

Variations of the Glass-Transition Temperature in the Imidization of Poly(styrene-*co*-maleic anhydride)

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ABSTRACT: The imidization of poly(styrene-*co*-maleic anhydride) (SMA) was conducted, and the glass-transition temperatures (T_g 's) of the resulting products were measured with differential scanning calorimetry. The contributions from functional groups of maleic anhydride, *N*-phenylmaleamic acid, and *N*-phenylmaleimide to T_g were examined. T_g increased in the order of SMA < styrene-*N*-phenyl maleimide copolymer < styrene-*N*-phenyl malea-

mic acid copolymer and followed the Fox equation. T_g of the imidized products of SMA could be controlled by the conversions of both ring-opening and ring-closing reactions. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2418–2422, 2007

Key words: poly(styrene-*co*-maleic anhydride); imidization; glass-transition temperature

INTRODUCTION

The glass-transition temperature (T_g) is an important intrinsic characteristic that influences the properties of a polymer and limits its applications. Three methods to adjust T_g according to a given application are as follows: (1) copolymerizing monomers A and B in a certain A/B ratio,^{1,2} (2) blending polymers PA and PB in a certain PA/PB ratio,^{3,4} and (3) modifying polymer PA with monomer B or polymer PB.^{5,6} For method 1, the A/B ratio is controlled by the reactivity ratios and is not adjustable in some cases; for instance, the product of their reactivity ratios is close to zero. For method 2, the properties of the blend are affected by the miscibility and compatibility of PA and PB. For method 3, it is flexible and convenient to obtain the desired degree of modification. Therefore, polymeric modification is the most feasible way of acquiring polymeric materials with a specific T_g .

Poly(styrene-*co*-maleic anhydride) (SMA) has excellent properties, such as good heat resistance and

adjustable compatibility, when blended with styrenic polymers and polar polymers.^{7–10} To improve the heat resistance further, the imidization of SMA with amine group compounds has been conducted by many researchers and companies. The resulting poly(styrene-*co*-maleimide)^{11,12} is extremely heat-resistant because of the rigid and bulky maleimide group. Besides the styrene group, the imidization product derived from SMA may consist of maleic anhydride groups, maleamic acid groups, and maleimide groups.¹³ Therefore, if the relationship between these groups and T_g is revealed, we could prepare various imidization products of SMA by controlling the reaction conversion to meet the requirements for different applications.

In this article, various imidization products of SMA with different compositions were synthesized by the direct imidization of SMA with aniline (ANL), and their T_g 's were measured with differential scanning calorimetry (DSC). Furthermore, the Fox equation was adopted to correlate the T_g values and compositions of the imidization products.

EXPERIMENTAL

Samples

ANL, ethyl benzene, tetrahydrofuran, anhydrous methanol, hexane, hydroxyl potassium, and acetone were all analytical-reagent-grade and were used as

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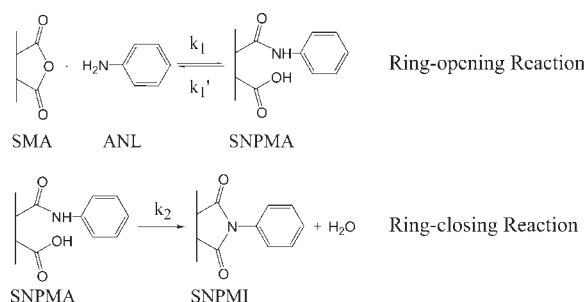
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TABLE I
Characteristics of SMA

| Sample | Anhydride content | M_n | M_w/M_n |
|--------|-------------------|---------|-----------|
| SMA216 | 16.63 mol % | 126,900 | 2.0 |

M_n , number-average molecular weight; M_w , weight-average molecular weight.



Scheme 1 Imidization mechanism of SMA and ANL.

TABLE II
Chemical Structures of the Various Polymers

| Polymer | Chemical structure |
|----------------|--------------------|
| SMA | |
| SNPMA | |
| SNPMI | |
| S-MA-NPMA | |
| S-NPMA-NPMI | |
| S-MA-NPMA-NPMI | |

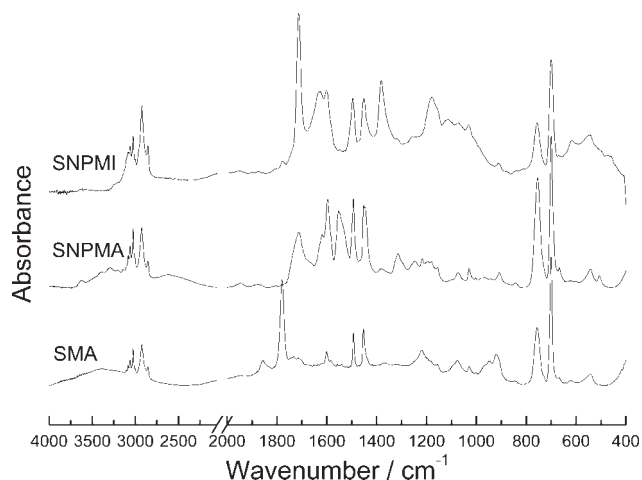


Figure 1 FTIR spectra of SMA, SNPMA, and SNPMI bipolymers.

received. A random SMA, shown in Table I, was synthesized with the method described in our previous publications.^{9,10}

The imidization mechanism is shown in Scheme 1. The imidization samples were prepared according to our previous publication.¹⁴ The compositions of the imidization samples were determined by both electronic conductance titration and Fourier transition infrared (FTIR) spectrometry (model 5700, Thermo Nicolet).

DSC experiments

The DSC measurements were performed with a DSC-7 (PerkinElmer) from 50 to 180°C. The temperature was calibrated with an indium standard at a heating rate of 20°C/min. The glass-transition behavior was investigated at a heating rate of 20°C/min

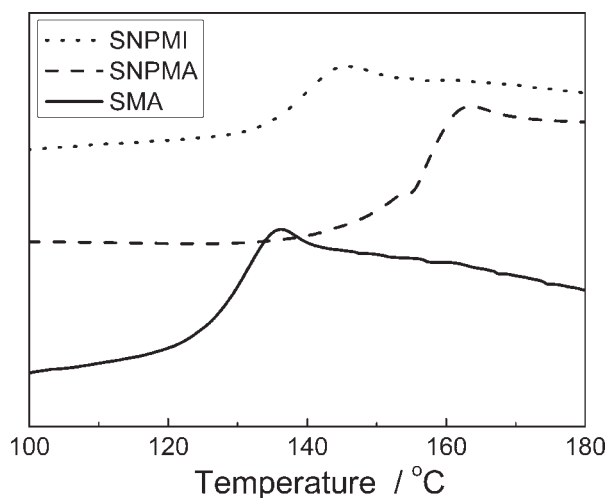


Figure 2 DSC traces of SMA, SNPMA, and SNPMI bipolymers.

TABLE III
T_g Values of SMA, SNPMA, and SNPMI Bipolymers

| Bipolymer | SMA | SNPMA | SNPMI |
|--------------------------|-------|-------|-------|
| <i>T_g</i> (K) | 401.1 | 429.6 | 409.5 |

only once because of more imidization of the samples incompletely imidized. *T_g* was estimated by the half-step method.

RESULTS AND DISCUSSION

Three copolymer systems were investigated in this article, and the chemical structures of the various resulting polymers are listed in Table II.

Bipolymer systems

Three bipolymers—SMA, a styrene-*N*-phenyl maleamic acid copolymer (SNPMA), and a styrene-*N*-phenyl maleimide copolymer (SNPMI)—were inves-

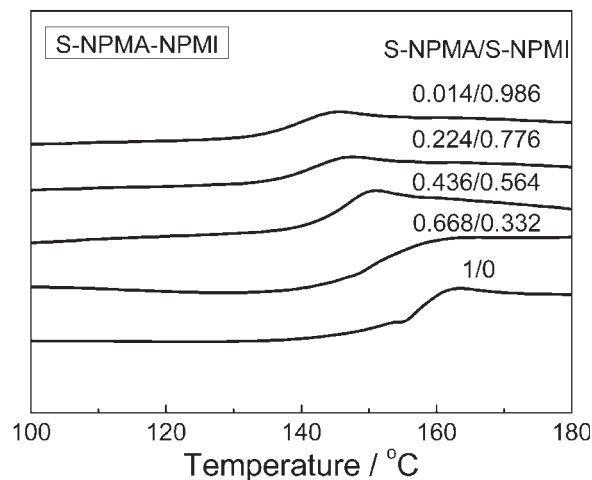
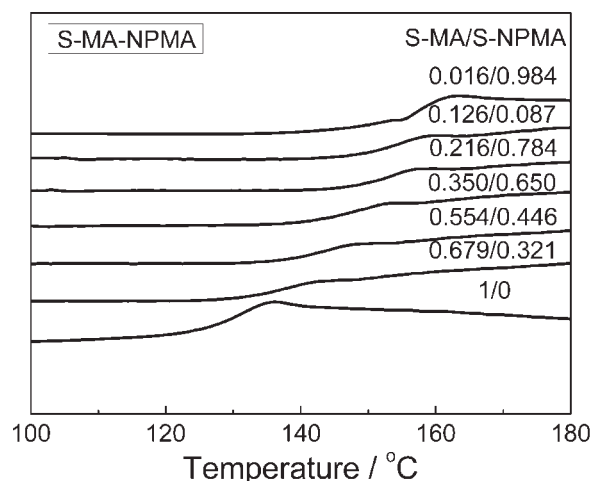


Figure 3 DSC traces of S-MA-NPMA and S-NPMA-NPMI terpolymers.

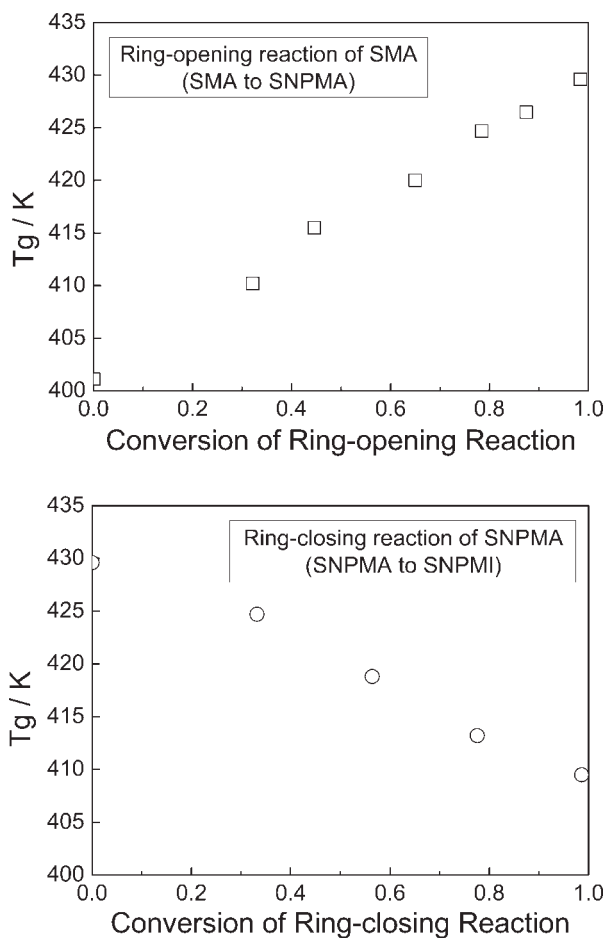


Figure 4 T_g versus the corresponding conversion of the ring-opening and ring-closing reactions.

tigated first. FTIR spectra of these three bipolymers are shown in Figure 1. The typical absorptions of SMA can be found at 1860 (C–O–C) and 1780 cm^{-1} (C=O); the absorptions of SNPMA are at 1700 (–N–C=O) and 1550 cm^{-1} (C–N–H); and the absorptions of SNPMI are at 1780 (C=O), 1700 (–N–C=O), and 1381 cm^{-1} (cyclo C–N–C).

The DSC traces of these bipolymers are shown in Figure 2, and their T_g values are listed in Table III. T_g of either SNPMA or SNPMI is higher than that of SMA because of the introduction of rigid phenyl rings. Furthermore, T_g of SNPMA is higher than that of SNPMI because of the existence of intermolecular hydrogen bonds between carboxylic acid groups. The loss of carboxyl and acyl amino groups leads to the lower T_g value of SNPMI. This phenomenon is very similar to the results of Yan and Zhu,¹⁵ and this indicates that T_g of poly[styrene-*co*-(*N*-4-carboxylphenyl)maleamic acid] with double carboxylic acid groups as the ring-opening product is higher than that of poly[styrene-*co*-(*N*-4-carboxylphenyl)maleimide] as the ring-closing product. Recently, Kuo et al.¹⁶ found a significant increase in T_g through

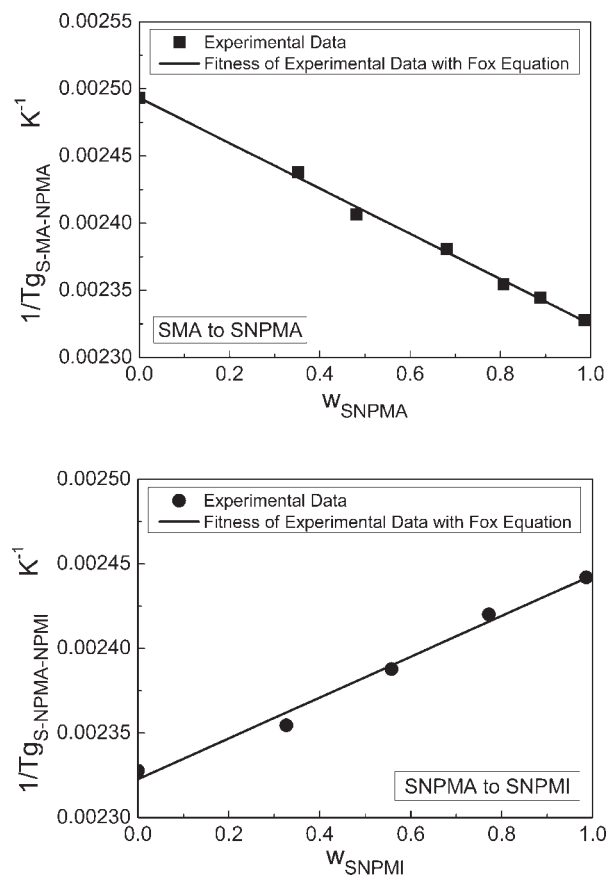


Figure 5 Comparison of the experimental data and calculation results from the Fox equation.

hydrogen-bonded copolymers. In fact, a previous study of Thomson et al.¹⁷ provided both experimental and theoretical analyses of hydrogen bonding in poly(amic acid)s, including the acid–acid interac-

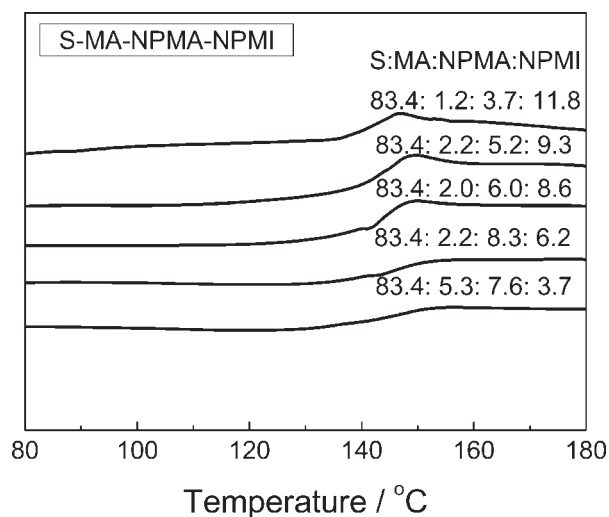


Figure 6 DSC traces of S-MA-NPMA-NPMI tetrapolymers of various compositions.

TABLE IV
Comparison of the Predicted and Experimental T_g Values for Tetrapolymers of Various Compositions

| Sample | S/MA/NPMA/NPMI molar ratio | T_g (K) | |
|--------|-------------------------------|-----------|-------|
| | | Calcd | Found |
| a | 83.4 : 5.3 : 7.6 : 3.7 | 416.6 | 416.8 |
| b | 83.4 : 2.2 : 8.3 : 6.2 | 418.8 | 419.1 |
| c | 83.4 : 2.0 : 6.0 : 8.6 | 415.9 | 416.3 |
| d | 83.4 : 2.2 : 5.2 : 9.3 | 414.8 | 414.6 |
| e | 83.4 : 1.2 : 3.7 : 11.8 | 413.4 | 413.5 |

S, styrene; MA, maleic anhydride; NPMA, *N*-phenyl maleamic acid; NPMI, *N*-phenyl maleimide.

tions, amide–amide interactions, and two other mixed interactions. In our view, these proposed hydrogen-bonded structures should exist and transform in the imidization of SMA.

Terpolymer systems

Two terpolymers—styrene–maleic anhydride–*N*-phenyl maleamic acid terpolymer (S–MA–NPMA) and styrene–*N*-phenyl maleamic acid–*N*-phenyl maleimide terpolymer (S–NPMA–NPMI)—were then investigated. The DSC traces are shown in Figure 3. Figure 4 shows that T_g increases first with increasing ring-opening conversion and then decreases with increasing ring-closing conversion.

Now the relationship between T_g of the random terpolymers and T_g of the component random bi-polymers can be considered. The Fox equation¹⁸ is based on free-volume concepts and can be expressed as follows:

$$\frac{1}{T_g} = \sum \frac{w_i}{T_{gi}} \quad (1)$$

where w_i is the weight fraction of monomer i and T_{gi} and T_g are the glass-transition temperatures of homopolymers i and their copolymers, respectively. The Fox equation can be extended as follows:

$$\frac{1}{T'_g} = \sum \frac{w'_i}{T'_{gi}} \quad (2)$$

where w'_i is the weight fraction of random copolymer component i and T'_{gi} is the glass-transition temperature of copolymer i . Then, if eq. (2) is applicable for a terpolymer, a plot of $1/T'_{gi}$ versus w'_i 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 good line relativity in Figure 5. Therefore, the Fox equation is suitable for our research systems.

Tetrapolymer systems

To obtain profound insight into our research, a series of styrene–maleic anhydride–*N*-phenyl maleamic acid–*N*-phenyl maleimide tetrapolymers (S–MA–NPMA–NPMIs) of various compositions were studied. The DSC traces are shown in Figure 6. As shown in Table IV, the T_g value predicted by the Fox equation matches exactly the experimental data. Therefore, it is feasible to control T_g by the adjustment of the compositions of S–MA–NPMA–NPMI.

CONCLUSIONS

Imidization products of SMA with various compositions were prepared, and their T_g values were measured with DSC. T_g increases in the order of SMA < SNPMI < SNPMA, and the T_g values of all the samples follow the Fox equation. This demonstrates that both the introduction of rigid phenyl rings and the presence of hydrogen-bonding interactions make great contributions to the enhancement of the thermal properties. This is attributable to intramolecular and intermolecular forces. The T_g values of the imidized products of SMA can be adjusted in a given range with multiple compositions of S–MA–NPMA–NPMI copolymers controlled by the conversions of both ring-opening and ring-closing reactions. The modification of a polymer with another monomer, such as the modification of SMA with amines, seems to be a flexible and convenient way of acquiring polymer materials with specific T_g values.

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