

# Thermal Analysis of Solution Copolymers of Styrene with *N*-Phenylmaleimide

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Received 11 January 2001; accepted 23 April 2001

**ABSTRACT:** Free-radical-initiated copolymerization of *N*-phenylmaleimide (NPMI) with styrene (St) at 110°C in a toluene solution initiated by AIBN was carried out by a semibatch method. The compositions of the copolymers were determined by using an elemental analyzer. The glass-transition temperatures of the copolymers were measured by differential scanning calorimetry. All the semibatch copolymers show a single glass-transition temperature that increases markedly with increasing NPMI content in the copolymers. The thermal stabilities of the copolymers were studied by using a programmed thermogravimetric analysis technique. Copolymers show a considerable increase in thermal stability and different degradation reaction mechanisms with increasing content of NPMI. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 417–422, 2002

**Key words:** thermal analysis; styrene; *N*-phenylmaleimide; solution polymerization

## INTRODUCTION

There has been considerable interest in the modification of commodity polymers to improve their properties to meet requirements for new applications. Copolymerization is one of the existing methods of improving polymers' properties.

The thermal stability of a polymer is an important aspect of its properties. Free-radical copolymerizations of styrene with various *N*-substituted maleimides to improve the thermal stability of polystyrene have been reported in many studies,<sup>1–4</sup> and nearly alternating copolymers were obtained. The kinetics of copolymerization has

also been studied.<sup>5–7</sup> In batch solution copolymerization, the desired copolymer structure is difficult to control by simply adjusting the monomer's composition because of the very low values of the reactivity ratios of St and NPMI.

Emulsion copolymerization of St with NPMI by the semibatch method has been reported,<sup>8</sup> although it is difficult to obtain a copolymer of high NPMI content because of the low solubility of NPMI in St. Thus, although many studies of copolymerizations of NPMI with St have been reported, the study of the effect of NPMI content on the thermal stability still remains to be investigated.

In this study the semibatch copolymerization of St with NPMI in toluene with 2,2'-azobis(isobutyronitrile) (AIBN) as an initiator was carried out to obtain NPMI–St copolymers of varying NPMI content. In addition the thermal stabilities of the copolymers were investigated.

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*Journal of Applied Polymer Science*, Vol. 83, 417–422 (2002)  
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**Table I** Solution Copolymerization Ingredients of St with NPMI

NPMI Feed Fraction (weight)	AIBN (g)	In Reactor		In Funnel		
		St (g)	Toluene (mL)	St (g)	NPMI (g)	Toluene (mL)
0	0.04	4.0	5	0	0	10
0.1	0.04	3.2	5	0.4	0.4	10
0.2	0.04	2.4	5	0.8	0.8	10
0.3	0.04	1.8	5	1.0	1.2	10
0.4	0.04	1.2	5	1.2	1.6	10
0.5	0.04	0.6	5	1.4	2.0	10
0.6	0.04	0	5	1.6	2.4	10

## EXPERIMENTAL

### Materials

St used in the experiment was distilled under reduced pressure after removal of the inhibitor by washing twice with 5% NaOH solution and several times with water. NPMI was prepared by a one-step method<sup>9</sup> and recrystallized several times from the ethanol/water mixture (volume ratio 1 : 2). AIBN was recrystallized from ethanol.

### Copolymerization

Copolymerization was carried out in a dried, clear 100-mL four-necked flask equipped with a stirrer, a thermometer, a condenser, and a nitrogen duct. Portions of toluene and monomer were added to the flask, then stirred over 10 min under nitrogen before half of the AIBN solution was added to the system. The residual monomer and AIBN solution was gradually added to the system over a period of about 1 h after it had been heated to about 110°C. The ingredients are shown in Table I. Copolymerization was stopped by decreasing the temperature and pouring the product into a large amount of ethanol. The copolymer was isolated by filtration and washed repeatedly with hot methanol to remove the residual monomer and AIBN. The obtained copolymer was then dried under vacuum at 60°C until a constant weight was attained. Weighing the obtained copolymer provided the weight conversion of NPMI–St copolymerization.

### Copolymer Analysis

The composition of the copolymer was calculated on the basis of the nitrogen content in the copolymer measured by using a Perkin–Elmer elemen-

tal analyzer (Model 240; Perkin Elmer Cetus Instruments, Norwalk, CT).

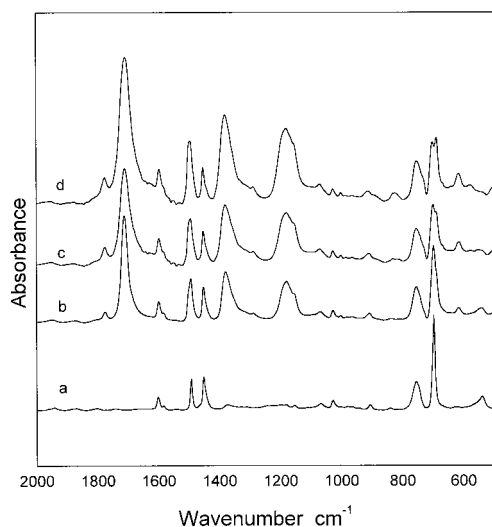
The copolymer's  $T_g$  was measured using a Shimadzu DT-40 differential scanning calorimeter (DSC; Shimadzu, Tokyo, Japan) with  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> as reference material at a heating rate of 20°C/min under nitrogen. The  $T_g$  was taken from the midpoint of the DSC trace transition of the second scanning.

Thermogravimetric analysis was carried out by means of Shimadzu DT-40 thermogravimeter (TG) at a heating rate of 10°C/min.  $T_{d50}$  was obtained when the weight loss of the copolymer reached 50%.

## RESULTS AND DISCUSSION

The structural change in the copolymer was investigated by using an FTS-40 IR spectrophotometer. FTIR spectra of both semibatch copolymers and PSt are shown in Figure 1. Typical absorptions of the copolymer representing the NPMI moiety are found at 1180 (C–N), 1381 (five-member ring), and 1710 cm<sup>-1</sup> (C=O). The characteristic absorptions of PSt are at 1454 and 1498 cm<sup>-1</sup>, reflecting the semicircle stretch and mixed C–H bending of a monosubstituted benzene ring. The intensity ratio of the 1180 and 1454 cm<sup>-1</sup> absorptions was found to be sensitive to composition and to increase with increasing NPMI content.

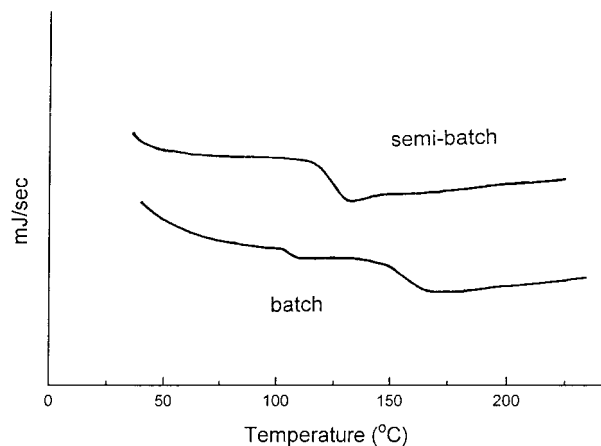
The polymerization conditions and other characteristic parameters are shown in Table II. As seen from the table, even though the copolymerization was performed by a semibatch method, the molar fractions of NPMI in copolymers  $F_1$  are not equal to  $f_1$ , the molar fractions of NPMI in the monomer feed mixture. Normally,  $F_1$  is closer to



**Figure 1** FTIR spectra of semibatch copolymers. NPMI mole fraction: (a) 0; (b) 0.202; (c) 0.352; (d) 0.510.

0.5 than  $f_1$  is for all the copolymerizations. It should also be noted that the conversion is significantly enhanced with increasing NPMI feed content. This is in agreement with the previous study, which showed that there is a maximum copolymerization rate at the proper monomer ratio.<sup>7</sup>

Monomers producing alternating copolymers in the conventional sense of free-radical polymerization are classified as specific acceptor monomers presenting large  $e$  values in combination with electron-donor monomers<sup>10</sup> such as NPMI with St. In normal solution copolymerization, NPMI and St have a strong tendency to complex and form alternating copolymers rather than random copolymers.<sup>2</sup> The strong tendency for alternation is also predicted by the copolymerization with very low reactivity ratios for both monomers. The monomers tend to alternatively copolymerize until one of them is consumed and then the remaining monomer tends to homopolymerize. Figure 2 shows the comparison of the DSC curves of batch and semibatch copolymers of the same monomer feed compositions. The difference is ob-



**Figure 2** DSC curves of semibatch and batch copolymers with the same monomer feed composition.

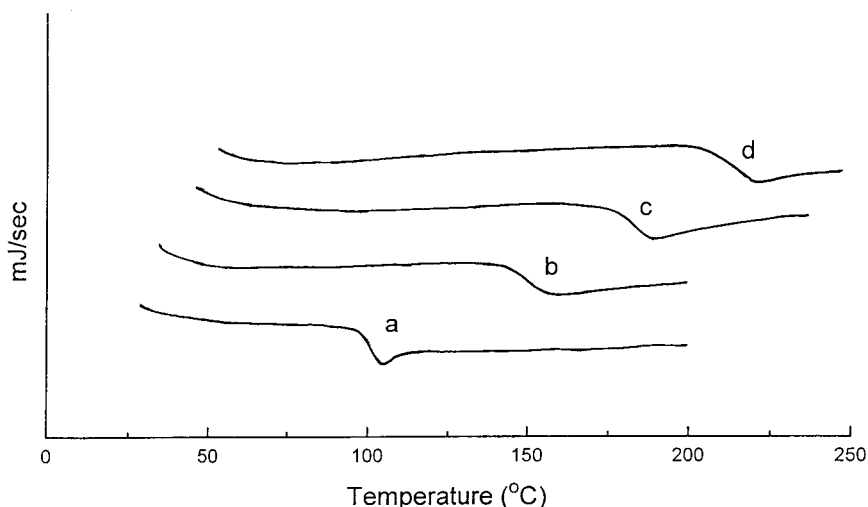
vious: the semibatch copolymer has one single glass transition at 123.7°C, but the batch copolymer has two glass transitions at 156.8 and 106.5°C, respectively, which to a considerable degree is related to the results of the emulsion copolymers of St and NPMI with acrylonitrile.<sup>11</sup> This shows that the copolymer is a mixture of varying NPMI–St compositions. The glass transition of the copolymer with a significantly higher NPMI–St composition shows that the copolymer consists mainly of copolymers with more NPMI moieties than that of average composition. Thus the glass-transition temperature of this batch copolymer is higher than that of the semibatch copolymer (the composition of the semibatch copolymer is not equal to the feed composition either as described below); however, the glass-transition temperature is not very close to the value of the alternative copolymer of NPMI and St.<sup>8</sup> This shows that the reactivity ratio is perhaps not so small at higher temperature and in a solution different from that of the reference.<sup>2</sup> The lower one is very close to the  $T_g$  of PSt, which indicates that the system tends to homopolymerize at the later reaction stage.

The DSC curves of the semibatch copolymers are shown in Figure 3. Figure 4 shows plots of

**Table II** Monomer Feed and Copolymer Composition

$f_1^a$	0	0.063	0.131	0.205	0.286	0.375	0.474
Yield (wt %)	42.5	47.5	52.5	51.3	55.0	60.0	62.5
$F_1$	0	0.124	0.202	0.334	0.352	0.403	0.510
$w_1$	0	0.191	0.296	0.455	0.475	0.529	0.634

<sup>a</sup> 1 represents NPMI.



**Figure 3** DSC curves of semibatch copolymers. NPMI weight fraction: (a) 0; (b) 0.296; (c) 0.475; (d) 0.634.

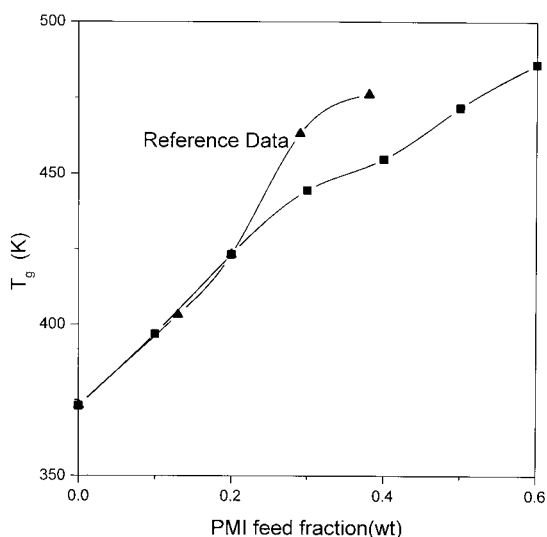
glass-transition temperatures of NPMI–St copolymers against the monomer feed weight fraction. Only slight differences between the glass-transition temperatures of reference data<sup>8</sup> and our experimental results were found when the NPMI feed content was not too great.

The copolymers obtained in solution copolymerization covered the complete composition range in weight fraction  $w_1$ , with increments from 0 to 0.634, as can be seen in Table II and Figure 5. This seemed a good series to examine with regard to the effect of the composition on the glass-transition temperature, which is difficult to obtain in emulsion or batch solution copolymerization of NPMI with St.

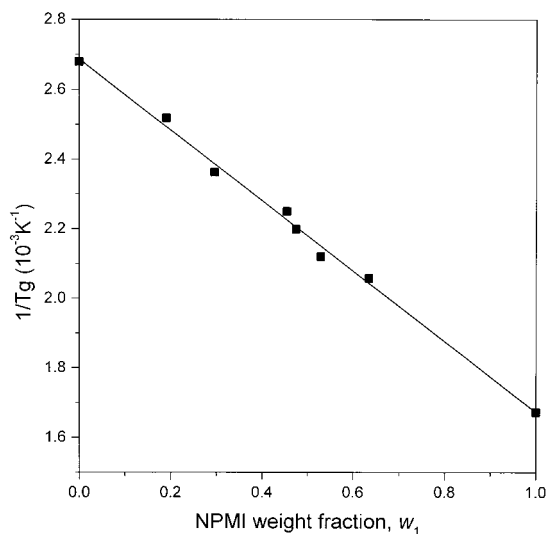
Now the relationship between the glass-transition temperatures of random copolymers and the glass-transition temperatures of the component homopolymers can be considered. The Fox equation<sup>12</sup> is based on free volume concepts and is expressed as follows:

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (1)$$

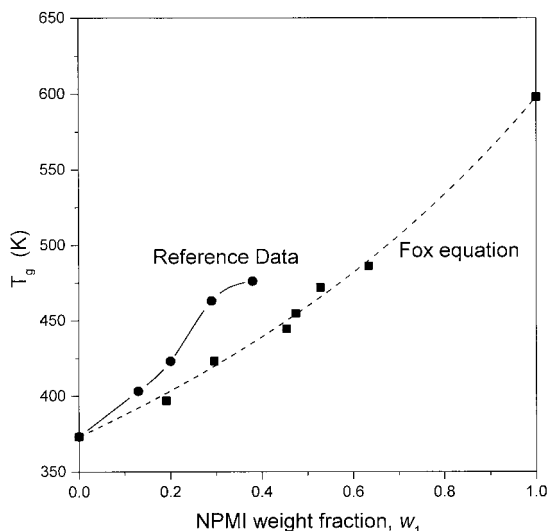
where  $w_1$  and  $w_2$  are the weight fractions of monomers 1 and 2, respectively; and  $T_{g1}$ ,  $T_{g2}$ , and  $T_g$



**Figure 4** Effect of NPMI content on  $T_g$  of copolymers.



**Figure 5** Relation of glass-transition temperatures to composition according to a plot suggested by the Fox equation.

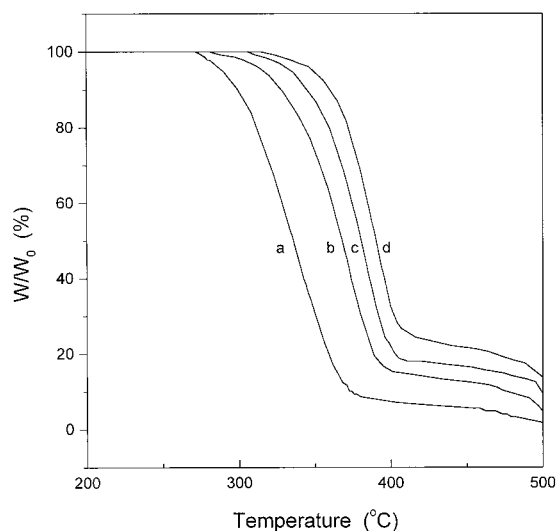


**Figure 6** Relation of glass-transition temperatures to compositions.

are, respectively, the glass-transition temperatures of homopolymers 1 and 2 and their copolymers. Then, if eq. (1) holds for a copolymer, a plot of  $1/T_g$  against  $w_1$  will be a straight line having a slope of  $(1/T_{g1}) - (1/T_{g2})$  and an intercept of  $1/T_{g2}$ . The plot is shown in Figure 5. There is a good line relativity with  $R^2 = 0.9953$ , and  $T_{g1}$  for poly(*N*-phenyl maleimide) of 598 K is obtained.

In a majority of the cases, triads such as BA\*B, BA\*A, or AA\*A, where A\* may contribute different  $T_g$ 's to the copolymer and the systems, do not give linear Fox-type plots. Therefore, the results in the NPMI–St system also indicate that A\* (NPMI or St) may have contributed the same  $T_g$  when it was in different triads such as BA\*B, BA\*A, and AA\*A.<sup>13</sup>

The glass-transition temperatures were plotted against the compositions of copolymers in Figure 6 and the differences between the reference data and our results are obvious. This is mainly because the copolymer compositions were assumed to be equal to the feed compositions in the



**Figure 7** Thermogravimetric analysis diagrams (10°C/min). NPMI mole fraction: (a) 0; (b) 0.202; (c) 0.352; (d) 0.510.

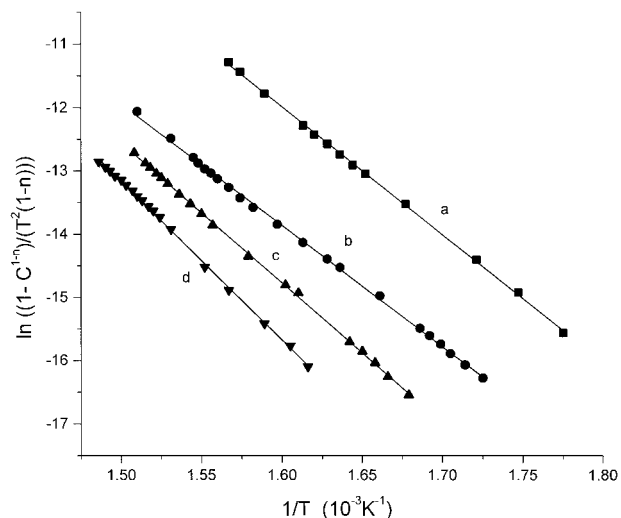
reference, whereas they were calculated from the elemental analysis results in our study. This fact also indicates that the copolymer compositions are not exactly equal to the monomer feed compositions, even though they were copolymerized by a semibatch method. The Fox equation line was plotted by assuming the glass-transition temperature of poly(*N*-phenylmaleimide) to be 598 K. It can be found that the Fox equation exactly fits the experimental data.

The thermal stability of the copolymer has been arbitrarily defined as a function of the initial decomposition temperature ( $T_{di}$ ), the half-weight loss temperature ( $T_{d50}$ ), and maximum weight loss rate temperature ( $T_{max}$ ) at particular environmental conditions described previously. Experimental results of some of the copolymers are given in Table III. For the purpose of comparison, the thermograms on the studied series of copolymers are shown in Figure 7.

The results show that the thermal stability tends to increase as the NPMI composition in-

**Table III** Thermogravimetric Analysis Results of Copolymers

$w_1$	0	0.296	0.475	0.634
$T_{di}$ (°C)	273.5	293.1	306.1	332.1
$T_{d50}$ (°C)	335.1	368.1	379.6	389.1
$T_{max}$ (°C)	336.5	372.7	384.0	392.3
Reaction order, $n$	2.0	1.5	1.3	1.1
$E_a$ (kJ/mol)	172.33	161.51	184.09	209.06
$R^2$	0.9990	0.9989	0.9997	0.9993



**Figure 8** Thermogravimetric analysis plot of  $\ln\{(1 - C^{1-n})/[T^2(1 - n)]\}$  versus  $1/T$ . NPMI mole fraction: (a) 0; (b) 0.202; (c) 0.352; (d) 0.510.

creases. Copolymer  $T_{di}$ ,  $T_{d50}$ , and  $T_{max}$  all increase with increasing NPMI composition. This is mainly attributed to the presence of 1,2-ethylenic units directly linked to styrene units.<sup>2</sup>  $T_{di}$  increases about 1.0°C per mol % of NPMI, and  $T_{d50}$  increases about 0.9°C per mol % of NPMI. However,  $T_{max}$  reaches its maximum when the NPMI mole fraction is about 0.5.

The following kinetic equation was assumed to hold for these thermal degradation reactions<sup>14</sup>:

$$\ln \frac{1 - C^{1-n}}{T^2(1-n)} = \ln \left[ \frac{AR}{\phi E} \left( 1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT} \quad (2)$$

where  $C = W/W_0$ ,  $W$  is the remaining weight, and  $W_0$  is the total weight;  $A$  is the frequency factor,  $\phi$  is the heating rate;  $R$  is the ideal gas constant;  $E$  is the activation energy; and  $n$  is the degradation reaction order. The activation energy  $E$  can be calculated when the plot of  $\ln\{(1 - C^{1-n})/[T^2(1 - n)]\}$  versus  $1/T$  has maximum linear correlation coefficient for a certain sample with different  $n$  values, where the slope gives the  $-(E/R)$  value. The plots of  $\ln\{(1 - C^{1-n})/[T^2(1 - n)]\}$  versus  $1/T$  of the samples are shown in Figure 8.

The degradation orders and reactivity energies are shown in Table III. When PSt was incorporated with 0.202 mol fraction of NPMI moieties, the degradation order changed from 2 to 1.5,

which perhaps indicates a different degradation mechanism. With increasing NPMI composition, the degradation order decreases further, reaching 1.1 when the mole fraction of NPMI is 0.51. Generally, the activation energy increases when the NPMI mole/weight fraction increases overall.

## CONCLUSIONS

Semibatch and batch solution copolymerization of NPMI with St produces copolymers of different structures and thermal properties. A semibatch copolymer has a homogeneous chain structure; its  $T_g$  increases with increasing NPMI content and follows the Fox equation. The thermal stability and degradation activation energy increase with increasing NPMI content in the copolymer, and the degradation reaction order decreases with increasing NPMI content.

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