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Poly(styrene-*co*-*N*-maleimide) Copolymers: Preparation by Reactive Extrusion, Molecular Characterization by FTIR, and Use in Blends

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ABSTRACT: Poly(styrene-*co*-*N*-maleimide) (NMI) copolymers were obtained from reactive extrusion experiments of poly(styrene-*co*-maleic anhydride) (SMA) with ammonia in small reaction times (2 min). As a result of this modification, materials with relatively high glass-transition temperatures have been obtained compared to the starting material, and this is believed to result mainly from hydrogen bonding between the maleimide groups. Qualitative and quantitative evidence has been obtained from an FTIR study performed on NMI-14 containing 14 wt % maleimide groups. This investigation revealed hydrogen bonding between the NH and carbonyl groups of the maleimide groups. A systematic FTIR spectroscopic study of the blend system consisting of NMI-14 and poly(styrene-*co*-2-vinylpyridine) (SPVP) was also performed. Direct evidence of hydrogen bonding involving the NH groups of NMI-14 and the nitrogen of the pyridine group in SPVP is presented.

Introduction

Copolymers of styrene and maleimide can be prepared by direct copolymerization of the monomers. The imide monomers, however, are quite expensive and polymerization by the free radical route usually yields 1:1 alternating copolymers.[1-4] One of the methods developed to prepare nonequimolar poly(styrene-*co*-maleimides) is to convert poly(styrene-*co*-maleic anhydrides) to the corresponding imide by reacting the copolymers with ammonia at 125–200 °C under pressure (60–150 psi) for 8–48 h in organic solvents.[5-7] This process eliminates the need for anhydrous ammonia, which is advantageous because ammonia is commonly sold as a 25–30% solution in water. Preparation in the autoclave, however, requires a suitable solvent, a suspending agent to prevent agglomeration of the final product, long reaction times, filtration and centrifugation to separate the solid from the liquid medium, etc.

Another approach is to perform this chemical modification by reactive extrusion. Moore[8] and Lambla[9] obtained imidized copolymers from SMA by previous treatment with ammonia and subsequent processing in the extruder. By this two-step process, Lambla obtained imide conversion levels of 78% at a screw speed of 20 rpm. As will be demonstrated in the first part of this paper, imidization can be accomplished in one step in the extruder by reacting poly(styrene-*co*-maleic anhydride) with aqueous ammonia in the melt within reaction times of 3 min.

In the second part of this paper, a systematic FTIR study of NMI-14 and miscible NMI-14/SPVP blends is reported and the role of hydrogen bonding is discussed. Polyimides have high glass-transition temperatures and may be blended with other thermoplastic polymers to increase the heat-distortion temperature of the latter. Miscibility of the blends as a function of composition has also been studied using differential scanning calorimetry.

Materials and Characterization Methods

A commercial SMA (Monsanto EX 3600) containing 25 wt % maleic anhydride (MA), 7 wt % methyl methacrylate (MMA), and 68 wt % styrene (Sty) with an intrinsic viscosity of 0.43 dL/g was used in this study (Figure 1a). Ammonia (28% aqueous solution from Baker) was used as received. The poly(styrene-*co*-*N*-maleimide) (NMI-14) with 14 wt % maleimide (MI) was obtained from Monsanto. The poly(styrene-*co*-2-vinylpyridine) (SPVP) with 30 wt % styrene and α-methyl-α-phenylsuccinimide from Aldrich were used without any further purification.

The degree of imidization of the samples was determined from titration of the residual MA groups using a MeOH/NaOH solution and from elemental nitrogen analysis using oxidative pyrolysis and the chemoluminescent detection of chemically bound nitrogen. Glass-transition temperatures (T_g) were measured on a Perkin-Elmer DSC-7 at a heating rate of 10 °C/min; the second run was used to determine T_g.

Fourier transform infrared (FTIR) vibrational spectroscopy was performed on a Digilab FTS-45 at a resolution of 2 cm^{-1}. A minimum of 15 scans were signal averaged, and the spectra were stored on a magnetic disk system. Spectra recorded at elevated temperatures were obtained by using a high-temperature cell mounted in the spectrometer and regulated by a heat controller with reported accuracy of ±0.1 °C. Samples for FTIR analysis were prepared by solution casting onto KBr windows from a 2% (w/v) solution in anhydrous THF. To ensure an even film thickness, a saturated THF environment was maintained during the evaporation process. The film was heated in a vacuum oven for 5 h at 200 °C prior to FTIR analysis. The films under study were sufficiently thin to be within the absorbance range where the Beer–Lambert law is obeyed (<0.8 absorbance units).

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker WM 250 from THF-d_8 solutions at 60 °C at a frequency of 62.9 MHz (^{13}C), a 60° pulse, and a

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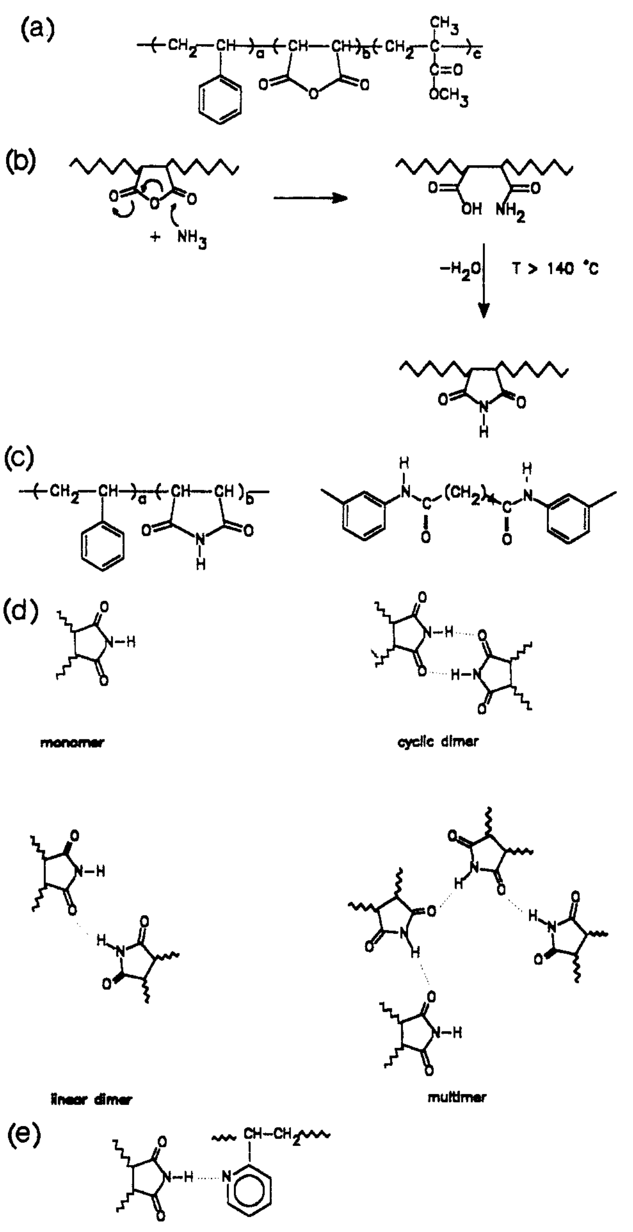

Figure 1. (a) Chemical structure of SMA. (b) Imidization reaction of an anhydride segment and a primary amine group. (c) Chemical structures of NMI-14 and MPD6 nylon. (d) Examples of self-association in NMI-14. (e) Representation of hydrogen bonding between SPVP and NMI-14.

scan amount of 21 728. ^{1}H-NMR scans at 250 MHz were also obtained at 60 °C from a deuterated THF solution.

Results and Discussion

Reactive Extrusion of Poly(styrene-*co*-maleic anhydride) (SMA) with Ammonia. An increase in glass-transition temperature is one of the objectives for the imidization of SMA. Figure 1b illustrates the imidization reaction. The process by which the SMA is reacted in the melt with ammonia in an extruder is called "reactive extrusion". Reactive processing in general has some distinct advantages over the conventional reaction in solution: (i) the absence of solvent leads to savings in raw materials and solvent-recovery systems, (ii) high amounts of the reacted species can be obtained since extruders can handle the high viscosity of polymers, (iii) the reaction kinetics can be accelerated as the reactions can be conducted in a large range of tempertures (70–500 °C) and pressures (0–500 atm), and (iv) a continuous production of ready-to-use materials is possible. Limitations of reactive extrusion, however, are (i) possible side, oxidation, or degradation reactions resulting from the high processing temperatures, (ii) decreased miscibility of coreagents, and (iii) slow diffusion of reagents in the polymer melt.

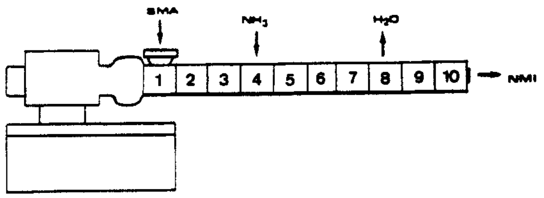

Figure 2. Leistritz configuration for the imidization reaction.

Table I. Characterization of Poly(styrene-*co*-*N*-maleimide) Polymers with Various Imidization Degrees

	MA (wt %)	MI (wt %)	Sty (wt %)	MMA (wt %)	conv (%)	T_g (°C)
SMA	25	0	68	7	0	154
NMI-1	15	10	68	7	39	165
NMI-2	10	15	68	7	60	169
NMI-3	7	18	68	7	72	172
NMI-4	4	21	68	7	86	176

The imidization reaction was performed in a Leistritz corotating twin-screw extruder containing 10 barrels, each set at varying temperatures (240–265 °C) (Figure 2). Aqueous ammonia was injected in the molten SMA at two injection ports of barrel 4 using a hydraulic pump. Reaction occurred in zones 4–7, after which venting was applied to eliminate condensation water and excess ammonia. It is important to emphasize that reproducible samples were obtained using similar processing conditions. Residence times of 2 min were determined at a screw rate of 100 rpm. No catalyst, solvent, or stabilizers were added. This reactive extrusion process in the melt allows amidation and ring closure in one step giving imidization.

Various NMI copolymers containing different maleimide levels were obtained (Table I) by varying the ammonia to maleic anhydride ratio in the extruder. From a limited number of extrusion experiments performed under various processing conditions, we believe that higher conversions of maleic anhydride to maleimide may be obtained and possibly total imidization if the process is optimized. Increasing the molar ratio of ammonia (3/1 ammonia vs maleic anhydride) did not affect the degree of conversion (Figure 3). Crucial factors pertaining to the optimization of the process appeared to be the venting of the condensation water evolved during imidization and the screw design.

NMR and FTIR analysis of the products indicated that imide rings were formed in the absence of amide or acid groups. A ^{13}C-NMR scan of NMI-4 compared to its parent SMA indicates a shift of the carbonyl from 173 to 179.6 ppm; this is consistent with the substitution of the maleic anhydride by the maleimide. In the ^{1}H-NMR spectrum, only a minor change in the polymer backbone is observed; a broad peak at 9.4 ppm is observed and assigned to the imide proton. Characterization by FTIR also supports the formation of imides; this is described in detail in the next part of this paper. The T_g's of the partially imidized copolymers, determined by DSC, are also presented in Table I. A significant increase of 20 °C in T_g is observed for NMI-4, reflecting a 21.5 mol % substitution of maleic anhydride by maleimide groups.

FTIR Characterization of Poly(styrene-*co*-*N*-maleimide) Copolymers. As mentioned above, substitution of maleic anhydride by maleimide increases the T_g

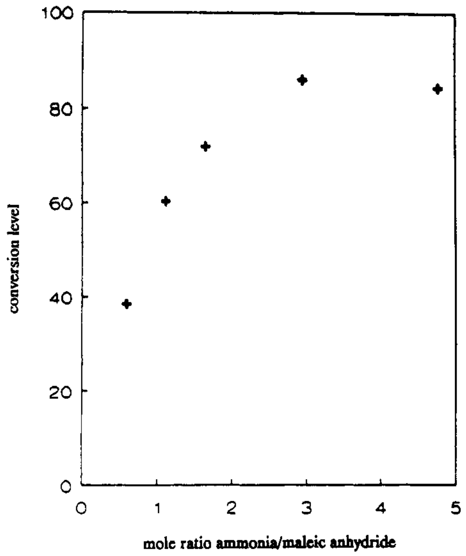

Figure 3. Influence of the mole ratio versus anhydride content on the conversion level of imide formation.

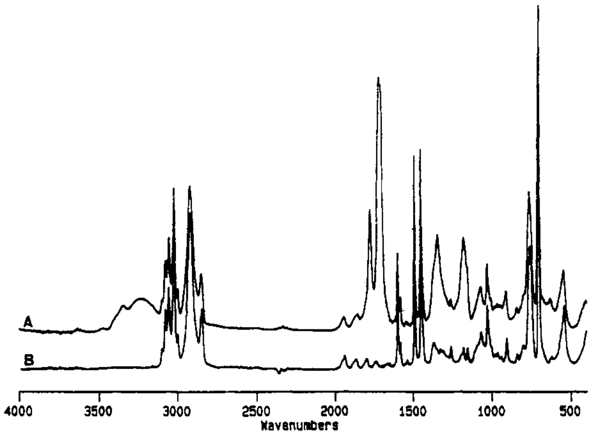

Figure 4. Comparison of FTIR spectra in the 3600–400-cm^{-1} region of (A) NMI-14 and (B) polystyrene recorded at room temperature.

significantly (Table I). It is believed that this increase in T_g can be explained predominantly on the basis of hydrogen bonding between the maleimide groups. Hydrogen bonding has been described in the literature for similar structures, including low-molecular-weight succinimides[10,11] and urazole-containing polymers.[12]

Information concerning the presence and the nature of hydrogen bonds in NMI copolymers has been gained from vibrational FTIR spectroscopy. Because of the very complex microstructure of the NMI copolymers which are composed of various segments (Table I), several of which are capable of forming hydrogen bonds, we decided to simplify the problem and study a model copolymer of styrene and maleimide containing 14% maleimide, denoted NMI-14. The spectroscopic data will be compared with results obtained for a poly(*m*-phenyleneadipamide) (MPD6) which is known to self-associate through hydrogen bonding (Figure 1c).[13]

Figure 4 compares the infrared spectrum of amorphous NMI-14 with that of atactic polystyrene, recorded at room temperature in the 3600–400-cm^{-1} range. The vibration modes due to the maleimide groups are easily distinguished. Upon cycling up and down in temperature, essentially identical spectra were obtained as illustrated in Figure 5. In this study, our attention has been focused on two major regions of the infrared spectrum of NMI-14: the NH stretching region from 3100 to 3600 cm^{-1} and the carbonyl stretching region from 1650 to 1800 cm^{-1}.

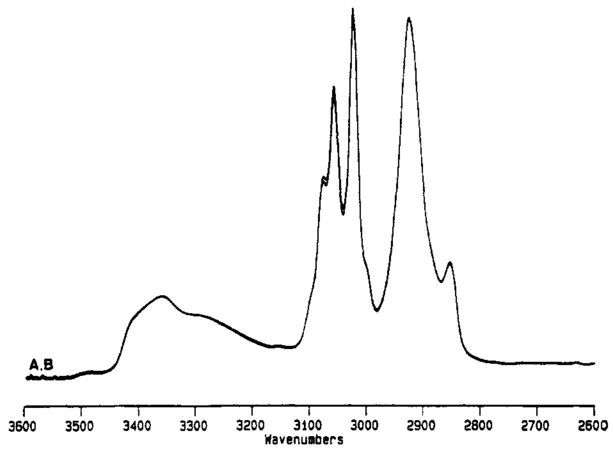

Figure 5. FTIR spectra of the NH stretching region after cycling up and down: (A) before cooling to 50 °C; (B) after cooling from 50 °C.

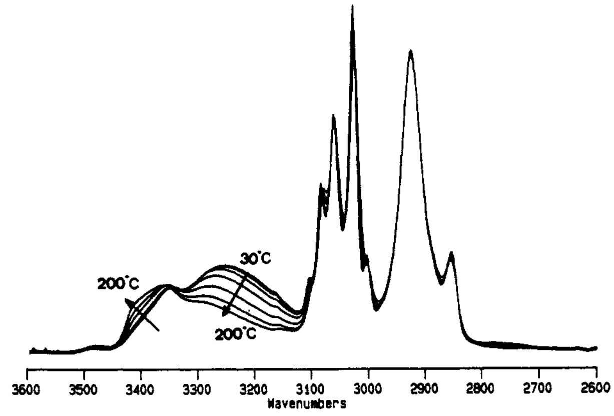

Figure 6. FTIR spectra in the 3600–2400-cm^{-1} region of NMI-14 recorded as a function of temperature (spectra recorded at 200, 170, 140, 110, 80, 50, and 30 °C).

NH Stretching Region. FTIR spectra of amorphous NMI-14 in the region from 3600 to 3100 cm^{-1} as a function of temperature are presented in Figure 6. The spectra were recorded on the same sample to compare the differences in absolute absorbance at various temperatures. Care was taken to minimize water absorption by heating the sample to 200 °C and recording the spectra as a function of decreasing temperature. For the spectrum at 30 °C a relatively narrow band at 3414 cm^{-1} is observed, attributed to the "free" NH stretching. A somewhat broader band that is approximately twice as broad as the "free" NH stretching is observed at 3352 cm^{-1} and is attributed to hydrogen-bonded dimers. Finally, a broad band centered at 3249 cm^{-1} is assigned to a wide distribution of hydrogen-bonded chainlike structures (multimers) of the maleimide groups. Figure 1d illustrates the range of multimers and dimers, both cyclic and linear, that one might expect to be present. We also caution that overtone and combination bands may occur in this region, which further complicates spectral interpretation.

An increase in temperature changes the distribution of the hydrogen-bonded species in a complex fashion.[14] For the "free" NH groups, an expected increase in intensity is observed. The intensity of the absorption band of the hydrogen-bonded groups, however, decreases markedly and the peak maximum shifts to higher wavenumbers as the temperature is varied from 30 to 200 °C. This rather large decrease in absorbance with temperature is not directly related to the transformation of the NH bonded groups to "free" ones but rather reflects the large variation of the absorption coefficient with the distance and

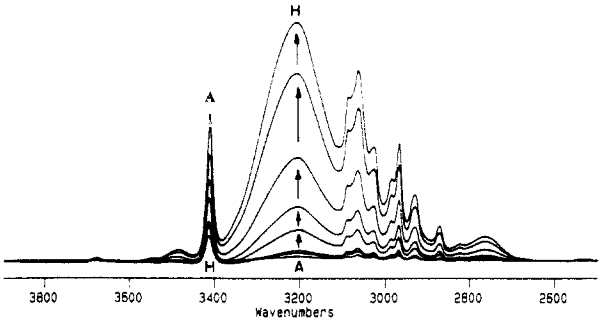

Figure 7. FTIR spectra in the 3600–2400-cm^{-1} region of α-methyl-α-phenylsuccinimide recorded at various concentrations: (A) 0.005, (B) 0.008, (C) 0.01, (D) 0.02, (E) 0.03, (F) 0.05, (G) 0.08 and (H) 0.1 M.

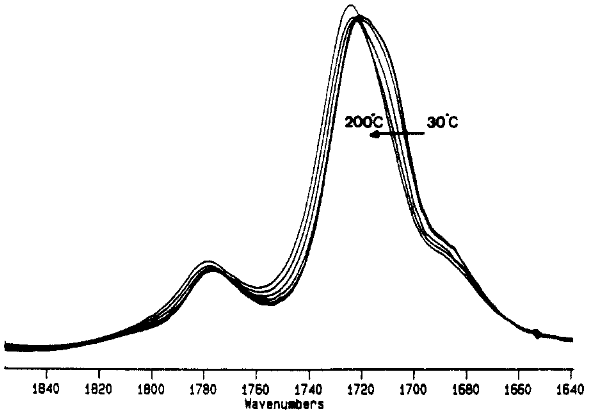

Figure 8. FTIR spectra in the 1900–1600-cm^{-1} region of NMI-14 recorded as a function of temperature (spectra recorded at 200, 170, 140, 110, 80, 50, and 30 °C).

geometry of the hydrogen-bonded species, the distribution of which changes with temperature.[14,15]

An indication of the relative enthalpy of hydrogen bond formation can be obtained from the difference in frequency of the "free" and hydrogen-bonded NH groups (multimers). For NMI-14 the frequency difference is 165 cm^{-1} at 30 °C, which is somewhat greater than that observed for amorphous polyamides (134 cm^{-1})[14] and significantly greater than for MPD6 (90 cm^{-1}).[13]

It is useful to compare the spectra of NMI-14 polymer with a model system that is less complicated. α-Methyl-α-phenylsuccinimide is an appropriate low-molecular-weight analog for NMI-14 that is soluble in CCl_4. Figure 7 shows the effect of dilution on the infrared spectrum of this compound. The "free" NH band at 3415 cm^{-1} increases upon dilution at the expense of the broad hydrogen-bonded band at 3207 cm^{-1}. These results are consistent with the trends noted above.

Carbonyl Region. At 30 °C three bands are observed in the 1700–1800-cm^{-1} region, which are attributed to NMI-14 carbonyl stretching modes (Figure 8). The first at ca. 1779 cm^{-1} is attributed to the in-phase carbonyl vibration of the imide group. Two other bands at 1726 and 1710 cm^{-1} are assigned to "free" and hydrogen-bonded out-of-phase carbonyl vibrations. With increasing temperature the hydrogen-bonded band decreases in intensity in favor of the "free" band. The in-phase vibration mode, on the other hand, does not appear too sensitive to hydrogen bonding. The shoulder observed at 1690 cm^{-1} is most probably ascribed to an oxidative product of polystyrene and is not observed when working under a nitrogen atmosphere. Supporting evidence for the band assignments of the "free" and the hydrogen-bonded carbonyl groups was obtained from spectra recorded from solutions of α-methyl-α-phenylsuccinimide in CCl_4 at various concentrations (Figure 9). Three well-resolved bands are discerned in the carbonyl region. As the solution is diluted, the band at 1737 cm^{-1} which is assigned to "free" carbonyl increases in intensity relative to that of the band at 1716 cm^{-1}, attributed to hydrogen-bonded carbonyl groups. The in-phase carbonyl absorption band at 1789 cm^{-1} remains essentially unaffected. These assignments are entirely consistent with those made for the analogous NMI-14 polymer.

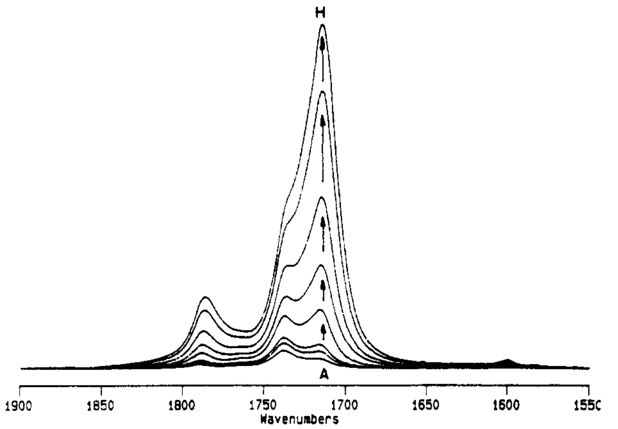

Figure 9. FTIR spectra in the 1990–1600-cm^{-1} region of α-methyl-α-phenylsuccinimide recorded at various concentrations: (A) 0.005, (B) 0.008, (C) 0.01, (D) 0.02, (E) 0.03, (F) 0.05, (G) 0.08, and (H) 0.1 M.

Spectra recorded at different temperatures are reproducible while cycling up and down in temperature, and one can visually detect the changing intensities of the bands at 1710 and 1726 cm^{-1}. Quantitative data were obtained by curve fitting of the carbonyl stretching region into two bands at 1726 and 1710 cm^{-1} using a least-squares iterative program previously described.[16] Several assumptions and restrictions were made when performing the curve fitting: (i) the band shape of the bonded carbonyl group was assumed to be Gaussian, (ii) a linear baseline was utilized from 1900 to 1550 cm^{-1}, and (iii) the curve fitting of the spectra was limited to a range between 1704 and 1744 cm^{-1}, which circumvents problems due to overlap contributions from neighboring absorption bands. Examples of curve fitting the carbonyl region at 30 °C and at 170 °C are shown in Figure 10. The fraction of "free" and hydrogen-bonded carbonyl groups f°_F and f°_{HB} for NMI-14 were obtained from $f^\circ_{HB} = 1 - f^\circ_F = A_{HB}/(A_{HB} + [a_{HB}/a_F]A_F)$, where the absorptivity ratio a_{HB}/a_F was assumed to be 1.2.[13] The results are presented in Table II. Note that only one in three carbonyl groups is hydrogen bonded at room temperature and that f°_{HB} decreases systematically with increasing temperature. A dimensionless equilibrium constant, K_B, that describes the self-association of NMI-14, assuming that the distribution of hydrogen-bonded species is "chainlike" and similar to that of polyamides or polyurethanes,[16] may be calculated from the relationship[13,16]

$$K_B = \frac{1 - f^\circ_F}{(f^\circ_F)^2}$$

Using the value of f°_F obtained at 170 °C (Table II), which is above the T_g of NMI-14 and facilitates equilibrium conditions, we calculated K_B to be 0.36. To compare the relative propensities toward self-association of comparable copolymers containing maleimide groups with those containing amide groups, we need to scale the equilibrium constants to a common reference volume. A convenient

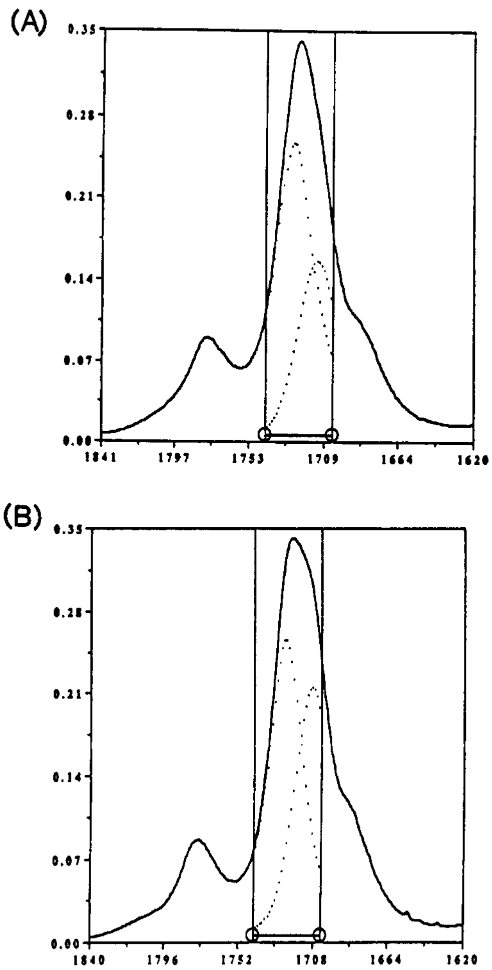

Figure 10. Curve fitting in the 1900–1600-cm^{-1} region of the spectrum of NMI-14 recorded at (A) 170 and (B) 30 °C.

Table II. Curve-Resolving Data of NMI-14

	free carbonyls			hydrogen-bonded carbonyls			
temp (°C)	posit (cm^{-1})	$w_{1/2}$ (cm^{-1})	A_F	posit (cm^{-1})	$w_{1/2}$ (cm^{-1})	A_{HB}	f°_F
200	1728	29	12.50	1714	28	3.82	0.80
170	1727	28	11.76	1713	27	4.00	0.78
140	1726	26	11.41	1711	24	4.02	0.77
110	1726	26	10.34	1711	25	5.02	0.71
80	1725	25	9.72	1710	25	5.56	0.68
50	1725	25	9.72	1710	25	5.56	0.68
30	1726	24	9.56	1710	25	5.72	0.67

reference volume, V_B^{ref}, is 100 cm^3/mol, and the relevant equation is[16]

$$K_B^{ref} = \frac{K_B V_B}{V_B^{ref}} = \frac{K_B V_B}{100}$$

The molar volume of an average repeat unit of NMI-14 that contains one maleimide group, which we refer to as the "specific" repeat,[16] is ca. 600 cm^3/mol, as estimated from group molar volume constants. Accordingly, the value of K_B^{ref} at 170 °C for a styrene-*co*-*N*-maleimide copolymer having a specific repeat of 100 cm^3/mol is ≈2.2. Using an identical procedure, we calculated from data obtained previously[13] that K_B^{ref} = 14.1 for an analogous copolymer having a specific repeat of the same reference volume and containing one amide group. Thus we may conclude, all other things being equal, that self-association of copolymers containing maleimide groups is significantly weaker than that of corresponding copolymers containing amide groups.

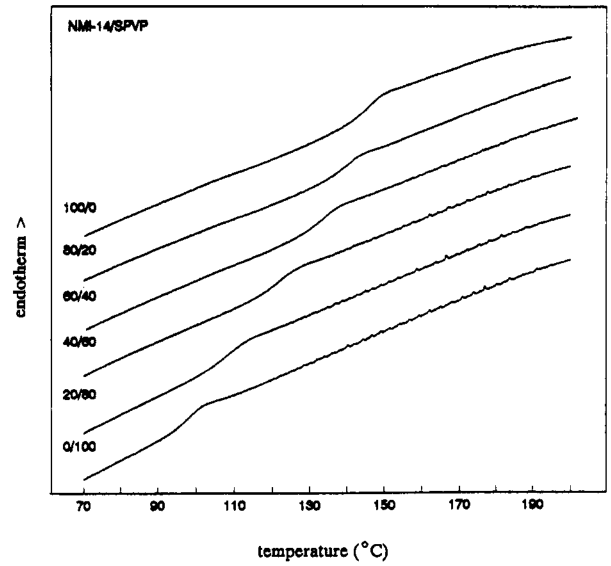

Figure 11. DSC curves of NMI-14/SPVP blends recorded at a heating rate of 10 °C/min.

Supporting evidence for the relatively small magnitude of K_B for NMI copolymers is found qualitatively in the recent work of Musto et al.[17] In this paper, *blends* of a polyimidazole (PBI) and an aromatic poly(ether imide), Ultem 1000, were shown to involve an imide NH to carbonyl interaction similar to that present in NMI-14 (self-association). Only a minor fraction of hydrogen-bonded carbonyl groups (=0.35 for a 50/50 blend) is observed in blends of comparable concentration of specific functional groups. This work contains some striking similarities to our results; a frequency for the free carbonyl groups is observed at 1725 cm^{-1} and for the hydrogen-bonded carbonyls at 1710 cm^{-1}.

Blends of NMI-14 with Poly(styrene-*co*-2-vinylpyridine) (NMI-14/SPVP). In general, the probability of finding miscible systems is enhanced if interassociation is favored over self-association.[18] The NH groups of NMI-14 can form hydrogen bonds with functional groups other than the carbonyl groups of the maleimide (self-association). Poly(styrene-*co*-2-vinylpyridine) (SPVP), for example, contains the pyridine moiety, which has a basic nitrogen capable of forming very strong hydrogen bonds with the imide (interassociation). In a miscible blend, a new distribution of hydrogen-bonded species is formed that includes "free" and hydrogen-bonded NH and carbonyl groups of NMI-14 and hydrogen-bonded NH to nitrogen of the pyridine groups in SPVP (Figure 1e). This distribution is dictated by the equilibrium constant values and temperature.

DSC characterization of the NMI-14/SPVP blends reveals single glass-transition temperatures that are intermediate between those of the pure components (Figure 11). A positive deviation of the experimental values from the Fox relation (Figure 12) suggests the presence of strong interactions.[19] The DSC results are consistent with a miscible system over the whole composition range, and there is no evidence of phase separation up to 300 °C.

FTIR Characterization of the Blends. Figure 13 shows spectra of NMI-14/SPVP blends of various compositions in the 3600–2400-cm^{-1} region. Increasing the concentration of SPVP in the blends has a marked effect on the distribution of the "free" and the hydrogen-bonded NH groups. At a composition of 40/60 NMI-14/SPVP, where there is an excess of vinylpyridine over maleimide segments, the "free" and the hydrogen-bonded NH groups

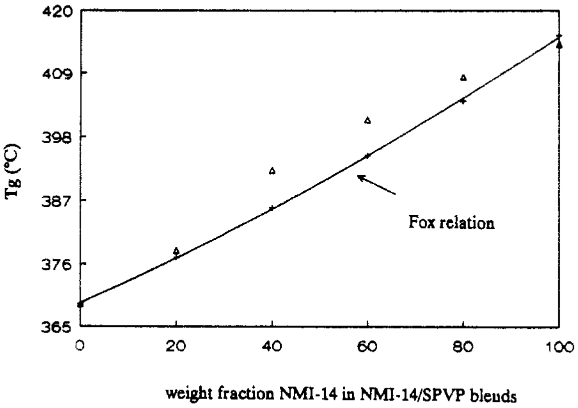

Figure 12. Comparison of experimentally and calculated T_g's for the NMI-14/SPVP blends obtained from DSC scans.

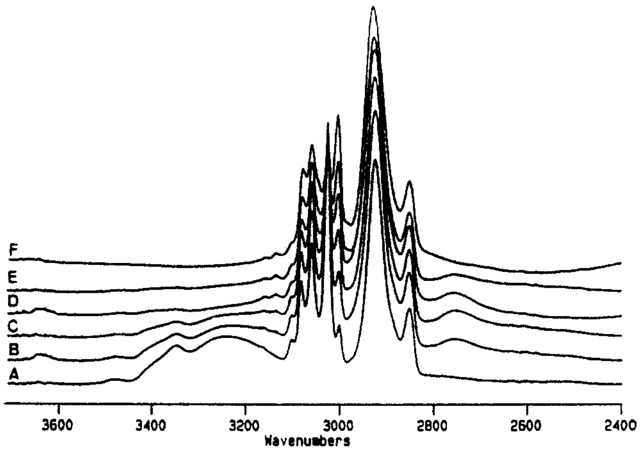

Figure 13. FTIR spectra in the 3600–2400-cm^{-1} stretching region of NMI-14/SPVP blends at various compositions recorded at room temperature: (A) 100/0, (B) 80/20, (C) 60/40, (D) 40/60, (E) 20/80, and (F) 0/100 NMI-14/SPVP.

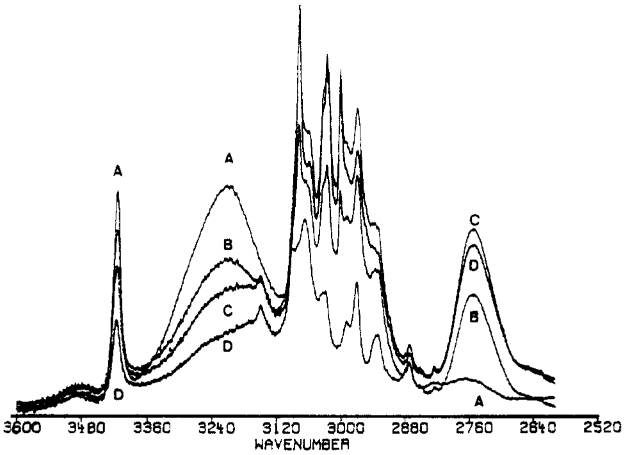

Figure 14. FTIR spectra in the 3600–2400-cm^{-1} stretching region of α-methyl-α-phenylsuccinimide (X)/pyridine (Y) mixtures recorded at various concentrations: (A) 0.05 M X; (B) 0.05 M X/0.05 M Y; (C) 0.05 M X/0.10 M Y; (D) 0.05 M X/0.15 M Y.

attributed to the self-association of maleimides are barely detected. However, a band at 2757 cm^{-1} is plainly seen and is ascribed to N–H···N interassociation.[20] The N–H···N interaction is much stronger than the N–H···C=O interaction, which implies that the equilibrium constant describing interassociation has a much greater value than that describing self-association. Similar results were obtained from an FTIR study of the model compound α-methyl-α-phenylsuccinimide mixed with pyridine at various concentrations in CCl_4. Spectrum A in Figure 14 represents a 0.05 M solution of the model imide compound

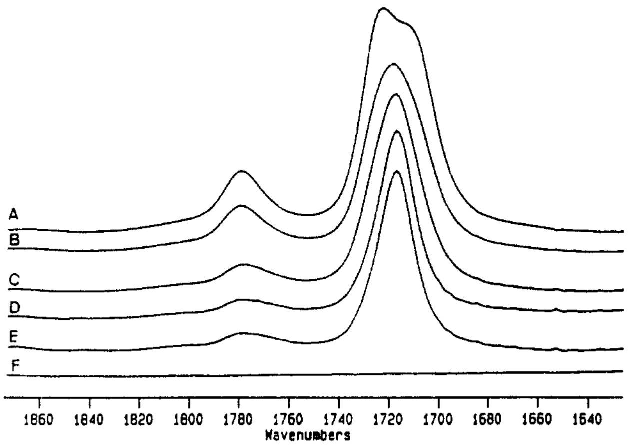

Figure 15. FTIR spectra in the 1900–1600-cm^{-1} region of NMI-14/SPVP blends at various compositions recorded at room temperature: (A) 100/0, (B) 80/20, (C) 60/40, (D) 40/60, (E) 20/80, and (F) 0/100 NMI-14/SPVP.

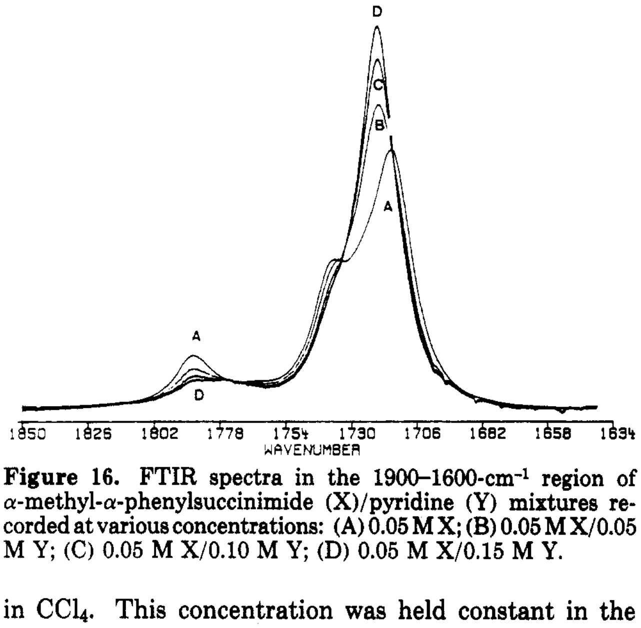

Figure 16. FTIR spectra in the 1900–1600-cm^{-1} region of α-methyl-α-phenylsuccinimide (X)/pyridine (Y) mixtures recorded at various concentrations: (A) 0.05 M X; (B) 0.05 M X/0.05 M Y; (C) 0.05 M X/0.10 M Y; (D) 0.05 M X/0.15 M Y.

in CCl_4. This concentration was held constant in the various solutions and the pyridine concentration was varied from 0.05 to 0.15 M. From these spectra one can clearly see the distribution of "free" NH groups, and N–H···C=O multimers change in favor of the N–H···N hydrogen bonds with increasing pyridine concentration (spectra B–D). In the 1600–1900-cm^{-1} region of the NMI-14 spectrum, three carbonyl bands described as above are observed (Figure 15A). SPVP does not absorb in this region. Upon increasing the concentration of SPVP in the blend, the "free" and hydrogen-bonded carbonyl bands at 1726 and 1710 cm^{-1} merge into a single band at 1717 cm^{-1}. As the interassociation of maleimide–pyridine groups is much stronger than the self-association of maleimide groups, the fraction of N–H···N groups dominates over that of N–H···O=C. Hence, the predominant structure present is shown in Figure 1e. This is a symmetrical structure anticipating single in-phase and out-of-phase carbonyl stretching modes, which is consistent with the bands observed at 1780 and 1717 cm^{-1}, respectively. Unfortunately, it is not feasible to accurately determine the fraction of "free" carbonyl groups and thus the value of the interassociation constant.

Finally, the results obtained for the model compound α-methyl-α-phenylsuccinimide mixed with pyridine at constant imide concentration confirms this spectral interpretation (Figure 16).

Conclusions

Copolymers of *N*-maleimides are readily produced from poly(styrene-*co*-maleic anhydride) via a one-step imidization with ammonia using reactive extrusion. These polymers have significantly higher T_g's than their poly(styrene-*co*-maleic anhydride) parents. Large amounts of ready-to-use materials may be obtained in small reaction times (2 min) without catalysts, suspending agents, solvents, processing aids, or stabilization products. Screw design and devolatilization of the condensation water appear to be primary factors controlling the imidization kinetics.

FTIR characterization of a model amorphous poly(styrene-*co*-*N*-maleimide) copolymer containing 14 wt % maleimide, NMI-14, revealed that self-association occurs through hydrogen bonding between the NH and carbonyl groups of the imides. Band assignments of the hydrogen-bonded imide groups were supported by a FTIR study of a low-molecular-weight analog, α-methyl-α-phenylsuccinimide, at various concentrations in CCl_4.

An equilibrium constant describing the self-association of NMI-14 was calculated from quantitative FTIR data of the fraction of hydrogen-bonded carbonyls. By scaling to a common reference volume, it was determined that the self-association of maleimides is significantly weaker than that of amides. The interassociation between maleimide and pyridine groups, however, is relatively strong, and the NMI-14 copolymer was found to be miscible with a poly(styrene-*co*-2-vinylpyridine) copolymer.

Conversion of styrene-*co*-maleic anhydride to styrene-*co*-*N*-maleimide copolymers not only raises the T_g significantly but also increases the probability of finding miscible or partially miscible polymer blend systems.

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