Direct Polymer Reaction of Poly(styrene-*co*-maleic anhydride): Polymeric Imidization

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ABSTRACT: Using direct polymer reaction of poly(styrene-co-maleic anhydride) (SMA), a synthesis of copolymer of styrene and N-aryl succinimide (SMI) has been investigated. SMI copolymers were synthesized from SMA copolymers by a concerted two-step reaction, which consisted of the condensation reaction (step 1) of SMA with aromatic amine to prepare a precursor, succinamic acid, for imide formation and the cyclodehydration reaction (step 2) of succinamic acid. In this article, the application of Searle's preparation method of N-aryl or N-alkyl maleimide to the direct polymer reaction for SMI was attempted. Compared with synthesis of monomeric imides, the imide formation in polymeric condition appeared to be a little more sensitive to the reaction condition. The optimum condition for maximum conversion was examined in terms of time, temperature, and the amount of reactants. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1187–1196, 1999

Key words: poly(styrene-*co*-maleic anhydride); styrene–*N*-aryl succinimide copolymer; polymer reaction; *N*-aryl succinimide

INTRODUCTION

As a representative alternating copolymer, poly-(styrene-co-maleic anhydride) (SMA) has been focused in studying the behavior of copolymerization.^{1,2} Compared with general purpose thermoplastics, SMA has a higher thermal stability and exhibits a good miscibility when mixed with styrenic polymers,^{3–5} providing a wide range of application in industrial use. Recently, industrial interests are aroused in the field of surface treatment or modification of styrenic polymers as well.

When heated above 250°C, however, an evolution of gaseous material after thermal breakdown and a severe thermal deformation were reported as critical drawbacks in application, as well as its poor weatherability due to the presence of anhydride functional group. To overcome these critical defects, the introduction of a new thermally stable group has been examined, and cyclic imide was well reputed for that purpose. At present, most of the research to modify SMA is devoted to the application of maleimide instead of maleic anhydride at the polymerization step.^{6–9} In those approaches, however, there are some critical problems to be solved, as follows.

- 1. First, as said above, the tendency of alternation in copolymer sequence impedes the free design of the copolymer architecture.
- 2. A new synthesis of various kinds of maleimide as a monomer requires another investment to set up facilities for each case.
- 3. When the primary amine is attempted to attack maleic anhydride to form maleimide, the formation of adduct of maleic an-

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hydride with aminein the form of II is unavoidable (Scheme 1), requiring a very critical purification step.

4. In the case of maleic anhydride, of which the melting temperature is 52°C, there is no need to use a solvent under the conditions of normal radical polymerization. On the other hand, most kinds of maleimide melt about or above 100°C; thus, it is indispensable to the use of solvent.

Provided that the imidization of SMA can be accomplished as intended, however, it will be capable of establishing a continuous process from SMA polymerization to imidization and obtaining corresponding high efficiency in cost and operation. In the light of these facts, it is very meaningful to apply the direct polymer reaction for the improvement of SMA thermal property.

In this article, we scrutinized the optimum reaction condition of SMI formation by way of direct polymer reaction in terms of reaction time and temperature, and the kinds of catalysts and their necessary amounts.

EXPERIMENTAL

Materials

Aniline, *p*-chloroaniline, and *p*-toluidine were purified with the suggested method.¹⁰ Sodium ace-

tate, received in a moisture-free state, was further dried at 120°C for 12 h just before use. N,Ndimethylformamide (DMF) and triethylamine (TEA) was dried with 4-Å molecular sieve for longer than 3 days. Acetic anhydride, tetrahydrofuran (THF), and *n*-hexane were used as received. Anhydrous methanol was made through 24-h refluxing with BaO.

Polymer

SMA, purchased from Aldrich, is completely alternating copolymer due to its tendency to form charge transfer complex during general radical polymerization. The number- (M_n) and weight-averaged molecular weights (M_w) , measured with gel permeation chromatography (GPC) calibrated with standard polystyrene, were 13,5000 and 350,000, respectively. In Table I, the characteristics of SMA copolymer used at this study are summarized.

Polymer Reaction

The modification of SMA was carried out in two steps according to the method to synthesize N-phenylmaleimide, which was developed by Searle.¹¹ A given amount of SMA was placed in an Earlenmeymer flask with a magnetic stirrer, followed by addition of DMF, and a vigorous stirring was attempted to get a homogeneous solution. The concentration of SMA in DMF was chosen as low as 10 wt % to avoid interchain reaction instead of intrachain cyclization during the step of imidization. Thereafter, in a round-bottomed flask equipped with a nitrogen gas inlet, a refluxing condenser, and a mechanical stirrer, a required amount of aniline was placed, and the prepared SMA solution was added slowly through addition funnel. At room temperature, the reaction proceeded for 3 h (step 1).

Into the solution prepared above, acetic anhydride, sodium acetate, and TEA, of which the intended amounts were calculated based on the mole content of anhydride unit in SMA, were added simultaneously. The reaction was at-

Table I	SMA Copolymer	Used in	This	Study
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Designation	$M_n \; (\rm g/mol)^a$				
SMA	135,000	350,000	50.0	171.0	

^a Determined with GPC calibrated with standard polystyrene.

^b The value is provided from the supplier.

^c Measured with a heating rate of 10°C/min.

tempted with variation of time and temperature (step 2).

A solution obtained from the step 2 was slowly dropped into 10-fold excess of anhydrous methanol to get a precipitant. The crude product was dissolved/precipitated with THF/*n*-hexane, respectively, for washing, which was repeated five times. Finally, the product was dried *in vacuo* for 24 h at 100°C.

CHARACTERIZATION

Spectroscopic Analysis

Fourier transform infrared (FTIR) analysis was used to monitor the reaction and find out the optimum condition for cyclic imidization. A specimen for the infrared (IR) experiment was made through a direct casting on clean KBr window. The 1.5 wt % polymer solution was prepared with THF, and the resulting thickness of thin film on KBr window was determined to be about 500 nm. The instrument was a Perkin–Elmer 750X FTIR spectroscopy, and each spectrum was obtained from 50 scanned data at room temperature and 1 atm. The resolution was 1 cm⁻¹, and scanning was conducted at absorption mode.

To verify a complete cyclization and obtain absolute amount of cyclic imide, a nuclear magnetic resonance (NMR) experiment had been attempted. A sample was dissolved in d_6 -DMSO. The instrument was AC-80 FT–NMR of Bruker, and a spectrum was obtained from 50 scanned data at room temperature and 1 atm.

Thermal Analysis

Using a Perkin–Elmer DSC-4, a thermal analysis has been performed under an N₂ atmosphere. With a heating rate of 10°C/min, a second scan spectrum was collected to measure the glass transition temperature (T_g) , and the temperature at the half-height of the heat capacity change was taken as T_g .

RESULTS AND DISCUSSION

Measurement of Conversion

The conversion of cyclic anhydride to cyclic imide in SMA was monitored and quantified with FTIR. An IR spectrum was obtained from thin film, which was prepared by direct casting on KBr window with diluted polymer solution. Figure 1 shows three kinds of spectra: (a) exhibits the state before reaction, (b) is under reaction, and (c) is after reaction, respectively. As is well known, a typical doublet of anhydride unit can be seen at 1780 and 1860 cm^{-1} in Figure 1(a). After the reaction of SMA with amine [Fig. 1(b)], it is observed that a imide peak appearing at 1715 cm^{-1} accompanies a carbonyl peak of free carboxyl acid at 1680 cm⁻¹ and an NH wagging peak at 820 cm^{-1} , showing the existence of succinamic acid formed at the step 1. In Figure 1(c), which shows the state of completion of imidization, it is observed that the 1715 cm^{-1} peak increased and the 1680 and 820 cm⁻¹ peaks decreased correspondingly. Based on the changes of peaks at 1715, 1680, and 820 cm^{-1} , it is possible to monitor the degree of conversion from cyclic anhydride to cyclic imide in SMA. Due to the fact that the thickness is different for each casted specimen and that the absorption coefficient is also different for each peak, it is impossible to deduce the desired accurate value for conversion by means of a simple comparison between the changes of peaks interesting. In the case of our experiment, it was found that the peak at 700 cm^{-1} , exhibiting the out-of-plane bending motion of monosubstituted benzene ring, does not produce any change during the whole reaction. Therefore, all the areas of the interesting peak were normalized with that of peak at 700 cm^{-1} to remove the effect of thickness and of change of absorption coefficient. In fact, it may be thought that evaluation of conversion to imide should be provided through changes of strong carbonyl peaks in anhydride, carboxylic acid, and imide groups. However, due to their high absorbance and the vicinal position to each other, and the corresponding large overlap among each peak, it is very hard to find out the exact area of the objective peak and may become much harder as the areas considered decrease. On the other hand, a peak of medium intensity without any vicinal strong peaks, such as NH wagging peak at 820 cm⁻¹, can be more useful to monitor precisely the removal of carboxylic acid. Therefore, the peak at 820 cm^{-1} normalized with 700 cm^{-1} peak, as well as the 1715 cm^{-1} peak, was simultaneously used for monitoring this experiment.

Moreover, to obtain an absolute value of conversion, a NMR experiment has been attempted for the specimens of which cyclization was determined to complete through IR experiment. Figure 2 is a typical NMR spectrum of the SMI copoly-



Figure 1 FTIR spectra of (a) SMA copolymer before reaction, (b) a ring-opened state having succinamic acid, and (c) SMI copolymer after ring closure.

mer synthesized with SMA and *p*-toluidine. The protons of *p*-tolyl unit appear as a symmetric pseudoquartet in the range of 7.0-7.6 ppm, and its number is proportional to the conversion,

while the number of alkylbenzene unit, which shows a multiplet of aromatic protons around 7.2 ppm, is constant. Therefore, it was capable of obtaining the conversion to the imide unit



Figure 2 FT-NMR spectrum of SMI copolymer prepared from SMA and *p*-toluidine.

through the comparison of peak area of 7.0-7.3 ppm with that of 7.3-7.6 ppm.

Determination of Reaction Conditions

Because the formation of imide from anhydride results in the release of water molecules, dehydration is indispensable to facilitate the overall reaction. Up to now, various kinds of dehydrating methods has been attempted in the formation of imide group. When divided largely, there are two kinds in dehydrating method, as follows: thermal and chemical methods. Although most polyimides are generally produced by way of thermal dehydration of polyamic acid, the inherent thermal weakness of the SMA main chain would impede specimens to exposure to high temperature. Most of syntheses of monomeric imides favor using dehydrating agents such as acetic anhydride and P_2O_5 .^{12,13} When powerful dehydrating agents, such as trifluoroacetic anhydride, N,N'-dicyclohexylcarbodiimide, or ethyl chloroformate, are allowed to react with maleamic acid in the presence of tertiary amine, such as TEA, it is reported that maleisoimides are formed as the main products instead of maleimides. Other dehydrating agents yield the corresponding imides or mixtures of imides and maleisoimides.¹⁴ Recently, new polyimides containing succimide in their backbone were synthesized from aspartic acid using o-phosphoric

acid.¹⁵⁻¹⁷ Although the acid-catalyzed polycondensation using o-phosphoric acid was observed to yield polymers of high molecular weight without a by-product, the reaction condition is somewhat severe; the temperature is approximately 200°C or higher, and the solvent required is a mixture of mesitylene-sulfolane, which is hard to remove completely. Among them, the dehydrating system of acetic anhydride and alkali metal salts of acetic acid has been known as the easiest and most efficient one. According to the patent provided by Searle, the optimum condition for the formation of monomeric cyclic imide appears to be 2 mol of acetic anhydride and 0.2 mol of sodium acetate to 1 mol of maleic anhydride. Based on this result, the feasibility in the application of Searle's recipe to polymeric system was examined.

Figure 3 is a conversion map describing that the optimum amount of acetic anhydride is two times that of the amount of anhydride in SMA. As seen in Figure 4, a dramatic change in conversion to imide resulted when sodium acetate was used, and the optimum value was determined 20 mol % to the content of anhydride unit in SMA; surprisingly, all the amounts of acetic anhydride and sodium acetate are consistent with Searle's results. The reaction occurred in the acetic anhydride-sodium acetate system, which is described



Figure 3 The conversion map from SMA to SMI in the function of the amount of acetic anhydride. The reaction condition was kept at 0.2 to 1.0 mol (sodium acetate to anhydride in SMA) for each run.

in eqs. (2), (4), and (5) within Scheme 2. When anhydride ring in SMA is opened, acetic anhydride is going to react with succinamic acid, as depicted in eq. (2) (Scheme 2). Although the formation of anhydride intermediate through eq. (2) can be made, low nucleophilicity of succinamic acid in SMA may act as a rate-determining factor. A free acetate ion can easily retain equilibrium state to create acetate group in SMA, which is



Figure 4 The conversion map from SMA to SMI in the function of the amount of sodium acetate. The reaction condition was kept at 2.0 to 1.0 mol (acetic anhydride to anhydride in SMA) for each run.

much higher nucleophilic than succinamic acid [eq. (4) in Scheme 3]. It is why sodium acetate is indeed required.

Compared with the synthesis of monomeric imides, it is requested to shift the equilibrium state of reversible reaction (4) in Scheme 3 to increase the yield in conversion to imide for the polymer reaction. Owing to the highly viscous environments, the reversibility can draw a limit





to obtain high yield. For this purpose, TEA is adopted to modify equilibrium state. TEA is a strong nucleophile and is expected to easily abstract acidic proton from acetic acid formed by the reaction of sodium acetate, regenerating acetate ion. Thereafter, the equilibrium point can be shifted toward the formation of anhydride intermediate. That is, the function of TEA is to accelerate reaction (5) in Scheme 3. In addition, TEA can take acidic proton from succinamic acid as well as from acetic acid like sodium acetate does. Therefore, TEA may be recommended as a cocatalyst instead of sodium acetate. Compared with sodium acetate, however, the amount required in TEA as the co-catalyst appeared much higher. In fact, sodium acetate can be referred to as a catalyst because it is regenerated through eq. (5) (Scheme 3), unlike TEA, which is actually diminished as the reaction proceeds. The function of TEA was obvious, facilitating to reach to the steady state at which the required amount is





Figure 5 The conversion map from SMA to SMI in the function of the amount of TEA. The reaction condition was kept at 2.0 to 0.2 to 1.0 mol (acetic anhydride to sodium acetate to anhydride in SMA) for each run.

Figure 6 The conversion map from SMA to SMI in the function of temperature. The reaction condition was kept at 2.0 to 0.2 to 1.1 to 1.0 mol (acetic anhydride to sodium acetate to TEA to anhydride in SMA) for each run.



Figure 7 The conversion map from SMA to SMI in the function of time. The reaction condition was kept at 2.0 to 0.2 to 1.1 to 1.0 mol (acetic anhydride to sodium acetate to TEA to anhydride in SMA) for each run.

found equivalent to the anhydride content in SMA, as shown in Figure 5. So a system consisting of acetic anhydride, sodium acetate, and TEA was established as 1.0 to 0.2 to 1.1 mol to 1 mol of maleic anhydride in SMA.

A cyclization is accompanied by dehydration reaction, and due to its endothermic character, thermal energy is required to shift the equilibrium state of a reversible reaction to the formation of product. In fact, when reacted at 60°C or below, even 10 more h was not enough for the complete removal of succinamic acid. As shown in Figure 6, the conversion came to the steady state at 70°C. When reacted above 100°C, the formation of large amount of isoimide was observed through Fourier transform (FT)-NMR. In addition, a thermal breakdown of the unreacted anhydride group cannot be avoidable, so the optimum temperature was determined at 80°C. As expected, it is observed that a long reaction time is favored to obtain a high yield in cyclization, and Figure 7 shows that a cyclization at 70°C should be kept at least 5 h or more to do so.

Figure 8 shows the change of conversion in terms of the amount of aromatic amine, the reactant. Curves 8(a) and (b) are the results for *p*-

toluidine and for aniline, respectively, showing that the yield in imidization linearly increases with the amount of amine, and the amount above four times the equivalent of maleic anhydride seems ineffective. In addition, when situated under the same reaction condition, the yield for ptoluidine was much higher than that for aniline. This difference in yield seems to be caused by the difference in the electron density of aromatic amine. In the case of *p*-toluidine, the electron density increased by the electron-donating effect of methyl group results in an increase of nucleophilicity of N, causing higher reactivity and corresponding the higher yield than with aniline. However, in any case, it was impossible to accomplish a perfect transformation to the imide group; the maximum in the yield was 70 mol % for ptoluidine and 55 mol % for aniline, respectively. The incompleteness is deduced to be caused by the intrinsic character of polymer reaction, that is, the high viscosity and the corresponding limited mass transfer.

Thermal Property

Since our primary goal at this study was to enhance the thermal property of SMA, it is of im-



Figure 8 The conversion map from SMA to SMI in the function of the amount of (a) *p*-toluidine and (b) aniline. The reaction condition was kept at 2.0 to 0.2 to 1.1 to 1.0 mol (acetic anhydride to sodium acetate to TEA to anhydride in SMA) for each run.

Designation ^a	Composition (mol %)			
	Anhydride	Imide	Conversion (%)	T_g (°C)
$T24^{b}$	25.94	24.06	48.12	205
T36	13.68	36.32	72.64	207
T48	2.48	47.52	95.04	211.5
$C42^{c}$	8.45	41.55	83.10	219.7
$A46^{d}$	4.49	45.51	91.02	186.5

Table II Characterization of SMI Copolymers Synthesized

^a The number shows the approximate content of imide group in mol %.

^b T represents the *N*-tolyl succinimide group.

^c C represents the *N*-*p*-chlorophenyl succinimide group.

^d A represents the *N*-phenyl succinimide group.

portance to monitor the change in T_g for each SMI copolymer. Table II shows the results of characterization in terms of copolymer composition and T_g . All SMI successfully show higher T_g than SMA, as found in Table II and Figure 9. Interestingly, it is observed that there is a distinct gap in T_g according to the kind of side chain on the succinimde group. When the SMIs with comparable degree of conversion are compared, there is an order in T_g of SMI copolymer as follows: N-p-chlorophenyl > N-tolyl > N-phenyl group. That



Figure 9 Glass transition temperature of SMA and SMI copolymers with various *N*-aryl succinimide side chains.

order seems created by the difference in bulkiness and the polarity of the attached side group.

CONCLUSION

In this experiment, a mixture of acetic anhydride--sodium acetate-TEA was used as a dehydrating system for cyclic imidization. The overall trend for the formation of cyclic imide in high polymer was similar to that for monomeric maleimide synthesis, expressing that the method provided by Searle is useful to introduce cyclic imide groups into SMA, even at the macromolecular condition. In addition, in the case of polymer reaction, of importance is that higher temperature and longer reaction time should be applied than for the monomeric reaction, in which the reaction is accomplished spontaneously at room temperature or even a much colder condition. On the other hand, the perfect transformation of SMA to SMI appeared impossible due to the limited mass transfer in a polymer solution.

Although it was not capable of obtaining SMI, a binary copolymer consisting of only styrene and *N*-substituted cyclic imide, as found in thermal behavior, our efforts are thought meaningful in terms of polymer modification.

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