatives and have some photosensitive properties [6, 7]. There are many reports concerning polymers with the cyclobutane ring [8–11] and the cyclobutane ring and hydroxy and ketoethyl group together [12–14].

Reactivity ratios are among the most important parameters for composition equation of copolymers, which can offer information such as relative reactivity of monomer pairs and estimate the copolymer composition. Knowledge of the copolymer composition is an important step in the evaluation of its utility. Copolymer composition and its distribution are dependent on the reactivity ratios. The most common mathematical model of copolymerization is based on finding the relationship between the composition of copolymers and the composition of the monomer feed in which the monomer

reactivity ratios are the parameters to be determined [15, 16]. The calculation of the monomer reactivity ratios requires the mathematical treatment of experimental data on the compositions of copolymers and monomer feed mixtures. No studies on reactivity ratios in the copolymerization of 2-(3-mesityl-3-methylcyclobutyl)-2-ketoethyl methacrylate (MKEMA) with any commercial monomer are found in the literature.

The present article investigates the synthesis, structural, and thermal characterization of copolymers of MKEMA with acrylonitrile (AN) and styrene (ST) as well as the determination of reactivity ratios in the copolymerization.

## Experimental

### Materials

1,4-dioxane, chloroform, methanol, and ethanol (Merck) were used as received. MKEMA was prepared as reported [13]. AN (Aldrich) was freed from inhibitor by distillation under reduced pressure, and ST was freed from inhibitor by washing with 5% NaOH solution followed by distilled water, drying over anhydrous MgSO<sub>4</sub>, and distillation under vacuum. 2,2'-azobisisobutyronitrile (AIBN) was recrystallized from a chloroform–methanol (1:1) mixture.

### Copolymerization of 2-(3-mesityl-3-methylcyclobutyl)-2-ketoethyl Methacrylate with Acrylonitrile and Styrene

Copolymerizations of MKEMA with AN and ST using different proportions of MKEMA were carried out in glass

Table 1. Monomer composition in feed and in copolymer<sup>a</sup>

| Sample | Feed composition in mole fraction |                         | Conversion (%) | Elemental N (%) | Copolymer composition in mole fraction |                         |
|--------|-----------------------------------|-------------------------|----------------|-----------------|--|-------------------------|
|        | AN (M <sub>1</sub> )              | MKEMA (M <sub>2</sub> ) |                |                 | AN (m <sub>1</sub> )                   | MKEMA (m <sub>2</sub> ) |
| 1      | 0.20                              | 0.80                    | 10.0           | 1.35            | 0.23                                   | 0.77                    |
| 2      | 0.30                              | 0.70                    | 8.0            | 2.07            | 0.34                                   | 0.66                    |
| 3      | 0.40                              | 0.60                    | 9.0            | 2.71            | 0.39                                   | 0.61                    |
| 4      | 0.50                              | 0.50                    | 7.0            | 3.02            | 0.44                                   | 0.56                    |
| 5      | 0.60                              | 0.40                    | 8.0            | 4.51            | 0.55                                   | 0.45                    |
| 6      | 0.70                              | 0.30                    | 8.0            | 6.25            | 0.65                                   | 0.35                    |
| 7      | 0.80                              | 0.20                    | 9.0            | 8.82            | 0.74                                   | 0.26                    |

<sup>a</sup>Solvent: 1,4-dioxane; temperature: 65 ± 1 °C; initiator: AIBN (1% weight of the monomers); non-solvent: ethanol.

Table 2. Monomer composition in feed and in copolymer<sup>a</sup>

| Sample | Feed composition in mole fraction |                         | Conversion (%) | I <sub>A</sub> /I <sub>a</sub> | Copolymer composition in mole fraction |                         |
|--------|-----------------------------------|-------------------------|----------------|--------------------------------|--|-------------------------|
|        | ST (M <sub>1</sub> )              | MKEMA (M <sub>2</sub> ) |                |                                | ST (m <sub>1</sub> )                   | MKEMA (m <sub>2</sub> ) |
| 1      | 0.20                              | 0.80                    | 8.00           | 0.12                           | 0.17                                   | 0.83                    |
| 2      | 0.30                              | 0.70                    | 9.00           | 0.15                           | 0.27                                   | 0.73                    |
| 3      | 0.40                              | 0.60                    | 10.00          | 0.23                           | 0.44                                   | 0.56                    |
| 4      | 0.50                              | 0.50                    | 8.00           | 0.26                           | 0.51                                   | 0.49                    |
| 5      | 0.60                              | 0.40                    | 8.00           | 0.28                           | 0.53                                   | 0.47                    |
| 6      | 0.70                              | 0.30                    | 9.00           | 0.33                           | 0.60                                   | 0.40                    |
| 7      | 0.80                              | 0.20                    | 10.00          | 0.42                           | 0.68                                   | 0.32                    |

<sup>a</sup>Solvent: 1,4-dioxane; temperature: 65 ± 1 °C; initiator: AIBN (1% weight of the monomers); non-solvent: ethanol.

ampoules under N<sub>2</sub> atmosphere in 1,4-dioxane solution with AIBN (1%, based on the total weight of monomers) as an initiator. The reacting components were degassed by three-fold freeze-thawing cycles and then immersed in a oil bath at 65 ± 0.1 °C for a given reaction time. The reaction time was selected to give conversions less than 10% to satisfy the differential copolymerization equation [17]. After the desired time the copolymers were separated by precipitation in ethanol and reprecipitated from CH<sub>2</sub>Cl<sub>2</sub> solution. The polymers, purified by reprecipitation to avoid the formation of homopolymers. The polymers were finally dried over vacuum at 45 °C to constant weight. The amounts of monomeric units in the copolymers were determined by elemental analysis. The feed compositions and copolymer composition for the copolymerization of MKEMA-co-AN and MKEMA-co-ST are presented in Tables 1 and 2.

### Measurements

Infra-red spectra were measured on a Mattson 1000 FT-IR spectrometer. The <sup>1</sup>H and <sup>13</sup>C-NMR Spectra of the monomer and copolymers were recorded in CDCl<sub>3</sub> with tetramethylsilane as the internal standard using a Varian Gemini 200 MHz spectrometer. Thermal data were obtained by using a Shimadzu DSC-50 instrument and a TGA-50 thermobalance in N<sub>2</sub> atmosphere. Molecular weights ( $\bar{M}_w$  and  $\bar{M}_n$ ) of the polymers were determined using Waters 410

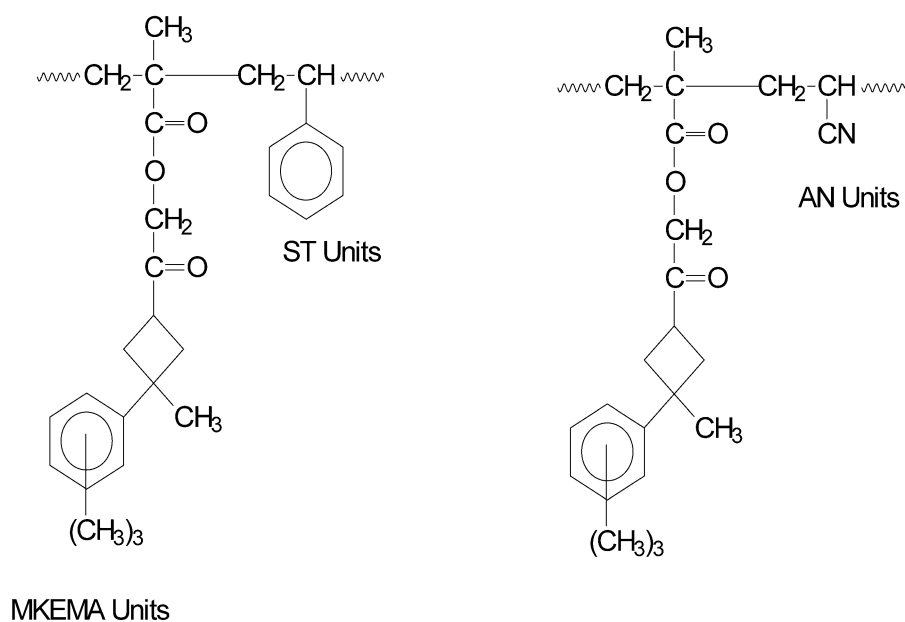
gel permeation chromatography equipped with a differential refractive index detector and calibrated with polystyrene standards. Elemental analysis were carried out by a LECO-932 microanalyzer.

## Results and Discussion

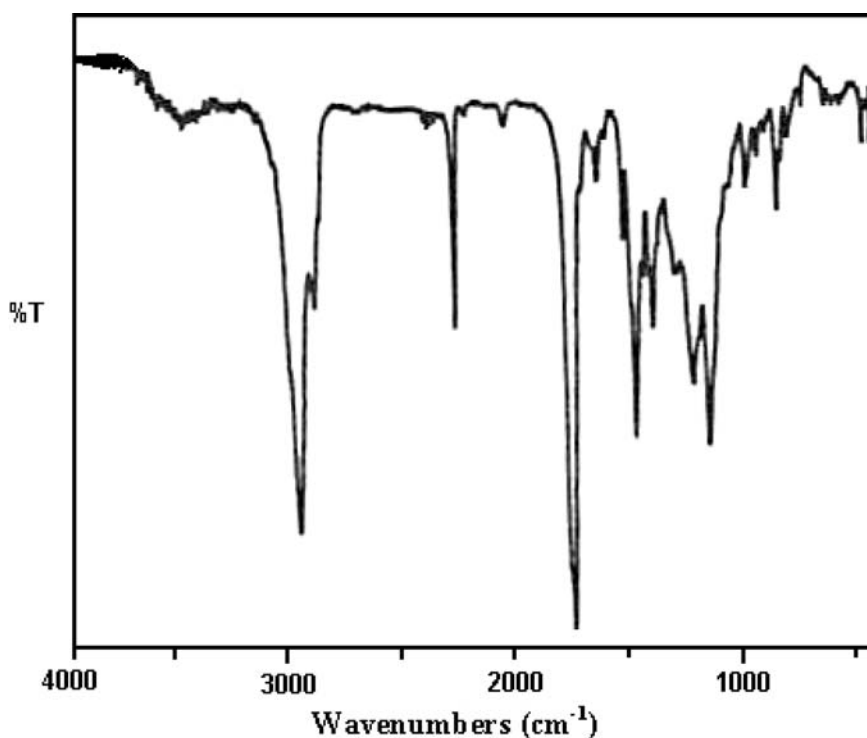
### Structural Characterization of the Copolymers

The constituent monomeric units of the copolymer are presented in Scheme 1.

The FTIR spectra of poly(MKEMA-co-AN) are shown in Figure 1. The FTIR spectra of the MKEMA-AN copolymers shows characteristic bands at 2200 cm<sup>-1</sup> (–C≡N), 1738 cm<sup>-1</sup> (–OC=O, and –C=O) 1510 cm<sup>-1</sup> (aromatic C=C stretchings), 3100 cm<sup>-1</sup> (aromatic C–H stretching vibrations), 1150 (–C–O). The <sup>1</sup>H-NMR spectrum of poly(pMKEMA-co-AN) are shown in Figure 2. <sup>1</sup>H-NMR (δ ppm): 6.5–6.73 (ArH), 4.62 (OCH<sub>2</sub>C=O), 2.7 (CH<sub>3</sub> protons on the mesityl ring), 2.2–3.3 (cyclobutane ring protons) 1.1–1.7 (–CH<sub>3</sub> on the cyclobutane ring and methylene protons in the polymer backbone). The <sup>13</sup>C-NMR spectrum of poly(pMKEMA-co-AN) are shown in Figure 3. <sup>13</sup>C-NMR (δ ppm): 205 (ketone carbonyl), 167 (ester carbonyl), 132–117 (ArC in polymer backbone), 75 (OCH<sub>2</sub>), 81



Scheme 1.

Figure 1. FTIR spectrum of copoly (MKEMA-AN)  $m_1 : m_2 : [26 : 74]$ .

( $-\text{C}\equiv\text{N}$ ), 42.5–38.9 (carbons in cyclobutane ring), 28.6 ( $\text{CH}_3$  in cyclobutane ring), 20.1, 22.0 ( $\text{CH}_3$  on polymer backbone).

Although the IR spectra of the MKEMA-ST (Figure 4) copolymers show characteristic bands at  $1740\text{ cm}^{-1}$  ( $-\text{OC}=\text{O}$ , and  $\text{C}=\text{O}$ )  $3100\text{--}3000\text{ cm}^{-1}$ ,  $1590\text{ cm}^{-1}$  (phenyl),  $1160\text{ cm}^{-1}$  ( $\text{C}-\text{O}$ ). The  $^1\text{H-NMR}$  spectra show broad peaks at 6.8–7.2 ppm (ArH), 4.62 ppm ( $\text{OCH}_2\text{C}=\text{O}$ ), 2.3–3.5 ppm (cyclobutane ring protons), 0.9–1.6 ppm (other aliphatic protons including those in the backbone).  $^{13}\text{C-NMR}$  peak assignments of this copolymer 125–148 ppm (aromatic ring protons), 203 (ketone carbonyl), 171 (es-

ter carbonyl), 44.2–41.6 (carbons in cyclobutane ring), 76.5 ppm ( $-\text{OCH}_2$ ), 37.2–40.5 ppm ( $-\text{C}-$  and  $\text{CH}$  protons in the backbone).

#### Molecular Weights of the Polymers

The molecular weights of the polymers were determined by GPC with polystyrene and tetrahydrofuran as the standard and solvent, respectively. The weight average ( $\bar{M}_w$ ) and number average ( $\bar{M}_n$ ) molecular weights and the polydispersity indexes ( $\bar{M}_w/\bar{M}_n$ ) of polymer samples are presented in Table 3. The PDIs of the polymers are close to 2.0. The theo-

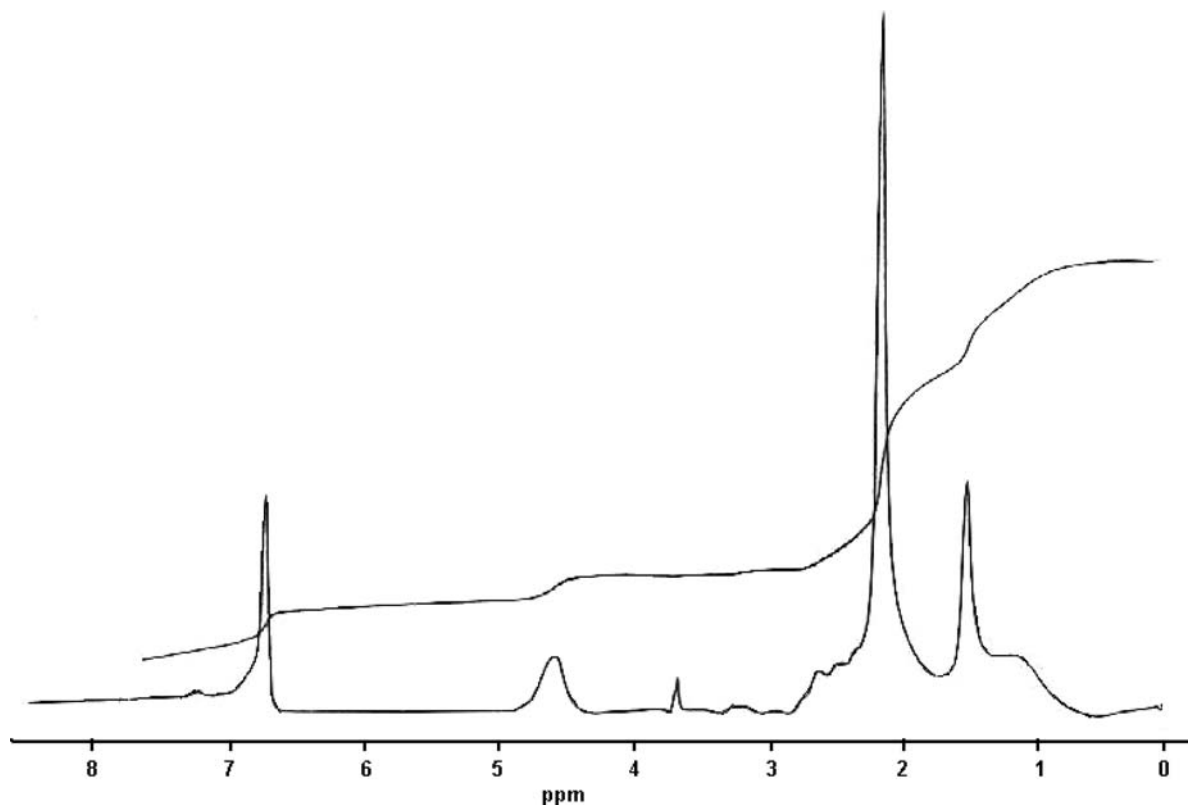


Figure 2.  $^1\text{H-NMR}$  spectrum of copoly (MKEMA-AN)  $m_1 : m_2 : [66 : 34]$ .

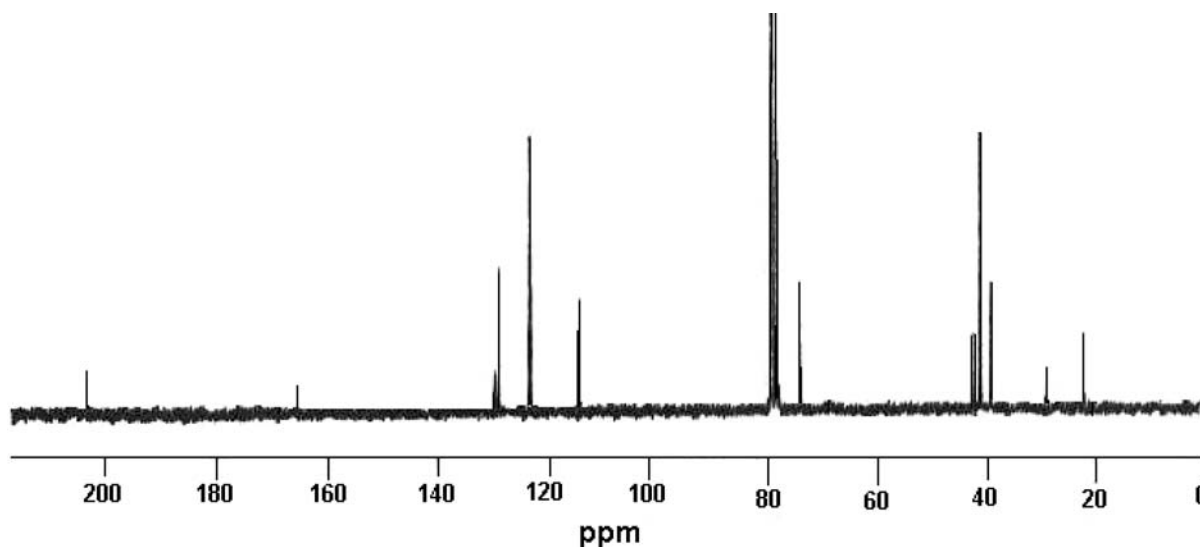


Figure 3.  $^{13}\text{C-NMR}$  spectrum of copoly (MKEMA-AN)  $m_1 : m_2 : [66 : 34]$ .

retical values of PDI for polymers via radical recombination and disproportionation are 1.5–2.0, respectively. The value of PDI in homopolymerization is also known to depend on chain termination.

#### Copolymer Compositions

Copolymerization of MKEMA with AN in 1,4-dioxane solution was studied for a molar fraction of MKEMA from approximately 0.80 to 0.20 in the feed. The amounts of monomeric units in the copolymers were determined by elemental analysis.

Table 3. The GPC result of the copolymers

| Poly(MKEMA-AN) | $M_w$  | $M_n$  | $M_w/M_n$ |
|----------------|--------|--------|-----------|
| 66/34          | 40,300 | 25,560 | 1,57      |
| 56/44          | 38,400 | 24,280 | 1,58      |
| 26/74          | 36,900 | 21,850 | 1,68      |
| Poly(MKEMA-ST) |        |        |           |
| 83/17          | 39,300 | 24,300 | 1,61      |
| 56/44          | 36,520 | 22,350 | 1,62      |
| 32/68          | 35,400 | 21,400 | 1,65      |

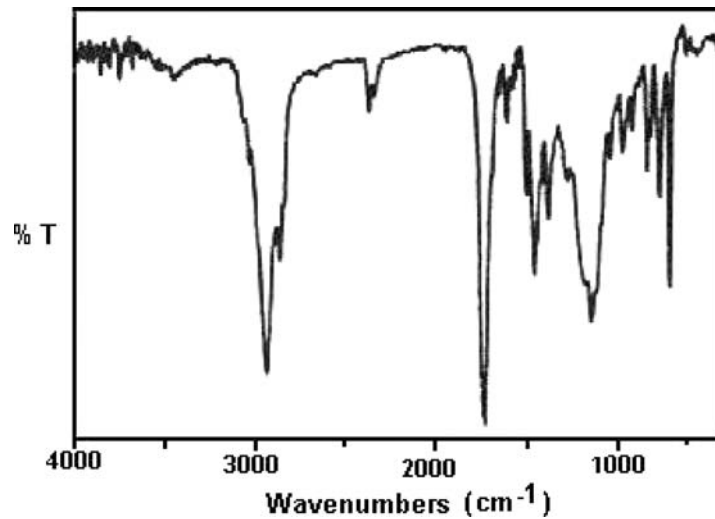


Figure 4. FTIR spectrum of copoly (MKEMA-ST)  $m_1 : m_2 : [83 : 17]$ .

Table 4. FR and KT parameters for copoly(MKEMA-AN) systems

| Sample no. | $F = M_1/M_2$ | $f = m_1/m_2$ | $G = F(f - 1)/f$ | $H = F^2/f$ | $\eta = G/(\alpha + H)$ | $\varepsilon = H/(\alpha + H)$ |
|------------|---------------|---------------|------------------|-------------|-------------------------|--------------------------------|
| 1          | 4.00          | 2.86          | 2.60             | 5.59        | 0.39                    | 0.84                           |
| 2          | 2.33          | 1.88          | 1.09             | 2.89        | 0.28                    | 0.73                           |
| 3          | 1.50          | 1.23          | 0.28             | 1.83        | 0.40                    | 0.63                           |
| 4          | 1.00          | 0.79          | -0.27            | 1.27        | -0.12                   | 0.55                           |
| 5          | 0.67          | 0.66          | -0.35            | 0.68        | -0.20                   | 0.38                           |
| 6          | 0.43          | 0.52          | -0.40            | 0.36        | -0.28                   | 0.25                           |
| 7          | 0.25          | 0.30          | -0.58            | 0.21        | -0.46                   | 0.17                           |

$$\alpha = (H_{\max} H_{\min})^{1/2} = 1.06.$$

Copolymer compositions of MKEMA with ST were determined by  $^1\text{H-NMR}$  spectral analysis. The assignment of resonance peaks in the  $^1\text{H-NMR}$  spectrum allow accurate determination of both kinds of monomeric units incorporated into the copolymers.

The following expression was derived to calculate the copolymer composition. Let  $m$  be the molar fraction of MKEMA and  $1 - m$  be that of ST in the copolymer. There are seven total aromatic protons (2H in MKEMA and 5H in ST) and 27 total aliphatic protons (24H in MKEMA and 3H in ST). Hence

$$\frac{2m_2 + 5m_1}{24m_2 + 3m_1} = \frac{\text{intensities of aromatic protons } I_A}{\text{intensities of aliphatic protons } I_a} \quad (1)$$

and on simplification it leads to

$$m_1 = \frac{24I_A - 2I_a}{21I_A + 3I_a}. \quad (2)$$

From Equation (2), the molar fractions of MKEMA in copolymers were determined by measuring the integrated peak heights of total aromatic proton signals and that of the total aliphatic proton signals of both monomer units.

#### Determination of Monomer Reactivity Ratios

The monomer reactivity ratios for the copolymerization of MKEMA with AN and ST were determined from the

monomer feed ratios and the copolymer composition. The Fineman–Ross (FR) [18] and Kelen–Tüdös (KT) [19] methods were used to determine the monomer reactivity ratios. The significance of parameters of FR and KT equations are presented in Tables 4 and 5. According to the FR method the monomer reactivity ratios can be obtained by the equation

$$G = Fr_1 - r_2, \quad (3)$$

where the reactivity ratios,  $r_1$  and  $r_2$  correspond to the AN with MKEMA monomers respectively. The parameters  $G$  and  $H$  are defined as follows:

$$G = \frac{F(f - 1)}{f} \quad \text{and} \quad H = \frac{F^2}{f} \quad (4)$$

with

$$F = \frac{M_1}{M_2} \quad \text{and} \quad f = \frac{m_1}{m_2}. \quad (5)$$

$M_1$  and  $M_2$  are the monomer molar compositions in feed and  $m_1$  and  $m_2$  the copolymer molar compositions.

Alternatively the reactivity ratios can be obtained using the KT method which is based on the equation

$$\eta = \left( r_1 + \frac{r_2}{\alpha} \right) \xi - \frac{r_2}{\alpha}, \quad (6)$$

where  $\eta$  and  $\xi$  are functions of the parameters  $G$  and  $H$ ,

$$\eta = \frac{G}{\alpha + H} \quad \text{and} \quad \xi = \frac{H}{\alpha + H}, \quad (7)$$

Table 5. FR and KT parameters for copoly(MKEMA-ST) systems

| Sample no. | $F = M_1/M_2$ | $f = m_1/m_2$ | $G = F(f - 1)/f$ | $H = F^2/f$ | $\eta = G/(\alpha + H)$ | $\varepsilon = H/(\alpha + H)$ |
|------------|---------------|---------------|------------------|-------------|-------------------------|--------------------------------|
| 1          | 4.00          | 2.13          | 2.12             | 7.53        | 0.23                    | 0.83                           |
| 2          | 2.33          | 1.50          | 0.77             | 3.57        | 0.15                    | 0.70                           |
| 3          | 1.50          | 1.13          | 0.17             | 1.99        | 0.05                    | 0.56                           |
| 4          | 1.00          | 1.04          | 0.04             | 0.96        | 0.16                    | 0.38                           |
| 5          | 0.67          | 0.79          | -0.18            | 0.60        | -0.08                   | 0.28                           |
| 6          | 0.43          | 0.36          | -0.78            | 0.53        | -0.38                   | 0.26                           |
| 7          | 0.25          | 0.20          | -1.00            | 0.31        | -0.54                   | 0.17                           |

$$\alpha = (H_{\max}H_{\min})^{1/2} = 1.53.$$

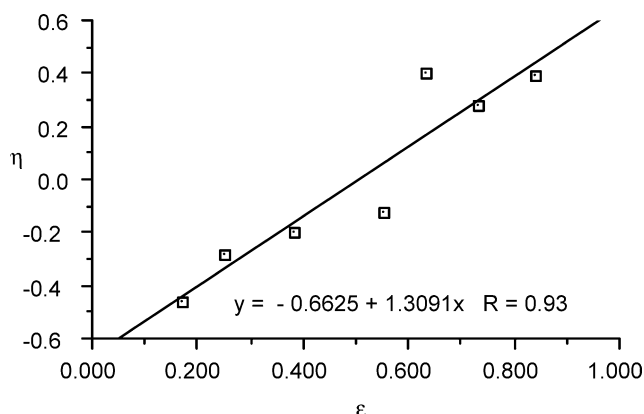


Figure 5. KT plot for copoly (MKEMA-AN)system.

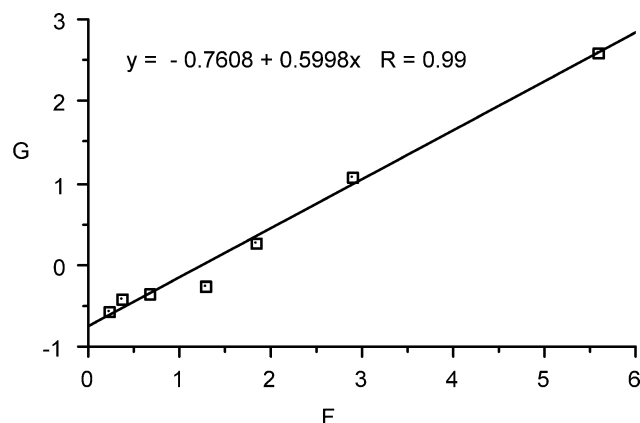


Figure 6. FR plot for copoly (MKEMA-AN)system.

and  $\alpha$  is a constant which is equal to  $(H_{\max}H_{\min})^{1/2}$ ,  $H_{\max}$ ,  $H_{\min}$  being the maximum and the minimum  $H$  values, respectively from the series of measurements. From the linear plot of  $\eta$  as a function of  $\xi$  the values of  $\eta$  for  $\xi = 0$  and  $\eta = 1$  are used to calculate the reactivity ratios according to the equations

$$\xi = 0 \implies \eta = -\frac{r_1}{\alpha} \quad \text{and} \quad \xi = 1 \implies \eta = r_2. \quad (8)$$

The graphical plots concerning the methods previously reported are given for poly(MKEMA-co-AN) in Figures 5, 6, whereas the reactivity ratios are summarized in Table 6.

In all cases and for all graphical methods the plots were linear indicating that these copolymerizations follow the

Table 6. Comparison of reactivity ratios by various methods

| System         | Methods | $r_1$ | $r_2$ | $r_1r_2$ | $1/r_1$ | $1/r_2$ |
|----------------|---------|-------|-------|----------|---------|---------|
| Poly(MKEMA-AN) | FR      | 0.59  | 0.76  | 0.45     | 1.69    | 1.32    |
|                | KT      | 0.65  | 0.70  | 0.46     | 1.54    | 1.43    |
|                | Average | 0.62  | 0.73  | 0.45     | 1.61    | 1.37    |
| Poly(MKEMA-ST) | FR      | 0.39  | 0.69  | 0.27     | 2.56    | 1.45    |
|                | KT      | 0.46  | 0.81  | 0.37     | 2.17    | 1.23    |
|                | Average | 0.43  | 0.75  | 0.32     | 2.33    | 1.33    |

conventional copolymerization kinetics and that the reactivity of a polymer radical is determined only by the terminal monomer unit.

For MKEMA and AN systems the  $r_2$  values are higher than the  $r_1$  values. The higher  $r_2$  value of MKEMA confirms the higher reactivity of MKEMA compared with that of AN. For MKEMA and ST systems the  $r_2$  values are higher than the  $r_1$  values. The higher  $r_2$  value of MKEMA confirms the higher reactivity of MKEMA compared with that of ST. The reactivity ratio values ( $r_1$  and  $r_2$ ) of copoly(MKEMA-AN) and copoly(MKEMA-ST) are less than one. The product  $r_1r_2$  indicates that the two system copolymerizes randomly in the polymer chain although there is a possible tendency for alternation.

### Glass Transition Temperatures

The glass transition ( $T_g$ ) temperatures were determined by a Shimadzu DSC-50. Samples of about 4–7 mg held in sealed aluminium crucibles and the heating rate of 20°C/min under a dynamic nitrogen flow (5  $\text{lh}^{-1}$ ) were used for the measurements. From DSC measurements  $T_g$  was taken as the midpoint of the transition region. The  $T_g$  values of poly(MKEMA), poly(AN), and poly(ST) obtained under the same conditions with the copolymers were found 115°C, 85°C and 105°C, respectively. The glass transition temperature of poly (MKEMA) is considerably higher than the other polymers. Apparently the bulky mesityl side group decreases the flexibility of the chain and the free volume, thereby increasing  $T_g$ .

Among the many strategies available for increasing the  $T_g$  of methacrylate polymers, the most promising is the replacement of the methyl group in the ester part of the

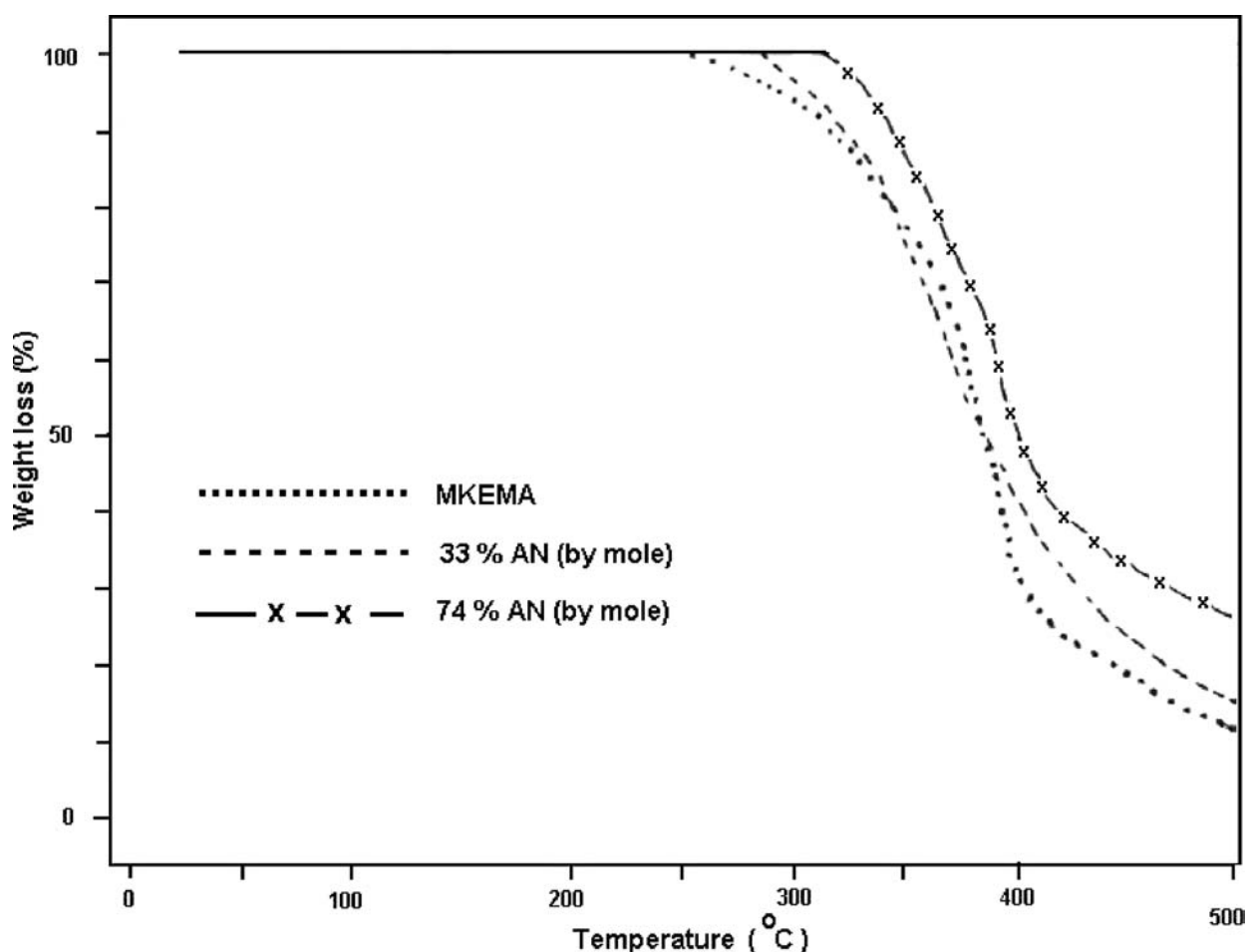


Figure 7. TGA curves of the copoly (MKEMA-AN) (heating rate 10 °C/min under a nitrogen atmosphere).

monomer. Sterically hindered and conformationally rigid cycloalkyl groups cause a significant increase in  $T_g$ . For example,  $T_g$  varies from 110 °C for poly(cyclohexylmethacrylate) to 194 °C for poly (bornyl methacrylate) and 200 °C for poly (isobornyl methacrylate [20]). Similarly, an increase in the polarity of the ester group causes an increase in  $T_g$ , which is observed in 4-cyanophenyl methacrylate ( $T_g$  155 °C) [21]. The  $T_g$  of the copolymers showed a gradual increase with an increase in the molar percentage of MKEMA.

In comparison to that of poly(AN), and poly (ST) the shift to higher temperature is also noted for all the copolymers studied and its magnitude is dependent on the increasing in MKEMA molar fraction in the copolymer chain. An increase in  $T_g$  of copolymers may be due to the introduction of comonomer into AN and ST, MKEMA, which increases the inter-molecular polar interactions between the molecular chains due to structure stretching. The results clearly indicate that  $T_g$  values of copolymers depend on the composition of comonomers and increase with increasing MKEMA contents in the polymer chain. These values are indicated in Table 7. It can be seen that the observed  $T_g$  increases with increasing MKEMA and presents a striking positive deviation with respect to linearity, which can be associated with a lower free volume, mobility and flexibility than a mixture of MKEMA and AN or ST units.

Table 7. Some TGA results and  $T_g$  values of the copolymers

| Polymer        | The temperature (°C) for a weight loss of |     |     |     | The residue (%) at 450 °C | $T_g$ |
|----------------|---|-----|-----|-----|---------------------------|-------|
|                | IDT <sup>a</sup>                          | 20  | 50  | 70  |                           |       |
| Poly(MKEMA)    | 250                                       | 325 | 385 | 410 | 19                        | 115   |
| Poly(AN)       | 320                                       | 370 | 490 | –   | 40                        | 85    |
| Poly(MKEMA-AN) |   |     |     |     |                           |       |
| 66/34          | 280                                       | 325 | 390 | 425 | 25                        | 109   |
| 56/44          | 298                                       | 351 | 400 | 465 | 32                        | 101   |
| 26/74          | 308                                       | 375 | 403 | 490 | 37                        | 93    |
| Poly(ST)       | 325                                       | 380 | 400 | 450 | 2                         | 105   |
| poly(MKEMA-ST) |   |     |     |     |                           |       |
| 83/17          | 287                                       | 348 | 385 | 420 | 11                        | 115   |
| 56/44          | 295                                       | 362 | 398 | 456 | 8                         | 108   |
| 32/68          | 300                                       | 381 | 413 | 485 | 6                         | 103   |

<sup>a</sup>Initial decomposition temperature.

#### Thermogravimetric Measurements of the Copolymers

The thermal stability of the copolymers was studied by programmed thermogravimetric analysis over a temperature range from room temperature to 500 °C under a nitrogen atmosphere. In Figures 7 and 8 the TGA thermograms of

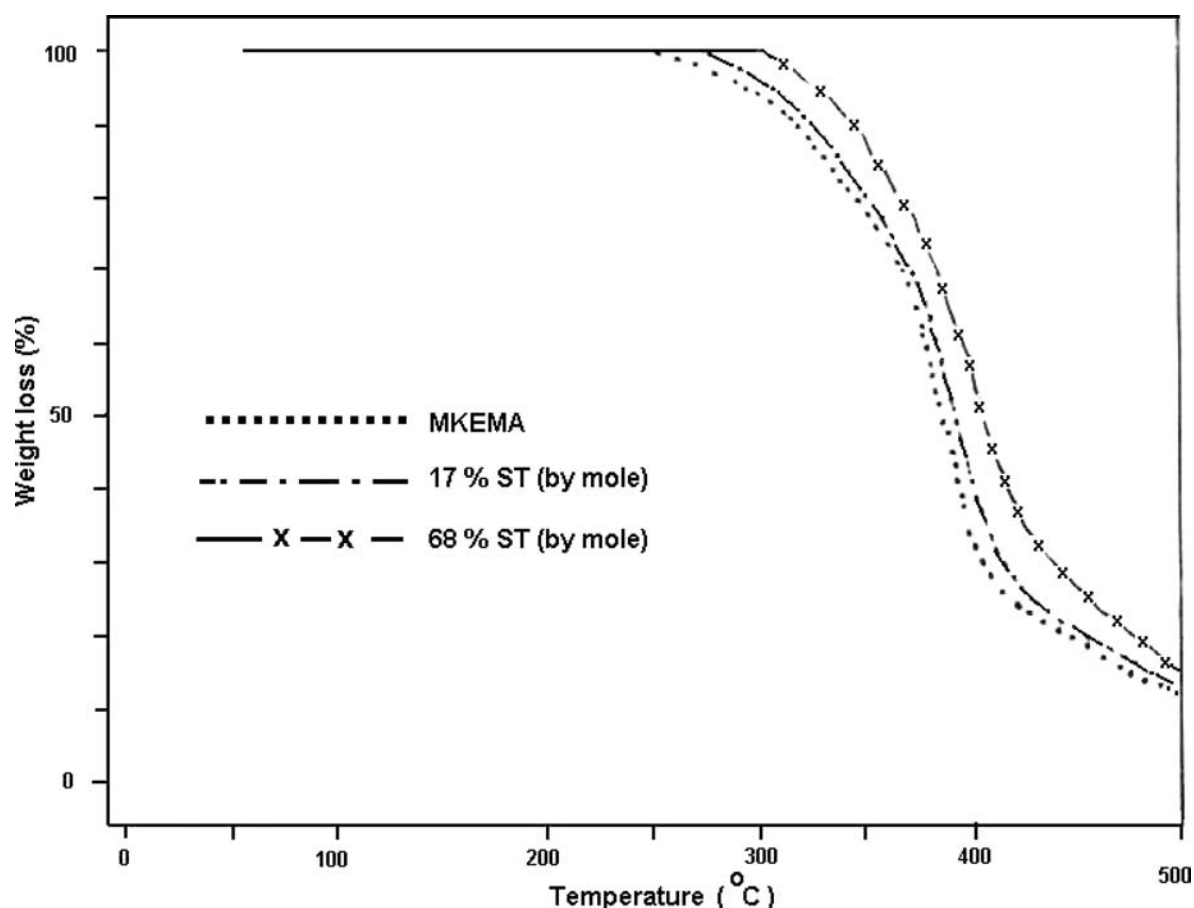


Figure 8. TGA curves of the copoly (MKEMA-co-ST) (heating rate 10°C/min under a nitrogen atmosphere).

polymers are shown. Some degradation characteristics of the copolymers are given in Table 7 by comparison with those of the homopolymers. The thermal stabilities of two copolymers are between those of the corresponding homopolymers. The homopolymers and all the copolymer samples showed a single decomposition step. The actual decomposition temperature range depends upon the composition of the constitutional monomeric units in the copolymer. The initial decomposition temperature and thermal stability of the copolymers increases with an increase in AN and ST monomers concentration. My results are in agreement [22, 23].

## Conclusion

Copolymers of MKEMA with AN and ST have been prepared by free radical polymerization in 1,4-dioxane at 65°C. The reactivity ratios of the copolymers were estimated using linear graphical methods. The  $r_2$  values were higher than the corresponding  $r_1$  values in all cases, meaning that a kinetic preference exists for the incorporation of MKEMA in the copolymer structure. The glass transition temperatures of the MKEMA with AN and ST copolymers were obtained and compared. The TGA studies concluded that the thermal stability of the copolymers increases with an increase of AN and ST in the copolymer chain.

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