

Synthesis and Comparative Study of Thermal Stabilities of the Imidization of Some Maleic Anhydride Copolymers

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ABSTRACT: In the present study, first, maleic anhydride-styrene (MA-St), maleic anhydride-allyl phenyl ether (MA-APhE), maleic anhydride-heptene-1(MA-Hp), and maleic anhydride-allyl propionate (MA-AP) copolymers have been synthesized in different solvents in the presence of azobisisobutyronitrile (AIBN) at 70°C. Then, these four copolymers have been reacted with aniline at 60°C in *N,N*-dimethyl formamide (DMF), and maleamic acid derivatives of these copolymers have been synthesized. Next, they have been obtained from their maleimide derivatives by heating under vacuum at 150°C. All these polymers have been character-

ized by Fourier Transform infrared spectroscopy (FTIR) and investigated their thermal properties by using differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA) methods. The analyses results showed that thermal properties of maleimide derivatives of maleic anhydride copolymers changed as depend on the neighbor monomers of maleic anhydride. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 2250–2254, 2006

Key words: polyimide; maleic anhydride; imidization; TGA; DSC

INTRODUCTION

It is well-known that polyimides are useful high performance materials because of their excellent thermal stability, high chemical resistance, high breakdown voltage, low thermal expansion, and low dielectric constants.¹ Polyimides are generally prepared through the ring-opening polyaddition of carboxylic dianhydrides with diamines, followed by thermal or chemical imidizations, and they have some significant disadvantages, such as low solubility and intermolecular and intramolecular charge-transfer-complex formation because of their characteristic structures.

Depending on requirement, many of maleic anhydride copolymers can be modified by reaction at maleic anhydride ring.^{2–6} In our laboratory, coterpolymers of maleic anhydride with different monomers are currently synthesized and characterized.^{7–9}

Thermal property is one of the most important properties for polymeric materials. Thus, thermal stability and thermal degradation kinetics may be significant for production and application. Thermogravimetric analysis (TGA) has been used for many years to evaluate polymer thermal stability. There are numerous studies of the thermal behavior of polyimides in the literature.^{10–15}

The aim of the study is to compare the thermal stability of maleimides synthesized by imidization reaction of aniline with the four copolymers of maleic anhydride. For thermal characterization of maleimides, DSC and TGA have been used.

EXPERIMENTAL

Materials

Maleic anhydride used after sublimation was obtained from Aldrich Chemical Company, UK. Heptene-1, *N,N*-dimethyl formamide (DMF) and styrene were obtained from Merck Chemical Company, Germany. Aniline was obtained from Merck Company; it was purified by distillation under vacuum (bp: 62.5°C). Allyl propionate was obtained from Peaxnm Company, Azerbaijan. Allyl phenyl ether was obtained from Fluka Chemie Company, Switzerland.

Modification and synthesis of maleic anhydride copolymers

The solvent, the amounts of the initiator and the monomers used in synthesis of four copolymers are given in Table I. All the monomers are 0.1 moles. The syntheses of the four copolymers have been carried out by using the solvents in the presence of AIBN initiator at 70°C for 1 h, and the amounts are given in Table I. The copolymers were purified by precipitation in propyl alcohol, and repeatedly washed with propyl

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TABLE I
The Amounts of the Materials Used in Synthesis of Four Copolymers

Copolymers	MA (g)	St (mL)	APhE (mL)	Hp (mL)	AP (mL)	AIBN (g)	Solvent
MA-St	19.6	20.0	–	–	–	0.2	Benzene
MA-ApHE	19.6	–	26.8	–	–	0.2	Butyl acetate
MA-Hp	19.6	–	–	20.0	–	0.2	Butyl acetate
MA-AP	19.6	–	–	–	25.0	0.2	Butyl acetate

alcohol to remove residual monomers, and dried at room temperature.

Next, the maleamic acid derivatives of these four copolymers were obtained by reaction of aniline with the copolymers at 60°C in DMF. The mole proportion of copolymer to aniline was 1 : 2. The amounts of the copolymers and aniline used for maleamic acid derivatives are given in Table II. Their maleimide derivatives have been later obtained by heating to 150°C under vacuum.

Characterization of the polymers

Unicam mark Mattson 1000 model FTIR was used for the spectrophotometer characterization of the copolymers prepared with KBr.

TGA and DSC experiments were carried out by using a Shimadzu TG-50 and DSC-50 at heating rate of 10°C/min under a flowing nitrogen atmosphere. The temperature was changed from 25 to 600°C. About 10 mg of the polymer samples were used in the examination. The gas flow rate was 25 cm³ min⁻¹.

RESULTS AND DISCUSSION

The copolymers of maleic anhydride have been synthesized via CT complexes. To represent all the copolymerization reactions, the mechanism of the MA-St copolymer is given in Scheme 1. The mechanisms of the maleamic acid and maleimide derivatives obtained from reactions of aniline with same copolymer are given in Scheme 2. The chemical formulas of the other copolymers are given in Scheme 3.

The spectroscopic analyses of all the polymers have been made, and the FTIR spectra of the MA copolymers and imide derivatives are shown in Figures 1

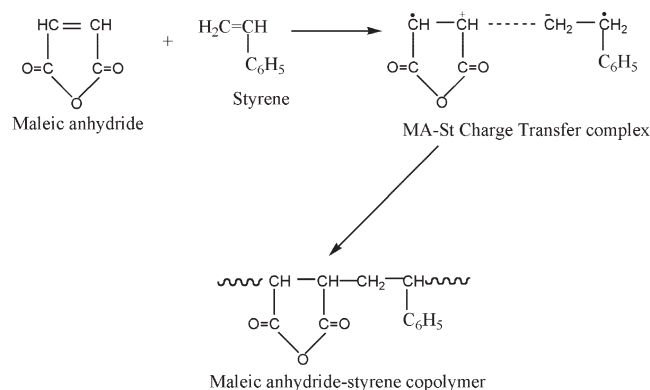
and 2, respectively. According to Figure 1, specific anhydride peaks appear at 1804 and 1855 cm⁻¹. As seen in Figure 2, these do not appear in maleimide derivatives.¹⁶ This proves that anhydride rings have been opened by aniline.

TG and DTG curves relating to MA copolymers and their maleimide derivatives are shown in Figures 3 and 4. Thermal stabilities of all the polymers can also be compared in quantity with each other by using some thermal parameters such as initial degradation temperature (T_i), half-time temperature (T_h), maximum rate temperature (T_m), final degradation temperature (T_f), maximum rate (R_m), and remained substance amount at maximum rate (C_m) given in Table III.

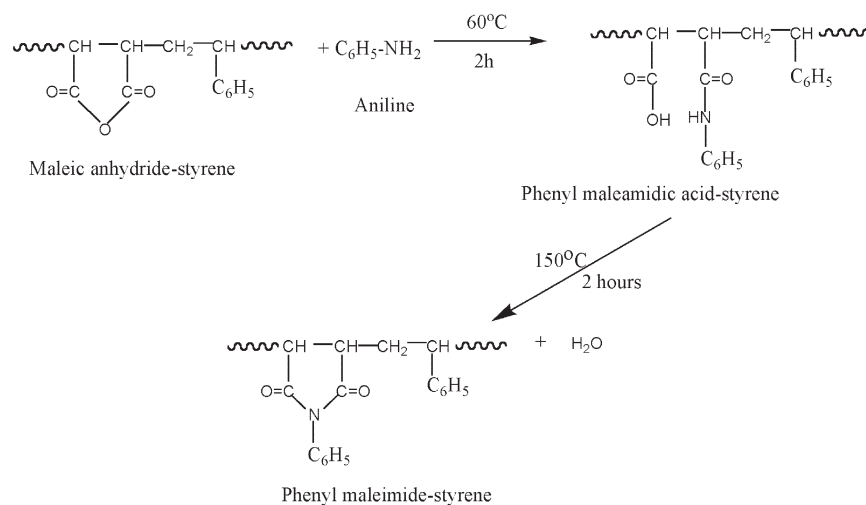
Until 300°C, the mass loss of the MA copolymers is approximately 10% in weight at first step of the thermal degradation. There must be two reasons for this mass loss. The first is that CO₂ and H₂O absorbed on the sample are removed by the effect of temperature, and the second is solvent removing. The main degradation reactions of the copolymers are carried out between 274 and 363°C. The degradation temperatures of MA-St and MA-Hp copolymers are higher than those of MA-AP and MA-ApHE copolymers, because MA-St consists of aromatic ring, while MA-Hp consists of long side branch. MA-ApHE also contains the aromatic structure; however, it is bound to the ether unit. Therefore, the aromatic ring in MA-ApHE does not affect the degradation temperature. The ini-

TABLE II
The Amounts of the Materials Used in the Synthesis of the Maleamic Acid Derivatives

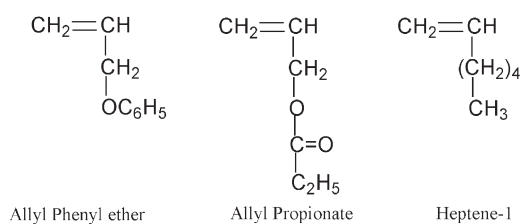
Maleamic acid derivatives	MA-St (g)	MA-ApHE (g)	MA-Hp (g)	MA-AP (g)	Aniline (mL)
MA-St/Aniline	5.0	–	–	–	5.0
MA-ApHE/Aniline	–	6.0	–	–	5.0
MA-Hp/Aniline	–	–	5.0	–	5.0
MA-AP/Aniline	–	–	–	5.5	5.0



Scheme 1 The mechanism of the formation of MA-St copolymer via charge transfer complexes.



Scheme 2 The mechanism of maleamic acid and maleimide derivatives of MA-St copolymer.



Scheme 3 The other three monomers used in the synthesis of the MA copolymers.

tial degradation temperature of the MA copolymers is in the sequence of MA-HP > MA-ST > MA-APhE > MA-AP.

The mass losses appeared at 300°C in MA copolymers have not been observed in the TGA curves of the

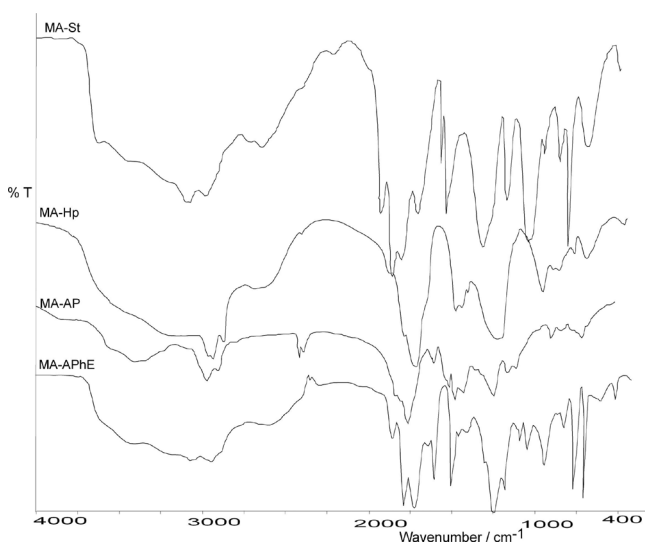


Figure 1 FTIR spectra of the MA copolymers.

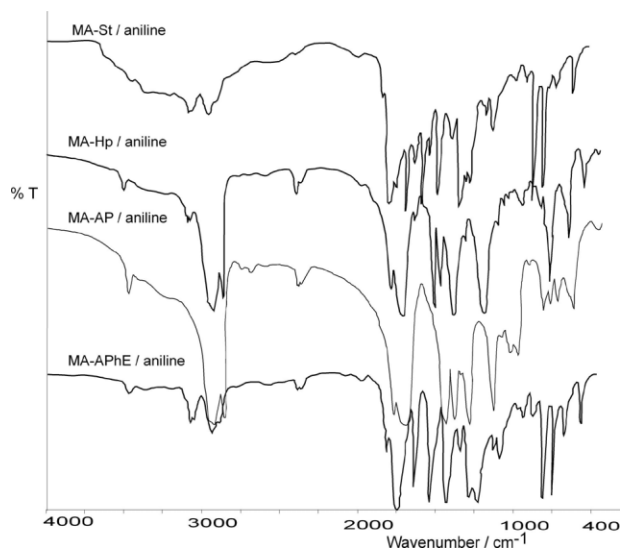


Figure 2 FTIR spectra of the maleimide derivatives of the MA copolymers.

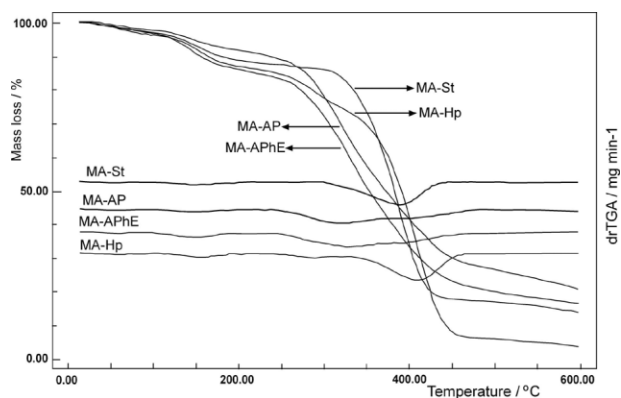


Figure 3 TGA-drTGA curves of the MA copolymers.

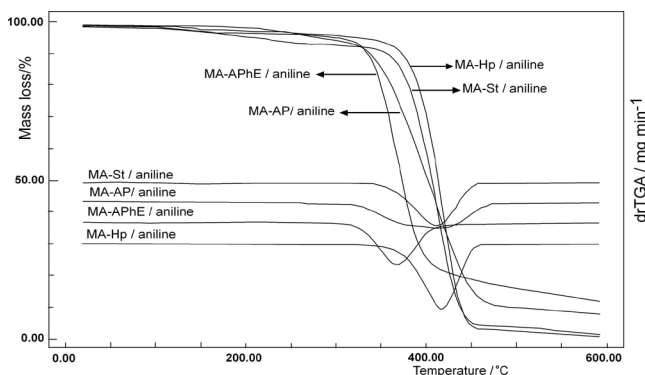


Figure 4 TGA-drTGA curves of the maleimide derivatives of the MA copolymers.

maleimide derivatives of the MA copolymers because of MA units in the copolymers. Initial degradation temperatures of MA copolymers are lower than those maleimide derivatives, because the MA copolymers easily absorb CO_2 and H_2O molecules because of their MA units. On the other hand, the main degradation temperatures of the maleimide derivatives are higher than those of MA copolymers. Initial degradation temperatures of MA copolymers are in the order of MA-HP/Aniline > MA-ST/Aniline > MA-AP/Aniline > MA-APhE/Aniline. In conclusion, because of the chemical formula of maleimide derivatives, they are more stable than MA copolymers.

The glass transition temperatures (T_g) of MA copolymers and their maleimide derivatives have been obtained from the DSC curves shown in the Figures 5 and 6. The values of the T_g and the degradation enthalpies obtained from these curves are given in Table IV. There are small differences in the T_g of the MA copolymers, in contrast to the maleimide derivatives. The reason of this is the complete opening of the anhydride rings in the backbone of the MA copolymers by the imidization reaction of aniline with MA units. The imidization reactions toughen the polymers. In the direction mentioned earlier, the degradation enthalpies of the maleimide derivatives are also higher than those of MA copolymers.

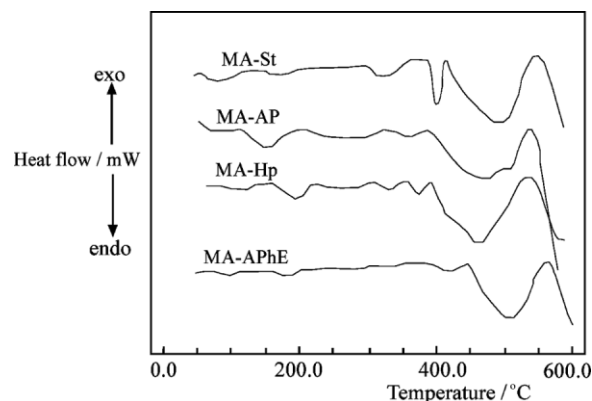


Figure 5 DSC curves of MA copolymers.

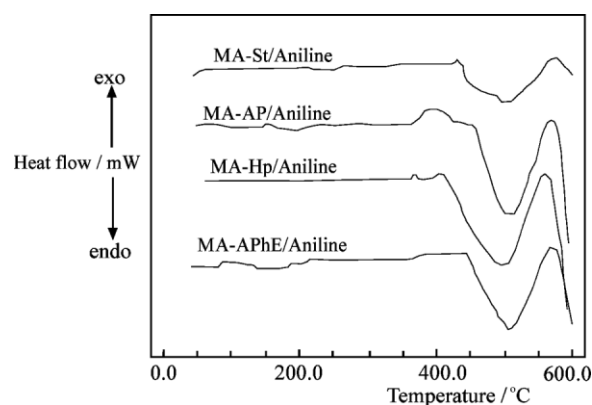


Figure 6 DSC curves of the maleimide derivatives of MA copolymers.

CONCLUSIONS

The maleimide derivatives of some MA copolymers have been successfully synthesized via the reaction of MA copolymers with aniline. All copolymers have been characterized by FTIR, and their thermal behaviors have been reported by TGA and DSC. These reports showed that it is possible to obtain the maleimide copolymers having better thermal stability via imidization of aniline with MA copolymers.

TABLE III
Thermal Parameters Relating with Thermal Degradation of the Copolymers

Copolymers	T_i (°C)	T_f (°C)	T_h (°C)	T_m (°C)	R_m (mg min^{-1})	C_m (%)
MA-St	339	421	382	386	0.0123	46
MA-St/Aniline	386	443	412	417	0.0243	41
MA-APhE	279	434	348	328	0.0081	62
MA-APhE/Aniline	347	406	380	372	0.0239	61
MA-AP	274	438	365	318	0.0077	72
MA-AP/Aniline	356	456	408	425	0.0155	42
MA-Hp	363	440	389	411	0.0147	32
MA-Hp/Aniline	392	448	417	420	0.0369	46

TABLE IV
Glass Transition Temperatures and the Degradation
Enthalpies Values of the Maleimide Derivatives and MA
Copolymers

Copolymers	T_g (°C)	$\Delta H/kJ g^{-1}$
MA-St	110	0.82
MA-St/Aniline	210	1.05
MA-APhE	105	1.20
MA-APhE/Aniline	125	1.08
MA-AP	107	1.00
MA-AP/Aniline	190	1.09
MA-Hp	120	1.82
MA-Hp/Aniline	—	2.21

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