

Radical Copolymerization of *N*-(4-Acetyl phenyl)-maleimide and Styrene: Monomer Reactivity Ratios and Thermal Properties

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ABSTRACT: Copolymers containing *N*-(4-acetyl phenyl)-maleimide (NAPMI) and styrene (ST) at different compositions have been prepared by radical copolymerization. FTIR, ¹H-, and ¹³C NMR and elemental analysis techniques were used on the identification of polymers. The monomer reactivity ratios were estimated using the Kelen-Tüdös (KT) and Fineman-Ross (FR) graphical methods. Structural parameters of the copolymers were obtained calculating the dyad monomer sequence fractions. A thermal study of the obtained copolymers related to the *N*-(4-acetyl phenyl)male-

imide content has been carried out taking into account several theories predicting the dependence of the glass transition temperature on the copolymers composition. The T_g s are linearly distributed between T_g s of homopolymers and in all cases, single, well-defined T_g s are obtained. Glass transition temperatures increase with the increase of molar fraction of *N*-(4-acetylphenyl)maleimide. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 964–970, 2004

Key words: radical polymerization; glass transition

INTRODUCTION

The importance of copolymerization has been very soon realized in polymer science leading to an enormous amount of work both experimental and theoretical. 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. Copolymerization is the most successful and powerful method for effecting systematic changes in polymer properties.¹ The incorporation of two different monomers, having diverse physical and/or chemical properties, in the same polymer molecule in varying proportions leads to the formation of new materials with great scientific and commercial importance.² Copolymerization modulates both the intramolecular and intermolecular forces exercised between like and unlike polymer segments, and consequently, properties such as glass transition temperature, melting point, solubility, crystallinity, permeability, dyeability, adhesion, elasticity, and chemical reactivity may be varied within wide limits. The utility of copolymerization is exemplified on the one hand by the fundamental investigations of structure property relations,³ and on the other hand by the wide range of commercial applications.⁴ The elucidation of copolymer struc-

ture (copolymer composition, monomer sequence distribution) and kinetics (propagation rate coefficients) are the major concerns for the prediction of copolymer properties and the correlation between structure and properties. Among the various copolymerization reactions radical copolymerization is the most important because it does not demand rigorous experimental conditions and can be applied to a large variety of monomers, leading to the formation of new materials.

Monomer reactivity ratios are generally determined at low conversions. In the classic terminal model of copolymerization, it has been suggested that, for a given pair of monomers, the instantaneous copolymer composition is a function of instantaneous feed only.⁵

It is well known that *N*-substituted maleimide and styrene represent monomer pairs with a strong tendency toward radical alternating copolymerization;^{6–13} moreover, after copolymerization, the thermal stability of polystyrene, which is widely used as a conventional plastic, will be greatly improved. So far, the copolymerization of *N*-butyl maleimide (NBMI) and styrene, *N*-4-hydroxy phenyl maleimide (NHPMI) and styrene has been reported in literature.^{14–17}

In this presentation, we report on the synthesis and characterization of copolymers of *N*-(4-acetyl phenyl)-maleimide and styrene. In this work, the monomer reactivity ratios were determined by several linear methods, and predictions concerning the monomer sequence distribution are provided. The glass transition temperature of the copolymers is determined and compared with several theoretical equations. Conse-

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quently, the influence of the size of the monomer on the copolymer structure and properties is discussed.

EXPERIMENTAL

Materials

Maleic anhydride, 4-amino acetophenone, ethanol, and styrene (Merck) were used as received. Pyridine, 1,4-dioxane and dimethylsulphoxide (Aldrich) were used as received. 2,2'-Azobisisobutyronitrile was recrystallized from chloroform-methanol. All the other chemicals were analytical grade commercial products. They were used without any further purification.

Measurements

IR spectra of the monomer and copolymers were recorded on a Mattson 1000 FTIR spectrometer. ^1H - and ^{13}C -NMR spectra of the copolymers were recorded in CDCl_3 with tetramethylsilane as the internal standard using a Varian Gemini 200 MHz NMR spectrometer. Elemental analyses were carried out by a LECO-932 microanalyzer. Thermal analysis was performed in nitrogen atmosphere at a heating rate of $10^\circ\text{C} \cdot \text{min}^{-1}$. Thermogravimetric data were obtained by using a Shimadzu DSC-50 instrument and a TGA-50 thermobalance. Molecular weight (\bar{M}_w and \bar{M}_n) of the poly(NAPMI-co-ST) (55.0% NAPMI by mol) was determined using Waters 410 gel permeation chromatography equipped with a RI detector and calibrated with polystyrene standards.

Synthesis of the monomer (NAPMI)

The NAPMI monomer was synthesized according to the usual method of synthesis for RMI compounds,^{18,19} which was prepared from the reaction of maleic anhydride and 4-aminoacetophenone, as reported previously.²⁰

Copolymerization

Copolymerizations of NAPMI and ST using different proportions of NAPMI were carried out in glass ampoules under N_2 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 threefold freeze-thawing cycles and then immersed in a oil bath at $60 \pm 0.1^\circ\text{C}$ for a given reaction time. For estimating monomer reactivity ratios, copolymerization experiments were terminated at less than 10% conversion. The copolymers were separated by precipitation in methanol and reprecipitated from 1,4-dioxane solution. The polymers, purified by reprecipitation to avoid the formation of homopolymers. The polymers were finally dried over

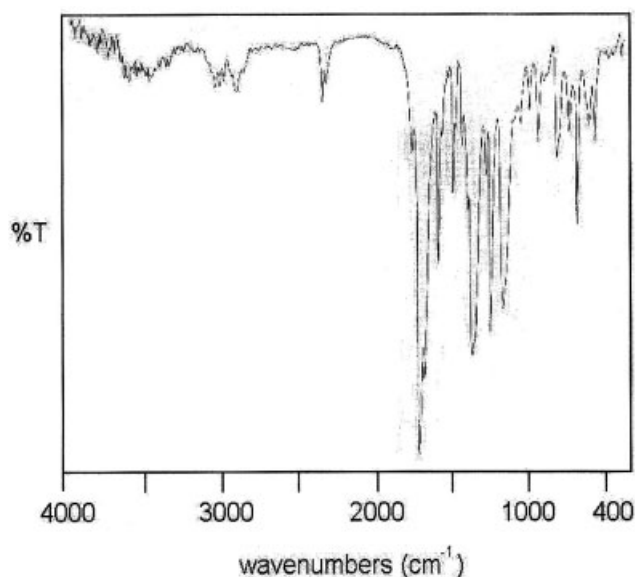


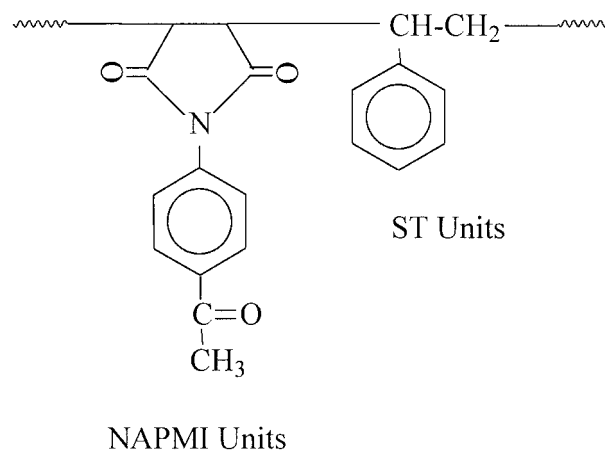
Figure 1 The FTIR spectrum of a poly(NAPMI-co-ST) (42.0% NAPMI by mol).

vacuum to constant weight. The amounts of monomeric units in the copolymers were determined by elemental analysis.

RESULTS AND DISCUSSION

Characterization of poly(NAPMI-co-ST)

The constituent monomeric units of the copolymer are as follows:



The FTIR spectrum of a poly(NAPMI-co-ST) (42.0% NAPMI by mole) is shown in Figure 1. The IR spectra of the copolymers show strong absorptions at 1780, 1730, and 1690 cm^{-1} due to $\text{C}=\text{O}$ stretching of imide and ketone groups, respectively. A strong band at about 1610 cm^{-1} corresponds to the pendant olefin group, which is flanked by a ketone and phenyl group in NAPMI unit. The aromatic $\text{C}=\text{C}$ stretchings are

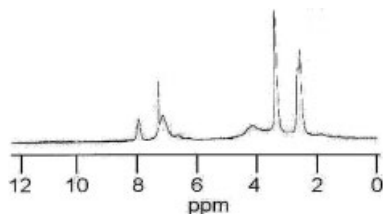


Figure 2 The ^1H NMR spectrum of a poly(NAPMI-co-ST) (42.0% NAPMI by mol).

observed at 1510 cm^{-1} . Peaks at 3100 cm^{-1} is due to aromatic C—H stretching vibrations. Peaks at $770\text{--}750\text{ cm}^{-1}$ may due to aromatic C—H out of plane bendings, and those at 1440 cm^{-1} may be assigned to CH_3 bending vibrations.

The ^1H -NMR spectra of poly(NAPMI-co-ST) (42.0% NAPMI by mol) is presented in Figure 2. The multiplet resonance signals at 8.1–6.9 ppm correspond to the aromatic protons of the NAPMI and ST units. The resonance signals at 3.2–3.6 and 3.8–4.4 ppm corresponds to the ring CH, CH—CH_2 protons of copolymer. A signals at 2.4–2.8 ppm originate due to methyl protons of NAPMI unit.

The proton decoupled ^{13}C -NMR spectrum of poly(NAPMI-co-ST) (42.0% NAPMI by mol) is shown in Figure 3. Chemical shift assignments were made from the off-resonance decoupled spectra of the copolymers. Resonance signals at 198 and 178 ppm corresponds to carbonyl carbon of imide group in NAPMI unit. The ketone carbonyl carbon resonance is observed at 172 ppm. Resonance signals at 145 ppm may be assigned to the olefinic carbon, which is attached to the aromatic and maleimide rings. The other aromatic carbons are observed 136–121 ppm. The methylene and methyne carbons of polymer backbone show signals at 55 and 52 ppm, respectively. The signals due to ring methyne carbon in the NAPMI and ST unit are observed at 46 and 45 ppm, respectively. The methyl group of NAPMI shows resonance signals at 28 ppm.

The GPC system calibrated with polystyrene in tetrahydrofuran (THF) showed that the weight-average molecular weight of the poly(NAPMI-co-ST) (55.0% NAPMI by mol) was 67,300 [(polydispersity index (PDI), 1.92)]. The PDI of the copolymer is close to 2.0. The theoretical values of PDI for polymers produced via radical recombination and disproportionation are 1.5–2.0, respectively.^{21,24} PDI:1.92 suggest that there must be some combination for the termination. Besides combination, some disproportionation and/or transfer is also probable.

Copolymer compositions

Copolymerization of NAPMI with ST in chloroform solution was studied for a molar fraction of NAPMI

from approximately 0.80 to 0.20 in the feed. The amounts of monomeric units in the copolymers were determined by elemental analysis.

Determination of monomer reactivity ratios

The monomer reactivity ratios for the copolymerization of NAPMI with ST were determined from the monomer feed ratios and the copolymer composition. The Fineman-Ross (FR),²⁵ the Inverted Finemann-Ross (IFR),²⁵ and Kelen-Tüdös (KT)²⁶ methods were used to determine the monomer reactivity ratios. According to the FR method the monomer reactivity ratios can be obtained by the equation:

$$G = Fr_A - r_S \quad (1)$$

where the reactivity ratios, r_A and r_S correspond to the *N*-(4-acetyl phenyl)maleimide and styrene monomers, respectively. The parameters G and F are defined as follows:

$$G = X(Y - 1)/Y \quad \text{and} \quad F = X^2/Y \quad (2)$$

with

$$X = M_A/M_S \quad \text{and} \quad Y = dM_A/dM_S \quad (3)$$

where M_A and M_S are the monomer molar compositions in feed, and dM_A and dM_S the copolymer molar compositions.

The inverted FR method is based on the equation:

$$G/F = r_A - (1/F)r_S \quad (4)$$

The plots of the G vs F values and the G/F vs $1/F$ values yield the reactivity ratios r_A and r_S from the intercept and the slope of the graphs.

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

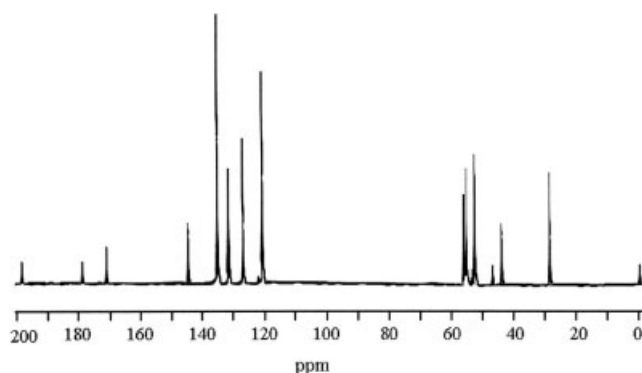


Figure 3 The ^{13}C NMR spectrum of a poly(NAPMI-co-ST) (42.0% NAPMI by mol).

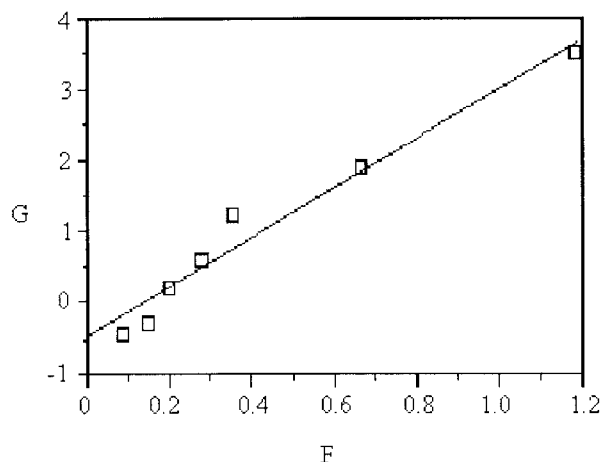


Figure 4 FR plots for the NAPMI and ST copolymers.

$$\eta = (r_A + r_S/\alpha)\xi - r_S/\alpha \quad (5)$$

where η and ξ are functions of the parameters G and H :

$$\eta = G/(\alpha + F) \quad \text{and} \quad \xi = F/(\alpha + F) \quad (6)$$

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

$$\xi = 0 \Rightarrow \eta = -r_A/\alpha \quad \text{and} \quad \xi = 1 \Rightarrow \eta = r_S \quad (7)$$

The graphical plots concerning the methods previously reported are given in Figures 4–6, whereas the reactivity ratios are summarized in Table I.

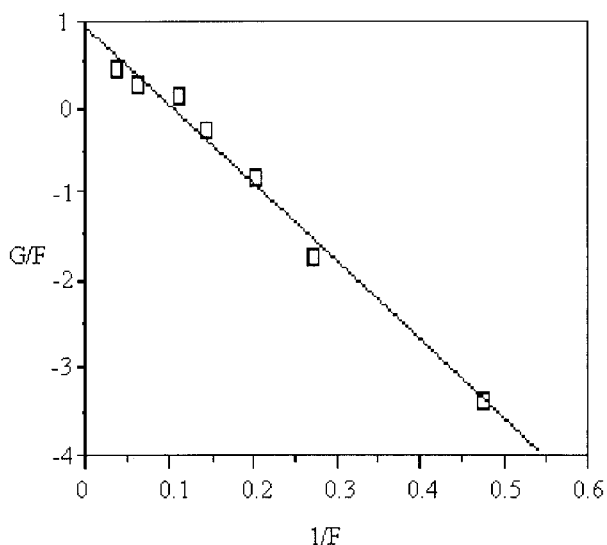


Figure 5 IFR plots for the NAPMI and ST copolymers.

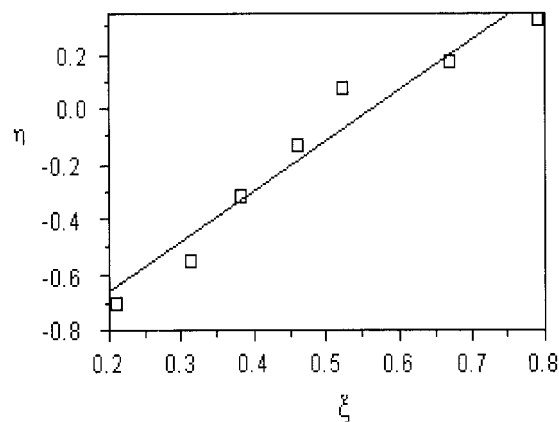


Figure 6 KT plots for the NAPMI and ST copolymers.

In all cases and for all graphical methods the plots were linear indicating that these copolymerizations follow the conventional copolymerization kinetics and that the reactivity of a polymer radical is determined only by the terminal monomer unit.

For all systems the r_A values are higher than the r_S values. This result shows that the incorporation of NAPMI units in the copolymer structure is kinetically favored by increasing the styrene monomer. The single parameter that can best describe the copolymer structure is the product of the reactivity ratios $r_A \cdot r_S$.

The higher r_A value of NAPMI confirms the higher reactivity of NAPMI compared with that of ST, and the copolymer sequence will be alternating in structure with more NAPMI. NAPMI and ST have approximately equal reactivities towards the poly(NAPMI) radical, but NAPMI is about four times more reactivity than ST towards the poly(ST) radical. The copolymer will have a strong tendency toward radical alternating copolymerization.

The reactivity ratios determined up to 1990 were collected by Müller and Braun.^{27,28} The recent work²⁹ agrees with the values reported for the styrene, somewhat higher r_P value of *N*-phenyl maleimide (NPMI) confirms the higher reactivity of NPMI compared with that of styrene (NPMI–ST) system. In that system, the monomer NPMI was the more active one $r_{\text{NPMI}} = 0.047$; $r_{\text{ST}} = 0.012$. In the other work,¹³ *N*-(4-hydroxy phenyl)maleimide (NHPMI) with styrene (ST), the monomer reactivity values was calculated as $r_{\text{NHPMI}} = 0.161$ and $r_{\text{ST}} = 0.058$. In our case, the monomer NAPMI was also more active. The reactivity ratios obtained from the two methods were in good agreement within the experimental error. Comparing NPMI, NHPMI, NAPMI to ST it should be stated that two monomers (NPMI and NAPMI) show similar copolymerization behaviour. The reactivities of these monomers are close together. Due to the presence of the phenyl groups, two monomers are highly susceptible to the addition of radicals leading to relatively

TABLE I
Reactivity Ratios for the Copolymers NAPMI and ST

| Method | r_A | r_S | $r_A \cdot r_S$ | $1/r_A$ | $1/r_S$ |
|---------|-------------------|-------------------|-----------------------|---------|---------|
| F-R | 0.051 ± 0.004 | 0.015 ± 0.003 | 7.65×10^{-4} | 19.60 | 66.67 |
| I-F-R | 0.070 ± 0.007 | 0.018 ± 0.008 | 1.26×10^{-3} | 14.28 | 55.56 |
| K-T | 0.060 ± 0.003 | 0.016 ± 0.002 | 9.6×10^{-4} | 16.67 | 62.50 |
| Average | 0.060 ± 0.005 | 0.016 ± 0.004 | 9.9×10^{-4} | 16.85 | 61.58 |

^a Temperature: 60 ± 1 °C; solvent: 1,4-dioxane; initiator: 2,2'-azobisisobutyronitrile (1%); nonsolvent for precipitation: ethanol

stable adducts. Although there is a small decrease at monomer reactivity ratio values of NAPMI-ST copolymers as monomers without acetyl substitution, there is a question as to whether the para derivative should behave similarly. Styrene is known to form alternating copolymer with maleimides and the same behavior is manifested in this study as well.

The statistical distribution of the dyad monomer sequences M_A-M_A , M_S-M_S , and M_A-M_S were calculated using the method proposed by Igarashi:³⁰

$$X = \phi_1 - \frac{2\phi_A(1 - \phi_A)}{1 + [(2\phi_A - 1)^2 + 4r_A r_S \phi_A(1 - \phi_A)]^{1/2}} \quad (8)$$

$$Y = (1 - \phi_A) - \frac{2\phi_A(1 - \phi_A)}{1 + [(2\phi_A - 1)^2 + 4r_A r_S \phi_A(1 - \phi_A)]^{1/2}} \quad (9)$$

$$Z = \frac{4\phi_A(1 - \phi_A)}{1 + [(2\phi_A - 1)^2 + 4r_A r_S \phi_A(1 - \phi_A)]^{1/2}} \quad (10)$$

where X , Y , and Z are the mol fractions of the M_A-M_A , M_S-M_S , and M_A-M_S dyads in the copolymer respectively and ϕ , the N -(4-acetyl phenyl)maleimide mol fraction in the copolymer. Mean sequence lengths ϕ_A and μ_S were also calculated using the following equations.³¹

$$\mu_A = 1 + r_A \frac{[M_A]}{[M_S]} \quad (11)$$

TABLE II
Structural Data for the Copolymers NAPMI and ST

| Sample | M_A-M_A | M_S-M_S | M_A-M_S | μ_A | μ_S |
|--------|-----------|-----------|-----------|---------|---------|
| 1 | 0.02 | 0.76 | 0.22 | 1.015 | 1.066 |
| 2 | 0.05 | 0.65 | 0.30 | 1.026 | 1.038 |
| 3 | 0.11 | 0.49 | 0.40 | 1.040 | 1.025 |
| 4 | 0.21 | 0.37 | 0.42 | 1.060 | 1.017 |
| 5 | 0.27 | 0.22 | 0.46 | 1.090 | 1.011 |
| 6 | 0.40 | 0.16 | 0.44 | 1.140 | 1.007 |
| 7 | 0.55 | 0.09 | 0.36 | 1.240 | 1.004 |

$$\mu_S = 1 + r_S \frac{[M_S]}{[M_A]} \quad (12)$$

The data are summarized in Table II, whereas Figure 7 display the variation of the dyad fractions with the N -(4-acetylphenyl)maleimide fraction in the copolymers.

Thermal analysis

Differential scanning calorimetry (DSC) was performed at a heating rate of $10^\circ\text{C} \cdot \text{min}^{-1}$ under nitrogen atmosphere. The thermal properties of the copolymers are influenced by their chemical structure and composition and the monomer sequence distributions. Several relationships have been employed to describe the effect of these parameters on the glass transition temperature of the copolymers.³² The simplest equation describing the effect of composition on T_g is the Gibbs-Di Marzio equation.³³

$$T_g = \phi_A T_{gA} + \phi_S T_{gS} \quad (13)$$

where ϕ_A , ϕ_S are the mol fractions of N -(4-acetyl phenyl)maleimide and styrene monomers, respectively, in

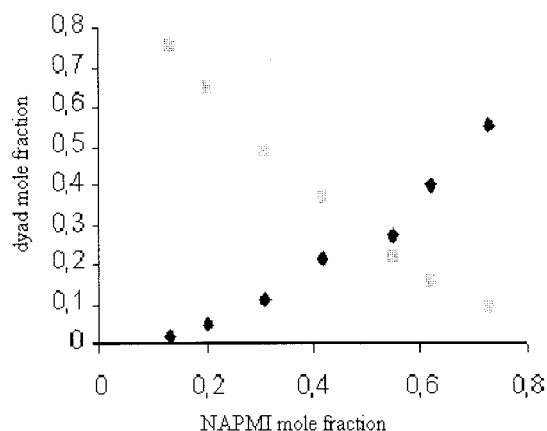


Figure 7 Dyad monomer sequence fractions vs the NAPMI mol fraction for the ST copolymers: M_A-M_A (◆), M_S-M_S (light shaded boxes) and M_A-M_S (▲) dyads.

the copolymer and T_{gA} , T_{gS} the glass transition temperatures of the two homopolymers, respectively.

A similar relationship was introduced by Fox:³⁴

$$1/T_g = w_A/T_{gA} + w_S/T_{gS} \quad (14)$$

where w_A and w_S are the weight fractions of *N*-(4-acetyl phenyl)maleimide and styrene monomers in the copolymer.

Based on the free volume concept Johnston proposed the following equation:³⁵

$$\frac{1}{T_g} = \frac{w_A P_{AA}}{T_{gAA}} + \frac{w_S P_{SS}}{T_{gSS}} + \frac{w_A P_{AS} + w_S P_{SA}}{T_{gAS}} \quad (15)$$

It is assumed that *AA*, *SS*, and *AS* or *SA* dyads have their own glass transition, T_{gAA} , T_{gSS} , and T_{gAS} , respectively. T_{gAA} and T_{gSS} can be considered as the glass transition temperatures for the respective homopolymers, where T_{gAS} is the glass transition temperature of the alternating copolymer *PA-alt-PS*. W_i is the weight fraction of the *i* component and P_{AA} , P_{SS} , P_{AS} , and P_{SA} are the probabilities of having various linkages. These probabilities can be calculated using the monomer reactivity ratios:³¹

$$P_{AA} = \frac{r_A}{r_A + \frac{[M_S]}{[M_A]}} \quad (16)$$

$$P_{AS} = \frac{[M_S]}{r_A[M_A] + [M_S]} \quad (17)$$

$$P_{SA} = \frac{[M_A]}{r_S[M_S] + [M_A]} \quad (18)$$

$$P_{SS} = \frac{r_S[M_S]}{r_S[M_S] + [M_A]} \quad (19)$$

TABLE III
Glass Transition Temperatures for the Copolymers
NAPMI and ST

| Sample m ₂ | ST (wt.%) | ^a (T _g) _{exp} (°C) | ^b (T _g) _{GM} (°C) | ^c (T _g) _F (°C) | ^d (T _g) _J (°C) |
|--------------------------|-----------|---|--|---|---|
| 0.87 | 77.0 | 128 | 135 | 125 | 127 |
| 0.80 | 66.0 | 152 | 152 | 137 | 145 |
| 0.69 | 52.0 | 170 | 177 | 157 | 162 |
| 0.58 | 40.0 | 194 | 200 | 179 | 195 |
| 0.45 | 29.0 | 228 | 233 | 206 | 220 |
| 0.38 | 23.0 | 254 | 249 | 224 | 234 |
| 0.27 | 15.0 | 270 | 275 | 254 | 268 |

^a Experimental result by DSC measurement.

^b Theoretical prediction using the Gibbs-Di Marzio equation.

^c Theoretical prediction using the Fox equation.

^d Theoretical prediction using the Johnston equation.

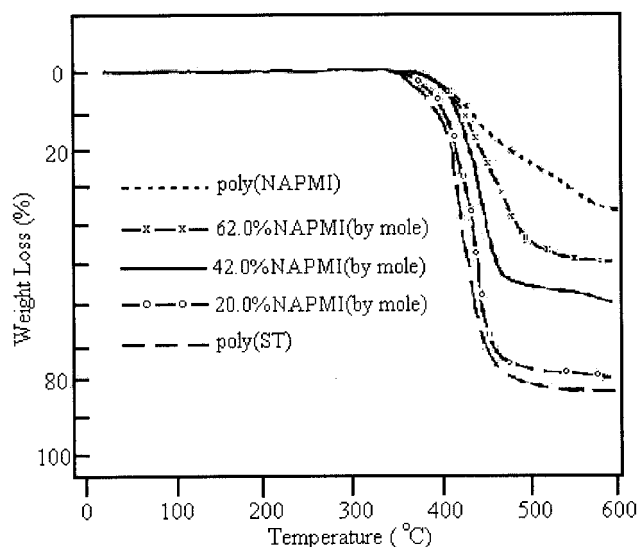


Figure 8 TG curves of the homo- and copolymers.

The experimental results concerning the T_g of the NAPMI and ST copolymers along with the predictions of the Gibbs-Di Marzio Fox and Johnston equations are given in Table III. It is obvious that large positive deviations are obtained by these three methods due to the fact that they are based only on thermodynamic and they do not take into consideration the monomer sequence distribution and the effect of their compatibility on steric and energetic interactions. Therefore, several models have been proposed that take into account these considerations. The thermal stability of the copolymers was studied by programmed thermogravimetric analysis over a temperature range from room temperature to 600°C under nitrogen atmosphere (see Fig. 8). The initial decomposition temperature for each copolymer and homopolymers taken from the first strong change in the slope of the thermogravimetric curve (See Fig. 8). All studied copolymers are stable at temperatures up to 380°C under the thermogravimetric conditions.

CONCLUSION

Copolymers of *N*-(4-acetyl phenyl)maleimide and styrene have been prepared by free radical polymerization in 1,4-dioxane at 60°C. The reactivity ratios of the copolymers were estimated using linear graphical methods. The r_A values were higher than the corresponding r_S values in all cases, meaning that a kinetic preference exists for the incorporation of styrene in the copolymer structure. This results was confirmed by the calculation of the monomer dyad sequences fractions. The glass transition temperatures of the NAPMI and ST copolymers were obtained and compared with the predictions provided by several theoretical models. The TGA curves of the copolymers show an in-

crease in the initial decomposition temperature with the increase in the concentrations of NAPMI unit in the copolymer.

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