

Kinetics and Simulation of the Imidization of Poly(styrene-*co*-maleic anhydride) with Amines

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Received 5 January 2005; accepted 26 April 2005

DOI 10.1002/app.23371

Published online 9 February 2006 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The imidization of poly(styrene-*co*-maleic anhydride) with amines may improve some of its end-use properties. The objective of this study was to examine the mechanism and kinetics with aniline (ANL) as an amine of the preparation of poly(styrene-*co*-*N*-phenyl maleimide). The reaction was carried out in a tetrahydrofuran solution at 25–55°C and in an ethylbenzene solution at 85–120°C. The extent of the reaction was determined by conductance titration, a new and simple method. Two consecutive reactions were involved in the imidization: ring opening to produce

an acido-amide group and ring closing to form a corresponding imide group. The imidization rate was greatly influenced by the reaction temperature and the molar ratio of ANL to the anhydride. A model for the imidization kinetics over a wide range of reaction temperatures and concentration ranges was developed and validated. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 2744–2749, 2006

Key words: poly(styrene-*co*-maleic anhydride); imidization; kinetics

INTRODUCTION

Poly(styrene-*co*-maleic anhydride) (SMA) has excellent properties, including good heat resistance and adjustable compatibility when blended with styrenic polymers and polar polymers.^{1–4} However, the hydrolyzation of anhydride groups and then degradation⁵ has been considered as a major hurdle to its applications. To overcome this problem, studies with cyclic or aliphatic imide groups instead of anhydride groups have been conducted. Poly(styrene-*co*-maleimide) (SMI) was first synthesized by Mitsubishi Monsanto Chemical Co.^{6,7} The thermal properties of SMI, including thermal stability and heat resistance, were strongly improved compared to those of SMA.

In general, SMI can be prepared either by the direct copolymerization of styrene and maleimide or by the imidization of SMA. Direct copolymeriza-

tion has the advantage that it is a simple process.^{8–10} However, the synthesis of the maleimide monomer is complex and expensive. More studies have focused on the direct imidization of SMA with primary amines^{11–18} in an attempt to establish an integrated process from SMA bulk polymerization to imidization and to achieve high efficiency in cost and operation. However, there have been few detailed kinetic studies of the reaction between the anhydride and amine in the polymeric and organic chemistry areas.

In this article, a quantitative description of the reaction course is presented. Further, the whole-range imidization kinetics of SMA and aniline (ANL) were experimentally investigated both in ethylbenzene (EB) and tetrahydrofuran (THF) solutions. A mathematic model was also developed and validated with the experimental data.

EXPERIMENTAL

Materials

ANL, EB, THF, anhydrous methanol, hexane, hydroxyl potassium, and acetone were all analytical reagent grade and were used as received. A random SMA with 16 wt % maleic anhydride (MAN) was synthesized in our laboratory.^{3,4}

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Contract grant sponsor: National Natural Science Foundation of China; contract grant numbers: 50390097 and 20310285.

Contract grant sponsor: Association Franco-Chinoise pour la Recherche Scientifique et Technique; contract grant number: PRA Mx02-07.

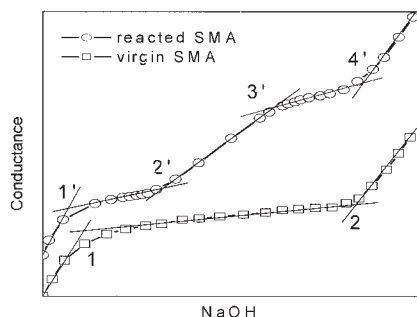


Figure 1 Typical conductance titration curve of the SMA copolymer before and after the ring-opening reaction: (1') maleic acid first H⁺, (2') maleamic acid, (3' and 4') maleic acid second H⁺ and maleic anhydride, (1) maleic acid first H⁺, and (2) maleic acid second H⁺ and MAN.

Imidization reaction in solution

The reaction was carried out in a jacketed reactor with an anchor agitator. The reaction temperature was controlled within $\pm 0.5^\circ\text{C}$. During each experimental run, a given amount of SMA was charged to the reactor, followed by the addition of THF or EB. The mixture was heated to a given temperature under strong agitation. After a homogeneous solution was obtained, the required amount of ANL was added into the reactor, and the reaction started to proceed.

Samples were collected at regular time intervals and dropped into a 10-fold excess of anhydrous methanol for precipitation and separation. The crude products were alternately dissolved with THF and precipitated with hexane three times. Finally, the purified products were dried *in vacuo* at 50°C for 24 h.

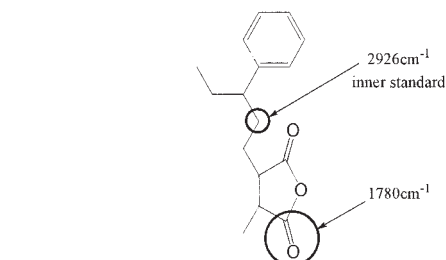
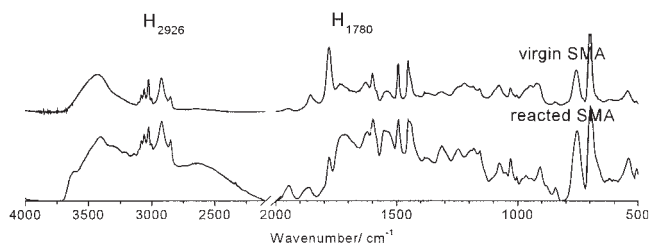


Figure 2 FTIR spectra of the SMA copolymer before and after the ring-opening reaction.

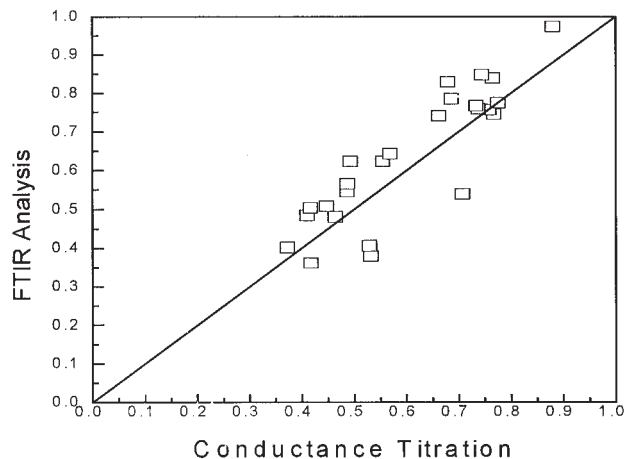


Figure 3 Comparison of the conversions of the anhydride groups at low temperatures after the ring-opening reaction without ring closing as measured by both FTIR analysis and the conductance titration method.

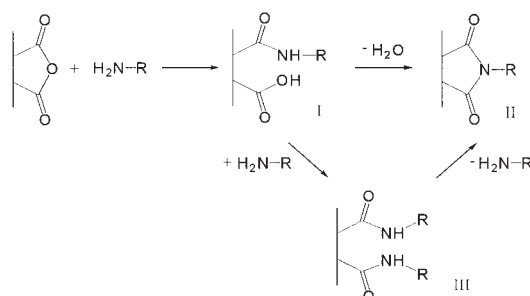
Sample composition analysis

The chemical compositions of the obtained products were analyzed by conductance titration in acetone with a 0.02 mol/L KOH-methanol solution. In a typical titration curve (Fig. 1), there were four equivalent points in sequence: the first proton of the maleic acid unit, the maleamic acid unit, the second proton of the maleic acid unit, and the MAN unit. On the basis of these points, the molar fractions of the maleic acid units, maleamic acid units, and MAN units could be directly measured. As shown in the following section, the results obtained from that method were in good agreement with Fourier transform infrared (FTIR) spectroscopy measurements. Furthermore, the residual maleimide units could be calculated by the subtraction of the molar fractions of the maleic acid units, maleamic acid units, and MAN units from the overall MAN units of SMA.

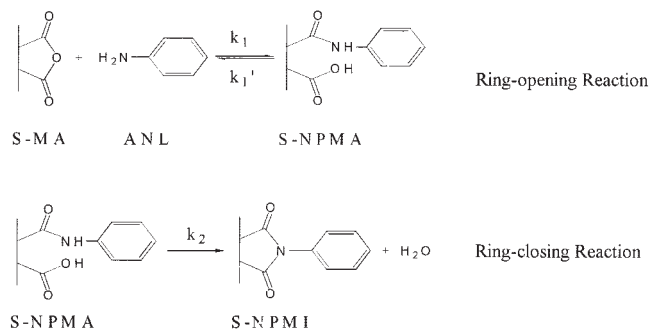
RESULTS AND DISCUSSION

Validation of the conductance titration method

Figure 2 shows the FTIR spectra of the SMA before and after the ring-opening reaction at low tempera-



Scheme 1 Several consecutive reactions between an anhydride and a primary amine.



Scheme 2 Imidization mechanism.

tures (25–45°C) without a ring-closing product. The height of the peak at 1780 cm^{-1} , associated with the anhydride residues, was normalized with that of the peak at 2926 cm^{-1} , which was associated with the $-\text{CH}_2-$ unit. The conversion of the anhydride groups was calculated as H/H_0 , where H_0 and H are the heights of the peak at 1780 cm^{-1} before and after the reaction, respectively. The corresponding conductance titration curves are shown in Figure 1. The conversion of the anhydride groups at low temperatures after only the ring-opening reaction without ring closing as obtained by the conductance titration method is compared with FTIR measurements in Figure 3. The results determined by both methods were in good agreement. This proved that the conductance titration was reliable, and it was simple to use.

Imidization mechanism

Tessier and Marechal¹⁹ indicated that several consecutive reactions between an anhydride and a primary amine could occur, as shown in Scheme 1, depending mainly on the reaction temperature. Their results showed that molar fraction of formation III was small and could be ignored. Furthermore, Hu and Lindt²⁰

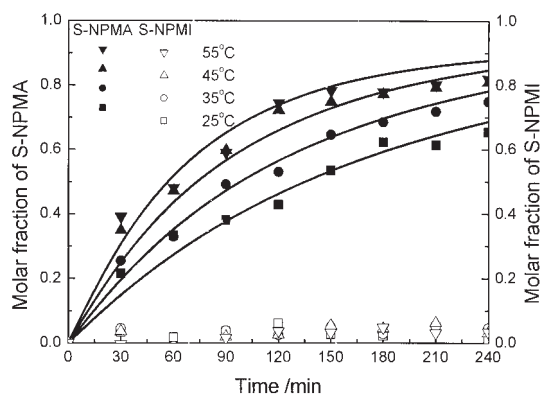


Figure 4 Molar fraction of S-NPMA and S-NPMI versus the reaction time at various temperatures (ANL/MAAn = 3 : 1). The symbols represent experimental points, and the curves represent kinetic model simulations.

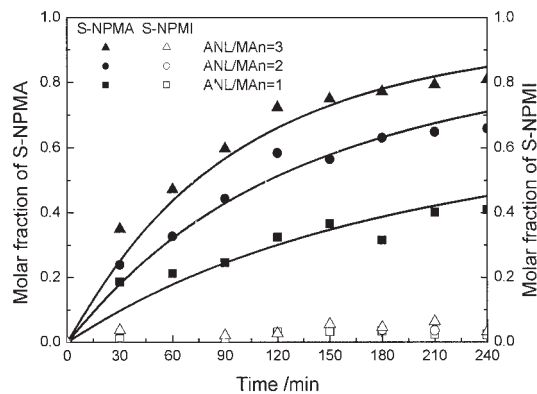


Figure 5 Molar fractions of S-NPMA and S-NPMI versus the reaction time for various ANL/MAAn molar ratios (temperature = 45°C). The symbols represent experimental points, and the curves represent kinetic model simulations.

revealed that the formation of I was a reversible reaction.

In this study, the mechanism shown in Scheme 2 was applied to the reaction between SMA and ANL: (1) the ring-opening reversible reaction of SMA to produce poly(styrene-*co*-*N*-phenylmaleamic acid) (S-NPMA) and (2) the ring-closing irreversible reaction of S-NPMA to obtain poly(styrene-*co*-*N*-phenyl maleimide) (S-NPMI).²¹

On the basis of this scheme, the overall reaction kinetics could be written as follows:

$$\frac{d(f[S - MA])}{dt} = -k_1 f[SMA][ANL] + k'_1 [S - NPMA] \quad (1)$$

$$\frac{d[ANL]}{dt} = -k_1 f[SMA][ANL] + k'_1 [S - NPMA] \quad (2)$$

$$\frac{d[S - NPMA]}{dt} = k_1 f[SMA][ANL] - (k'_1 + k_2)[S - NPMA] \quad (3)$$

$$\frac{d[S - NPMI]}{dt} = k_2 [S - NPMA] \quad (4)$$

where k_1 is defined as the forward rate constant of the ring-opening reaction, k'_1 the reverse rate constant of the ring-opening reaction, k_2 the forward rate constant of the ring-closing reaction, and f is the molar fraction of the maleic anhydride unit in the poly(styrene-*co*-maleic anhydride).

Mild-temperature reaction in THF solution

Because previous work^{20,22} has revealed that the ring-closing reaction of S-NPMA barely occurred at mild

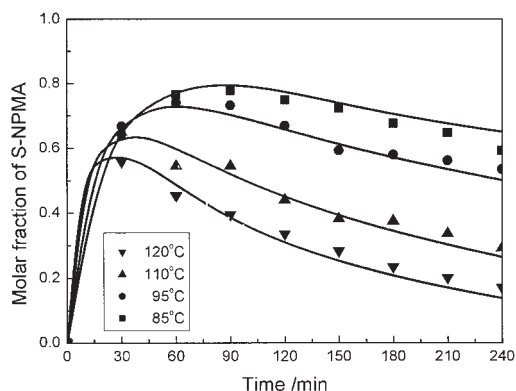


Figure 6 Molar fraction of S-NPMA versus the reaction time at various temperatures (ANL/MAN = 3 : 1). The symbols represent experimental points, and the curves represent kinetic model simulations.

temperature, the ring-opening reaction of SMA was our only focus of attention in the mild-temperature range.

The phenomena were proven by the homogeneous reaction of SMA and ANL in THF solution at temperatures between 25 and 55°C. When the reaction temperature was increased, the ring-opening reaction rate increased, as shown in Figure 4. As expected, S-NPMI obtained by the ring-closing reaction of SMA was indeed undetectable in this mild-temperature reaction.

As shown in Figure 5, an increase in the molar ratio of ANL to MAN groups on SMA backbone was favorable for the ring-opening reaction due to the increasing collision probability among the reactants. Lee and Ahn²² considered that this was due to the limited mass transfer in a polymer solution, and Hu and Lindt²⁰ indicated that the polymer reaction was affected by steric hindrance.

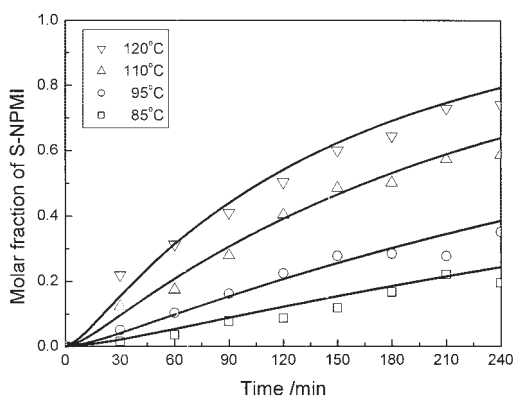


Figure 7 Molar fraction of S-NPMI versus the reaction time at various temperatures (ANL/MAN = 3 : 1). The symbols represent experimental points, and the curves represent kinetic model simulations.

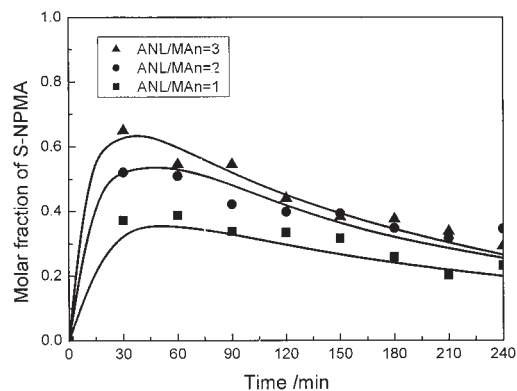


Figure 8 Molar fraction of S-NPMA versus the reaction time for various ANL/MAN molar ratios (temperature = 110°C). The symbols represent experimental points, and the curves represent kinetic model simulations.

High-temperature reaction in EB solution

In this part of the experiment, in addition to the ring-opening reaction, more attention was paid to the ring-closing reaction of S-NPMA during the high-temperature imidization process. EB was substituted for THF as the good solvent for the reaction because it was not a good solvent for the reaction in the mild-temperature range but became a good solvent at higher temperatures. As shown in Figure 6, the yield of S-NPMA as an intermediate product exhibited a maximum. Raising the reaction temperature unilaterally improved the ring-closing conversion, as shown in Figure 7.

Moreover, the higher the molar ratio of ANL to MAN was, the higher were the yield of S-NPMA (Fig. 8) and the ring-closure conversion (Fig. 9). These results imply that 100% imidization would be difficult to reach by only the addition of an excess of ANL. These results, together with those of Figure 7, also show that ring-closing reaction required high temperatures.

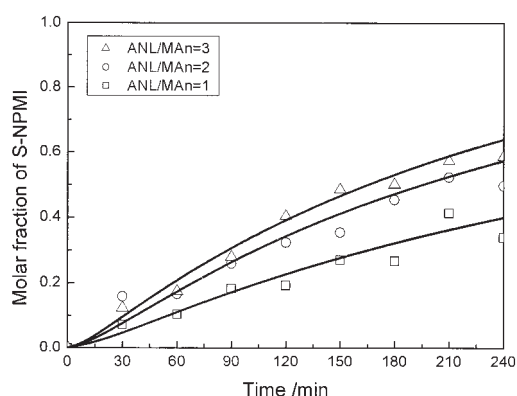


Figure 9 Molar fraction of S-NPMI versus the reaction time for various ANL/MAN molar ratios (temperature = 110°C). The symbols represent experimental points, and the curves represent kinetic model simulations.

TABLE I
Kinetic Rate Constants of the Imidization Based on Simulation

Solvent	T (°C)	k_1 [(mol/L)/s]	k'_1 (l/s)	k_2 (l/s)
THF	25–55	$1.12 \times 10^4 e^{-27,200/RT}$	$7.92 \times 10^4 e^{-60,700/RT}$	
EB	85–120	$1.10 \times 10^4 e^{-27,100/RT}$	$7.80 \times 10^4 e^{-61,000/RT}$	$9.45 \times 10^4 e^{-65,800/RT}$
THF + EB ^a	25–120	$1.10 \times 10^4 e^{-27,100/RT}$	$7.82 \times 10^4 e^{-61,000/RT}$	$9.49 \times 10^4 e^{-65,800/RT}$

T = temperature; R = universal gas constant.

^a Experimental data in THF and EB were used together to determine the kinetic rate constants.

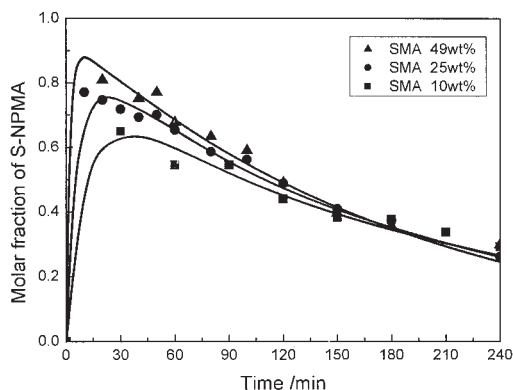


Figure 10 Molar fraction of S-NPMA versus the reaction time for various concentrations of SMA (ANL/MAN = 3 : 1; temperature = 110°C). The symbols represent experimental points, and the curves represent kinetic model simulations.

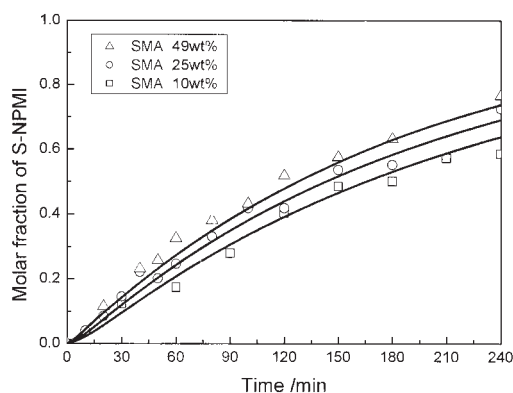


Figure 11 Molar fraction of S-NPMI versus the reaction time for various concentrations of SMA (ANL/MAN = 3 : 1; temperature = 110°C). The symbols represent experimental points, and the curves represent kinetic model simulations.

Kinetic parameters

Table I shows the values of the reaction rate constants based on the experimental data in mild-temperature THF solution and in high-temperature EB solution, respectively. The constants were very close under the two different solution conditions. This could be explained as follows. Both THF and EB were good solvents of the SMA and its products in the corresponding temperature ranges. The values of the reaction rate constants also revealed that the ring-closing reaction of S-NPMA depended very much on the temperature.

Effect of SMA concentration

The ring-closing reaction described previously is viewed as an intrachain cyclization process. Would it also follow an interchain process? If so, the cyclization by an interchain process would become more important with increasing concentration in SMA. Moreover, the kinetic data obtained in dilute solutions would not be applicable to concentrated reacting systems. Figures 10 and 11 compare experimental conversion data and the previous model predictions in a high-SMA-concentration system. The good agreement indicates that the mechanism of the imidization reaction followed Scheme 1 and

that its kinetics followed Scheme 2. The cyclization did not proceed through the interchain mode.

CONCLUSIONS

The kinetics of the imidization of SMA with ANL were investigated in tetrahydrofuran solution at 25–55°C and in ethyl benzene at 85–120°C, respectively. The extent of imidization was measured by conductance titration, a reliable and simple method. Two consecutive reactions were involved in the imidization process: reversible ring opening to produce S-NPMA and irreversible intrachain ring closing to form the corresponding S-NPMI. The imidization rate was greatly influenced by the reaction temperature and the molar ratio of ANL to MAN. A kinetic model was developed and the kinetic parameters within a broad reaction-temperature range and a wide SMA concentration range were determined and validated.

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