Dependence of Transition Temperatures and Enthalpies of Fusion and Crystallization on Composition in Polyaniline/Nylon Blends

Rafil A. Basheer*

Polymers Department, General Motors Research & Development Center, Warren, Michigan 48090-9055

Alan R. Hopkins and Paul G. Rasmussen

Center for Macromolecular Science and Engineering and Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109-1055

Received December 16, 1998; Revised Manuscript Received May 4, 1999

ABSTRACT: The properties of blends, cast from hexafluoro-2-propanol, of nylon 6 and of nylon 12 with polyaniline doped with various functionalized organic acids were investigated using differential scanning calorimetry and microscopy. The glass transition temperature of the as-cast and dried blends of polyaniline with either nylon displayed a composition-independent relationship indicative of a phase-separated morphology irrespective of the functionalization of the sulfonic acid dopant. Although electron microscopy data also showed phase-separated morphologies, the PANI domain size within the nylon matrix was found to be dependent upon the functionalized acid dopant. A decrease in the melting transition temperatures of nylon 6 and associated enthalpies with blend composition is attributed to the effects of dissociation and degradation processes occurring during thermal analysis. We suggest that the effusion of the resulting thermally induced species from within the polyamide domain disrupts the crystalline structure, leading to depression in the melting point and heat of fusion. Changes in other thermal transitions, such as melt and cold crystallizations and their enthalpies, were attributed similarly to products of PANI dissociation and degradation formed during thermal analysis.

Introduction

Remarkable improvement in the physical or mechanical properties of certain polymers may be achieved by blending with a second polymer without significantly compromising the desirable attributes of either component of the blend. For conducting polymers such as polyaniline (PANI), the discovery[1] of solution processability by doping (protonating) with functionalized organic acids has allowed the preparation of blends of polyaniline and a number of conventional polymers.[2,3] In attempts to overcome the brittle characteristics of PANI, blends with excellent mechanical and electrical properties have been made by judicious selection of the functionalized doping acid, the solvent, and the host polymer. Perhaps the most remarkable feature of this approach is the achievement of high blend conductivity values approaching those of the pure conducting component by using a PANI concentration which amounts only to a minor fraction of the total composition.[3] These high conductivity values have their origin in the complex phase-separated fibrillar network morphology of the blend, giving rise to percolation threshold values at volume fractions of polyaniline that are substantially lower than 1%. Such a phase-separated morphology is induced by the effect of the counterion trying to be at the interface of PANI and the host polymer during liquid−liquid phase separation.[2]

Not all blends of PANI and random coiled polymers have a phase-separated morphology. Stockton and Rubner[4] reported that the nonconducting form of PANI (PANI/EB) forms miscible blends with poly(*N*-vinyl-2-pyrrolidone) up to a concentration of 30 wt %, whereas the blend with the acid-doped PANI was phase-separated. The observation of phase separation was evident by the appearance of microaggregates in the resulting film. Ong and co-workers[5] reported miscible blends of poly(vinyl acetate) and of poly(2-ethyl-2-oxazoline) with PANI doped with selected functionalized acids. More recently, Byun and Im[6] investigated nylon 6/PANI composite films prepared by swelling nylon 6 with aniline, followed by oxidative polymerization with ammonium peroxydisulfate in the presence of a number of functionalized sulfonic acids. Using dynamic mechanical thermal analysis, they observed increased intensity and broadening of the tan δ peak of nylon 6 upon composite formation. Results from another investigation involving the X-ray diffraction of blends of nylon 6 and PANI cast from a solution of formic acid demonstrated the absence of any interaction between the two components of the blend even though thermal analysis in the same study showed a decrease in the melting point of the nylon upon blending.[7]

We have recently reported on the properties of blends of nylon 6 and of nylon 12 with PANI doped with a number of functionalized acid dopants, namely methanesulfonic acid (MSA), dodecylbenzenesulfonic acid (DBSA), and camphorsulfonic acid (CSA).[8,9] The primary objective of that study was to determine how the different counterions affect the morphology and conductivity of blends of PANI and two polyamides possessing different proportions of polar (amide) and nonpolar ($-CH_2-$) units.

The counterion of the organic acid dopant strongly influences the solubility of polyaniline in a specific solvent. For blend formation, such a solvent must be capable of codissolving polyaniline and the host polymer. For polar polymers, *m*-cresol has been the solvent of choice when blends of PANI with such polymers are considered. One of the problems associated with the use of *m*-cresol is the difficulty of its complete removal from the cast films. Residual *m*-cresol, which can be as high as 18% of the total blend, contributes to many of the observed physical and mechanical properties. Thus,

* Corresponding author.

10.1021/ma981935r CCC: $18.00
Published on Web 06/15/1999

conclusions drawn from experimental observations on such blends can have significant error. Hexafluoro-2-propanol (HFIP), which has a low boiling point, has been used successfully to prepare blends of PANI and polyamides.[8] In the present investigation, we report on the thermal analysis of films cast from HFIP to explore the phase behavior of blends of polyamides and doped PANI in an effort to better understand the remarkably high conductivity values of these blends.

Experimental Section

Polyaniline emeraldine base (PANI-EB) was prepared by oxidative polymerization of predistilled aniline at room temperature using $FeCl_3$. Details of the doping (protonation) process and of the molecular characteristics of undoped polyaniline and polyaniline salts are described elsewhere.[8] Molar doping of undoped polyaniline for each of the polyaniline salts was calculated from the mole ratio y = (moles of dopant)/(moles of phenyl-NH). Optimally, doped polyaniline requires a value of $y = 0.5$. Dopants used were as follows: camphorsulfonic acid (CSA), Aldrich, methanesulfonic acid (MSA), and dodecylbenzenesulfonic acid (DBSA), TCI America. Nylon 6 and nylon 12, Aldrich, were vacuum-dried at 75 °C for 24 h before solution blending. All polyaniline salt solutions were filtered using 0.5 μm size filter.

The filtered solutions of blends of undoped polyaniline and of doped polyaniline salts with polyamides were cast onto a Teflon-coated glass substrate. The cast films were immediately covered with a glass dish to allow for a slow evaporation of the solvent over a period of 24 h at room temperature. All films were then peeled off the Teflon-coated substrate and dried at 75 °C in a vacuum oven for approximately 24 h. From fluorine elemental analysis, the amount of residual HFIP solvent in the films was less than 0.5% (w/w). Casting from HFIP produced robust free-standing and solvent free polyaniline/nylon blend films. Blend compositions in terms of weight fractions of PANI/nylon were converted to volume fractions using film densities measured by calcium nitrate/water density gradient column as described elsewhere.[9]

Thermal analysis was performed using a differential scanning calorimeter (Perkin-Elmer DSC-7) calibrated with indium as the reference material. Typically, 10 mg of folded and predried (at 75 °C for 24 h) blend film sample contained in an unsealed aluminum DSC pan was used for each measurement. Scanning was conducted from −10 °C to about 20 °C above the melting point of the nylon under nitrogen gas at a heating rate of 10 °C/min. For the determination of melt crystallization transitions, samples were cooled from above the melting point of the nylon to room temperature at a cooling rate of 10 °C/min under nitrogen. In another experiment, samples were quickly removed from the DSC cell, which was at a temperature 30 °C higher than the melting point of the nylon, and quenched in liquid nitrogen. The thermograms of these samples were then recorded at a heating rate of 10 °C/min starting from −10 °C through the melting transition. Experiments involving dedoping (deprotonation) were carried out by immersing the blend films (nylon 6/PANI/CSA) in either ammonium hydroxide for a period of 24 h or methanol for a period of 7 days. The samples were then washed with water and dried under vacuum at 75 °C for 24 h. The enthalpies of the different thermal transitions (ΔH_f and ΔH_c) of the blends were calculated by digitally integrating the area of the endothermic and exothermic peaks and expressing the values in units of watts per gram. It is important to note that all values of the experimentally measured heats of transition quoted here have already been normalized (w/w) to account for the nylon phase in the blend.

Transmission electron microscopy observations were performed using a Philips electron microscope operated at a potential of 150 keV. A typical blend sample was prepared by embedding multiple films in epoxy resin followed by staining by RuO_4 and then microtoming to obtain sections of ≈100 nm. The microtomed (at room temperature) samples were captured on a 100 mesh size copper grid by floating in deionized water.

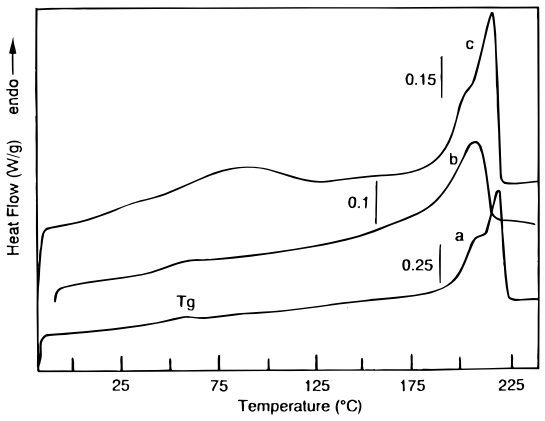

Figure 1. DSC thermograms of (a) nylon 6 and its blends with (b) 25% PANI/EB and (c) 10% PANI/MSA.

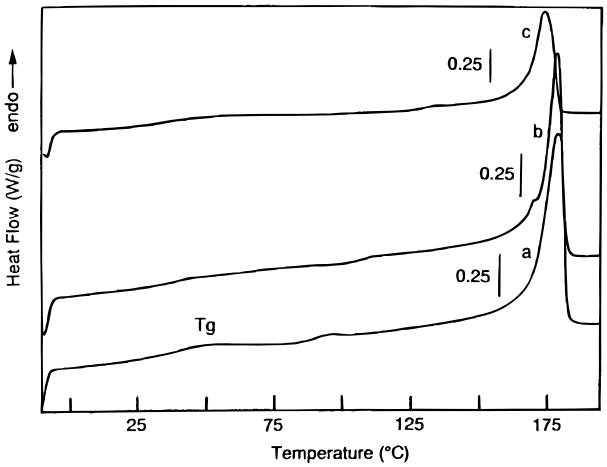

Figure 2. DSC thermograms of (a) nylon 12 and its blends with (b) 10% PANI/EB and (c) 25% PANI/DBSA.

Results and Discussion

Glass Transition. Differential scanning calorimetry (DSC) is the most common method of investigating polymer miscibility or the degree of interaction between the constituent polymers of a blend. Interaction on the molecular level between the amorphous phases of two polymers of sufficiently separated glass transition temperatures (T_g) leads to a single T_g. This is generally taken as an indication of polymer miscibility. A significant shift of the two T_g values toward some intermediate values is recognized as a sign of partial miscibility or interfacial interaction. Completely phase-separated blends show two T_g values corresponding to those of the pure components. Changes in other thermal transitions such as the melting point and the crystallization temperature and in their associated enthalpies have also been reported in blends of miscible polymers.[10]

Since both polyaniline emeraldine base form (PANI/EB) and polyaniline salts form (PANI/salt) do not exhibit a T_g or a melting point (e.g., PANI/EB shows only a broad exothermic peak associated with degradation and cross-linking), the thermal transitions and associated heats of the second polymer (nylon 6 or nylon 12) in a blend with PANI may be used to assess the level of polymer−polymer interaction.

Figures 1 and 2 show DSC thermograms of as-cast nylon 6, nylon 12, and representative examples of their blends with polyaniline. The thermograms of nylon 6

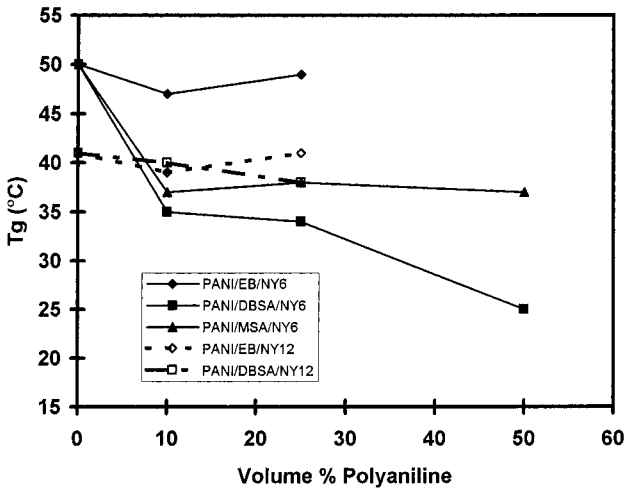

Figure 3. T_g/composition dependence for as-cast blends of PANI/nylon 6 and PANI/nylon 12.

and nylon 12 are similar to those reported in the literature.[11,12] In Figure 3, the glass transition temperatures of nylon 6 and of nylon 12 are plotted as a function of composition of as-cast blends with PANI/EB, PANI/MSA, and PANI/DBSA. The decrease in T_g from a value of 50 °C for pure nylon 6 film on increasing the polyaniline component volume fraction is attributed to plasticization by residual water. The plasticization of nylon 6 and other polyamides with water has been well documented.[13] As stated earlier, these samples were dried under vacuum for 24 h at 70 °C prior to DSC measurements. However, even brief exposure of a dried specimen of polyamide to ambient humidity causes large reduction in the glass transition temperature. The water absorption is generally enhanced in thin films compared to bulk materials, and the presence of the extremely hygroscopic polyanilinesulfonate salts in a blend with a polyamide leads to additional water absorption. In fact, the intensity of the broad endothermic peak that appears above the T_g of nylon 6 or nylon 12 (maximum around 100 °C) increases with the increase in the PANI/salt content of the blend. The marginal reduction in T_g for PANI/EB blends compared to the much larger drop in T_g for PANI sulfonate salt blends is due to the difference in the hydrophobic nature of the two forms of PANI. This is supported by thermogravimetric analysis which showed a weight loss at 125 °C of 3% and 1.5% for PANI/MSA/nylon 6 and PANI/EB/nylon 6 blends, respectively. Additional evidence for water plasticization of the nylon was obtained from T_g measurements on samples that were heated in the DSC cell at 110 °C for 1 h and then cooled to room temperature under nitrogen gas. The choice of drying at 110 °C was motivated by our desire to remove the water without subjecting the samples to excessively high temperatures and by results from TGA analysis which showed no additional weight loss from 110 to 150 °C. An exception to this behavior was observed for blends containing PANI/MSA where an additional weight loss of 0.5% was recorded at 150 °C. Table 1 shows the rise in T_g on drying the samples at 110 °C. Except for PANI/MSA/nylon 6 blends, the T_g values are only slightly lower than the T_g values of the corresponding pure nylon. The lower T_g observed for the dried PANI/MSA/nylon 6 may be due to incomplete removal of water by heat treatment. Due to the lower concentration of the amide group per unit mass, nylon 12 is much less hydrophilic than nylon 6 and, therefore, has a lower tendency for water absorption. This is

Table 1. Glass Transition Temperatures (°C) of Nylon 6 and Nylon 12 Blends with PANI Emeraldine Base and Salt Forms

		T_g			
nylon	PANI (vol %)	as-cast	dried at 110 °C	NH_3 treated	MeOH treated
nylon 6	0	50	49		
nylon 6	25% PANI/EB	49	49		
nylon 6	25% PANI/DBSA	34	47		
nylon 6	25% PANI/MSA	38	43		
nylon 6	25% PANI/CSA	34	47		
nylon 6	25% PANI/CSA			49	50
nylon 6	50% PANI/CSA			48	48
nylon 12	0	41	41		
nylon 12	25% PANI/EB	39	40		
nylon 12	25% PANI/DBSA	38	40		
nylon 12	25% PANI/MSA	37	39		
nylon 12	5% PANI/CSA	40	42		

evident by the small reduction in T_g in blends of nylon 12 and PANI from that of the pure component. The absence of a significant T_g −composition dependence in the dried samples clearly indicates a phase-separated morphology not only in blends containing PANI/EB but also in blends containing polyaniline salts. Furthermore, upon removal of the doping acid from a blend of nylon 6 and PANI/CSA either by neutralization with ammonium hydroxide or by extraction with methanol followed by drying at 110 °C, the measured T_g from either treatment was similar to that obtained for the corresponding as-cast and dried blend of nylon 6 and PANI/EB form (Table 1). Films of blends of PANI/EB with either nylon appear phase-separated under optical microscope while the blends containing PANI/CSA appear homogeneous (and transparent for low PANI/CSA concentration) with no obvious sign of phase separation.[14] However, the phase-separated morphology of either nylon/PANI/CSA blends is evident in their transmission electron microscopy micrographs in which dense network-like structure of PANI/CSA in the host polymer is clearly seen (Figure 4). A recent study using small-angle neutron scattering[9] provided no evidence of miscibility in any of the PANI/salt/nylon 6 blends. The scattering data, however, showed some deviation from the model of a simple two-phase system, suggesting a more complex phase-separated morphology. Thus, although these distinctly different sulfonic acids do not induce any pronounced interaction between the rigid polyaniline and the coil-like nylon chains, they do influence the degree and the nature of dispersion (domain size) of PANI in the host polymer. These characteristics in turn affect the electrical conductivity value of the blend.[2]

It is fundamentally difficult for a rigid-rod polymer to form miscible blends with flexible random coil polymers unless there exists strong intermolecular interaction to overcome the unfavorable entropic change of mixing.[15,16] Some miscible blends of PANI/salts with specific random coiled polymers have been reported. Of particular interest is the work of Goh et al.,[17] which provided evidence of miscibility in blends of PANI/salts and tertiary amide polymers. Unlike MSA, DBSA, and CSA, their functionalized acid dopants (like *p*-phenolsulfonic acid) seem capable of interacting with the functional group of the studied host polymers leading to miscibility. Hydrogen-bonding interaction at the phase boundary has been suggested[18] for a nylon 6/PANI/salt composite prepared by diffusion of aniline monomer into a nylon film and subsequent polymeri-

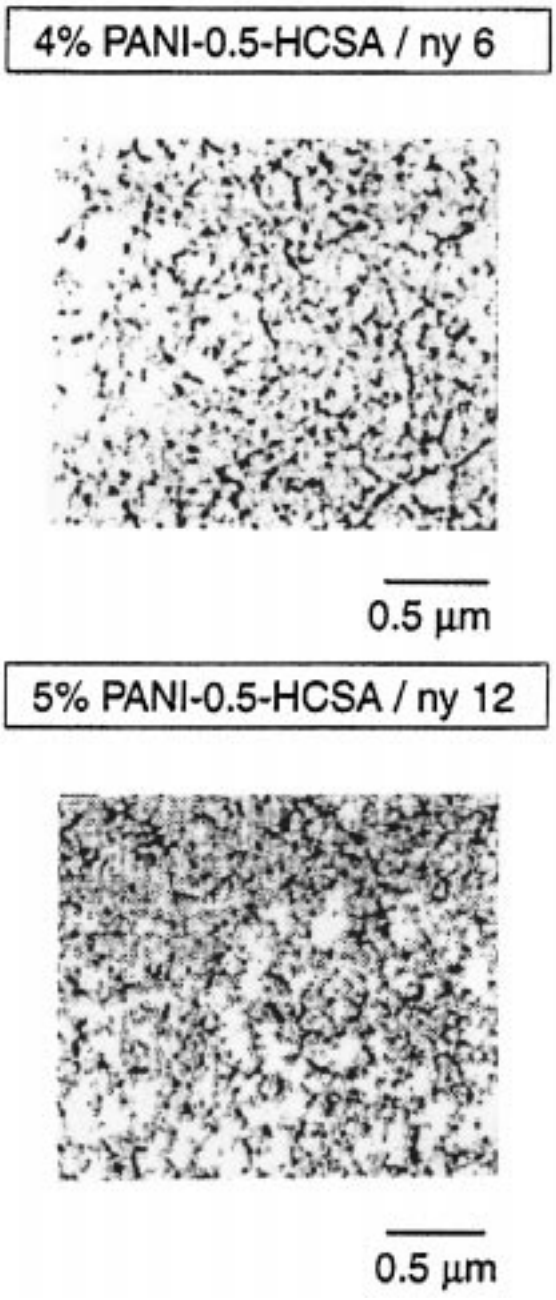

Figure 4. TEM micrographs of (a) nylon 6/PANI/CSA and (b) nylon 12/PANI/CSA. Dark areas of micrographs represent stained polyaniline salt in polyamide.

zation. The conclusion regarding the presence of such interactions at the interfacial regions is based on DMA analysis of biaxially stretched films which revealed a decrease in T_g of nylon 6 by 7 °C. This evidence, however, is not conclusive due to reported difference in the amount of crystallinity of the two materials.

Melting and Crystallization Transitions. The melting transitions of the as-cast nylon 6 and nylon 12 films are shown in Figures 1 and 2. The melting transition of nylon 6 exhibit the typical double endothermic peaks (at 213 and 221 °C) which have been observed for both solution and melt grown crystals.[11] The origin of the double melting transition lies in the existence of a series of metastable crystal structures which vary continuously in size and perfection. During the DSC measurements, the double endotherm results from three successive processes associated with crystal-

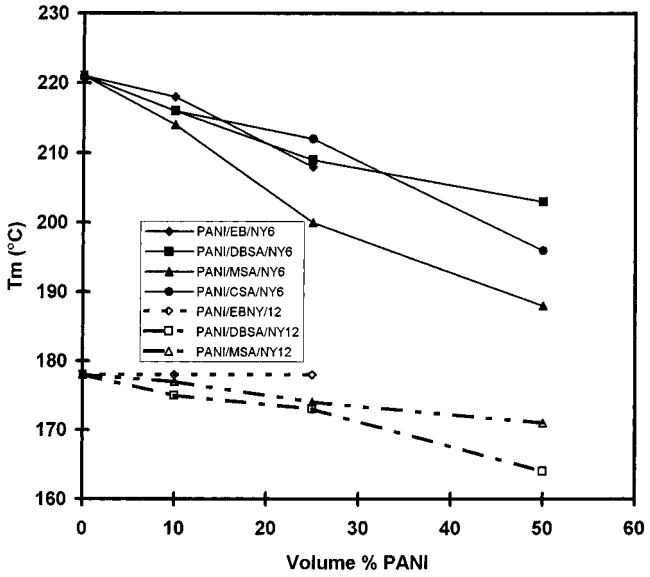

Figure 5. Melting transition temperatures vs composition of as-cast nylon/PANI blends.

line perfection, namely, melting, recrystallization, and remelting of the resulting more perfect crystals.[11]

The blends of nylon 6 with PANI/EB exhibited a single broad endotherm with a tail extending into the lower temperature region. In blends of nylon 6 and PANI/salts, the double melting peaks appear to merge and become relatively broader with increasing concentration (above 25%) of the PANI/salt component. This is also accompanied by a similar tail extending into the low-temperature region.

Figure 5 shows that the higher temperature melting transition peak T_m is depressed with increasing volume fraction of PANI component. The depression in T_m occurred not only in blends containing PANI/salt but also in those containing PANI/EB. Among the PANI/salts, PANI/MSA induced the highest drop in T_m while the lowest decrease was noted for PANI/DBSA. Usually the depression of the melting point in polymers is associated with molecular interaction between the constituent of the blends. However, these blends are phase-separated and as such should not display a T_m/composition dependence. Thus, the depression in T_m must be due to other species that were either preexisting or formed by thermally induced chemical reactions during the DSC run. Thermogravimetric analysis showed that PANI/EB undergoes decomposition and weight loss which begins around 170 °C and increases with increasing temperatures. In blends of nylon 6/PANI/EB, the degradation of PANI/EB, therefore, takes place long before the melting of nylon 6 crystals, and in the case of PANI/salts containing blends, deprotonation has been observed to take place at temperatures as low as 100 °C (for PANI/CSA).[19] In a study of the thermal stability of PMMA/PANI/CSA blend using optical microscopy, Heeger et al.[19] observed the formation of CSA crystals due to salt dissociation (deprotonation), which began above 100 °C. Similar dissociations are to be expected for PANI/MSA and PANI/DBSA. It should be noted that upon dissociation the resulting MSA, which is a liquid with a relatively small molecular mass and a low boiling point (167 °C), is expected to be more mobile than CSA and the much larger DBSA. Furthermore, in blends of nylon 6 and PANI/CSA, the free CSA resulting from dissociation subsequently decomposes at temperatures

(202 °C) near the melting transitions of nylon 6. The effect of dissociation and decomposition products of the PANI component is further inferred by the observed progressive decrease in T_m with repeated DSC scans. The low-temperature tail (Figure 1b) associated with the depressed and broadened main melting transitions indicates that the interaction between nylon 6 crystals and the products of dissociation and decomposition commence before the onset of these main melting transitions. We assumed that the effusion of these materials from within the interior of the blend with the rise in temperature disrupts the crystalline structure in a way similar to the reported effect of moisture. Heating of moisture containing crystalline spherulitic specimens of nylon 6 involves the fast effusion of trapped moisture from within the structure, causing disordering on the macroscale (disruption of spherulites) and microscale (decrease in crystalline perfection) levels.[20]

Additional evidence for the influence of degradation products on the melting point of nylon 6 is seen by comparison with the data of nylon 12/PANI blends. Blends of nylon 12 with either PANI/EB or PANI/salts invariably showed smaller depression in the melting point compared to the cases of the corresponding blends involving nylon 6 (Figure 5). At temperatures lower than the main melting of nylon 12, fewer PANI dissociation and decomposition products are formed. In this case, no disruption of the crystalline domain occurs as indicated by the absences of any depression in the melting transition of nylon 12 in a blend with PANI/EB (Figure 5). It is also interesting to note that PANI/DBSA (at 50% volume fraction) was more effective in lowering the melting point of nylon 12 than PANI/MSA. This observation is opposite to that noted for nylon 6 blends and suggests greater specific interactions between the DBSA which has a long hydrocarbon tail and nylon 12 which contains a greater number of $-CH_2-$ units in its structure than nylon 6.

Supporting evidence for the proposed role of PANI/salt dissociation on the depression of T_m is found from a parallel DSC measurements on nylon 6 containing pure CSA. The thermogram obtained (not shown) for a composite of the two materials at 25 vol % of CSA is similar to those recorded for nylon6/PANI/CSA blends. The measured melting point for the nylon 6/CSA composite was 209 °C. In the blend of nylon 6 which contains 50 vol % of optimally doped PANI/CSA, the proportion of CSA is roughly 20 vol % of the total blend. As noted earlier, the thermal treatment of PMMA or polyester blends containing PANI/CSA[19] resulted in dissociation of the PANI salt above 100 °C. The dissociation gradually increased with the rise in temperature, and complete deprotonation accompanied by initiation of CSA evaporation and decomposition of PANI network was reported above 200 °C. Similarly, it is reasonable to assume that, barring any stabilization effects, the PANI/CSA in nylon 6 blends completely dissociates into PANI and CSA above 200 °C. Thus, above 200 °C, a blend of nylon 6 containing 50 vol % of PANI/CSA must contain roughly 20 vol % of free CSA (before evaporation). Therefore, the melting transition temperature of a blend of nylon 6 containing 50 vol % of PANI/CSA should compare favorably with that of nylon 6 containing 25 vol % of pure CSA. However, the measured T_m (208 °C) of nylon 6/25 vol % CSA mixture is significantly higher than the T_m (196 °C) obtained for the nylon 6 blend containing 50 vol % of PANI/CSA even though the latter contains slightly lower volume concentrations of CSA (20 vol %). We have, therefore, concluded that the greater depression in the melting temperature in nylon 6/PANI/CSA relative to nylon 6/CSA composite is partly due to deprotonation and partly due to subsequent decomposition of the resulting PANI/EB.

Table 2. Enthalpy of Fusion (ΔH_f) of As-Cast Blends of Nylon 6 and Nylon 12 with PANI/EB and PANI/Salts

PANI (vol %)	ΔH_f (W/g) nylon 6	ΔH_f (W/g) nylon 12
0	75	80
10% PANI/EB	60	101
25% PANI/EB	41	130
10% PANI/MSA	67	88
25% PANI/MSA	42	77
50% PANI/MSA	18	73
10% PANI/CSA	71	
25% PANI/CSA	62	
50% PANI/CSA	63	
10% PANI/DBSA	73	87
25% PANI/DBSA	66	99
50% PANI/DBSA	72	111

The observed depression in the melting point on nylon 6 is accompanied by a decrease in the amount of crystallinity, particularly in blends involving PANI/MSA and PANI/EB components. This is evident by the decrease in the normalized heat of fusion with composition as shown in Table 2. Difficulties were encountered in the measurements of the heat of fusion due to the problem of separation of the heat capacity of the sample from the heat of fusion (baseline problem). This was particularly serious in samples when melting occurs over a wide temperature range. Furthermore, because nylon 6 has a range of metastable crystals with variable sizes, crystalline perfection becomes a subject of considerable concern since it is desirable to ascertain how much crystallization is due to initial solidification and how much is due to subsequent heating. Crystalline perfection can, therefore, lead to overestimation of the initial degree of crystallinity. The data of Table 2 represent the heat of fusion of all crystals, including those resulting from possible crystal perfection.

Compared to the case of PANI/MSA, the decrease in the amount of crystallinity with composition was comparatively small for nylon 6 blend containing PANI/CSA and practically negligible for the blend with PANI/DBSA. A very different behavior was noted for the blends of nylon 12 (Table 2). In this case, the heat of fusion actually increased as a function of composition (for PANI/EB and PANI/DBSA). Even PANI/MSA, which induced the greatest reduction in ΔH_f of nylon 6, produced a remarkably small effect on ΔH_f of nylon 12. This difference in behavior is again due to difference in the extent of dissociation and decomposition of PANI component at their respective melting transitions. The release of MSA, which has a relatively low molecular mass, at high temperatures (near melting point of nylon 6) can lead to greater disruption of the crystalline domains. This, in turn, results in the reduction in the size of the crystals and in the degree of crystallinity. Due to the lower melting point of nylon 12 and the insufficient amounts of degradation and volatilization products from the PANI component at that temperature, no detectable disruption in the crystalline structure occurs.

The increase in the heats of fusion observed for the blends of nylon 12 with PANI/EB and with PANI/DBSA may be due to increased heterogeneous nucleation

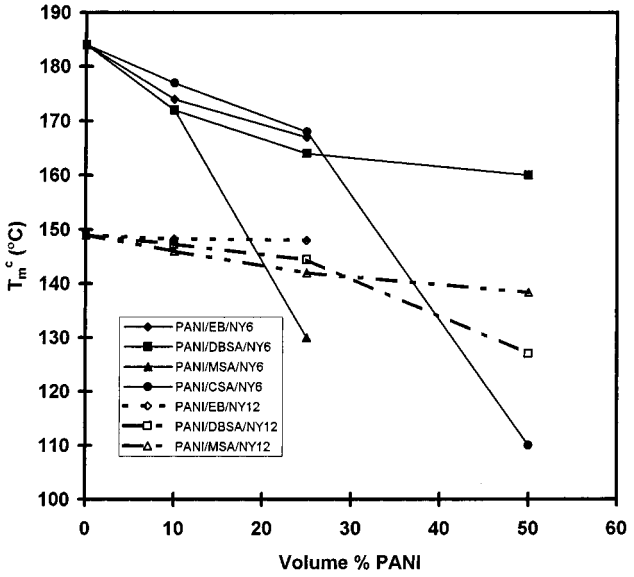

Figure 6. Melt crystallization temperature vs composition of PANI/nylon blends.

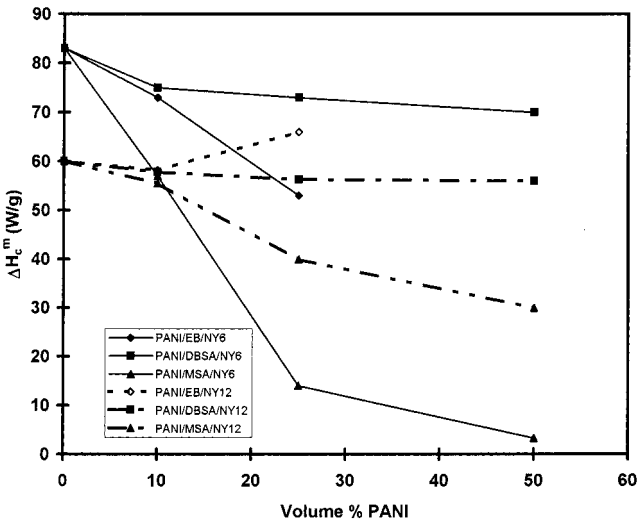

Figure 7. Heat of melt crystallization (ΔH_m^c) as a function of composition of PANI/nylon blends.

during solution crystallization or, alternatively, due to increased crystal perfection. Crystallization of polyamide solution in the presence of large amounts of foreign material had been shown to be nucleated by the surface of these objects as long as these surfaces are hydrophilic.[21] Increased nucleation often leads to increased crystallinity although the size of the individual crystals may actually decrease.

Changes in other thermal transitions of the nylon such as melt crystallization temperatures (T_c^m) and associated heats of transition were also observed as a result of blending with the PANI component. These results are given in Figures 6 and 7, which show the depression in T_c^m and the reduction in the associated heats of crystallization (ΔH_c^m) of nylon 6 and of nylon 12 as a function of composition. The specimen is cooled to room temperature from above the melting point of the nylon at a rate of 10 °C/min. Retardation of melt crystallization of both nylons, as evident from ΔH_c^m data, is more pronounced with PANI/MSA than with the other components of similar composition. For instance, ΔH_c^m values of both polyamides in the presence of PANI/DBSA is practically independent of composition. The T_c^m values, however, exhibited a dependence on counterion. The depression in T_c^m of nylon 6 blend with PANI doped with MSA is much larger than that of the corresponding blend with PANI doped with DBSA. Conversely, the incorporation of PANI doped with DBSA in a blend with nylon 12 (50 vol %) resulted in a significantly larger T_c^m depression compared to the incorporation of PANI doped with MSA. The difference in T_c^m dependencies of the two polyamides on the counterion may be explained in terms of greater interaction of the long hydrocarbon tail of DBSA with the polyamide having the larger number of $-CH_2-$ units in its structure. The absence of a substantial reduction in melt crystallization of either nylon (Figure 7) in blends with PANI/DBSA is attributed to the bulkiness of the DBSA structure. The much smaller MSA acts in a way similar to the known effects of diluents or solvents on melt crystallization of polymers.

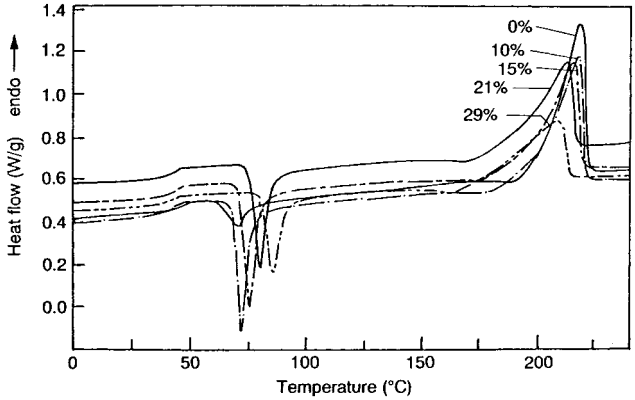

Figure 8. DSC thermograms of quenched nylon 6/PANI/CSA blends.

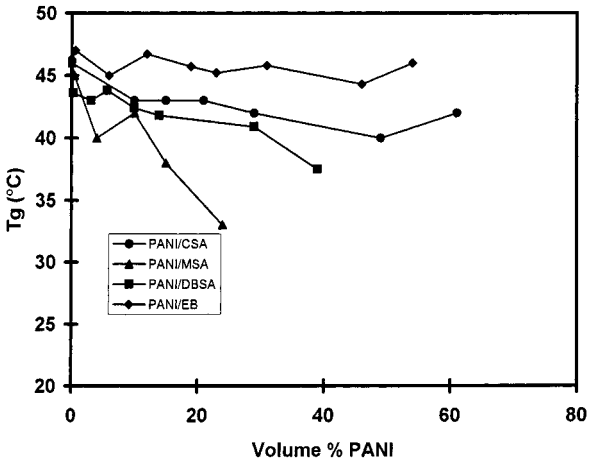

Figure 9. T_g vs composition of quenched nylon 6/PANI blends.

More information on the constituents of PANI component responsible for the changes in the various thermal transitions is obtained from samples of blends of nylon 6/PANI/salt quenched in liquid nitrogen from melt. Representative thermograms are given in Figure 8 for nylon 6/PANI/CSA blends. The glass transition temperatures of quenched samples of pure nylon 6 and of nylon 6/PANI blends (Figure 9) were slightly lower than the corresponding values of the dried as-cast films. The slight decrease in T_g is attributed to differences in the degrees of crystallinity of the as cast and quenched specimens. The glass transition temperatures of many polymers including polyamides have been shown to depend on the amount of crystallinity present in the

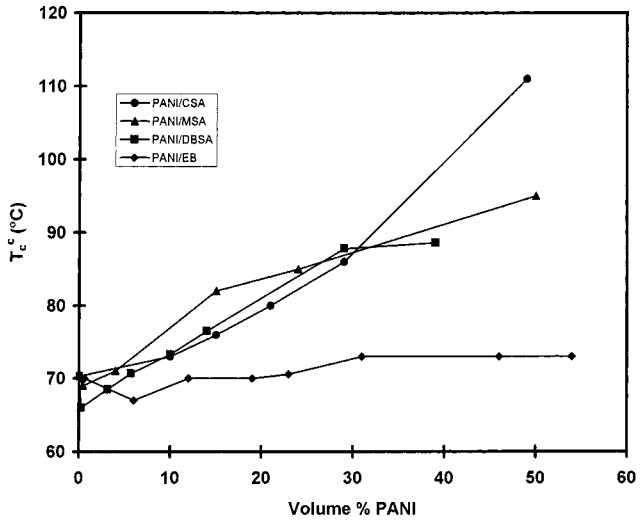

Figure 10. Cold crystallization temperature vs composition of quenched nylon 6/PANI blends.

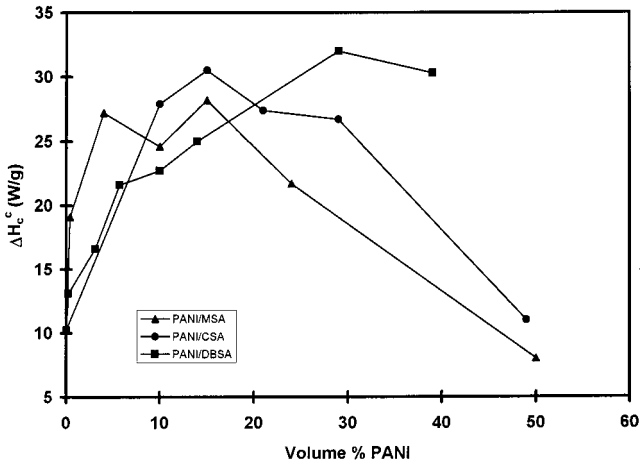

Figure 11. Dependence of enthalpy of cold crystallization on the composition of nylon 6/PANI/CSA blends.

material.[22,23] Excluding the effect of the degree of crystallinity on T_g, there seems to be little dependence upon the composition except for PANI/MSA where the decrease in T_g is due to plasticization of the nylon by free MSA.

Due to its low T_g, nylon 6 can easily crystallize from the glassy state (cold crystallization).[24] Crystallization is known to occur immediately above T_g as evident by the exothermic peaks observed for both pure nylon 6 and nylon 6/PANI blends (Figure 8). However, like crystallization from the melt, the cold crystallization temperature (T_c^c) varied as a function of blend composition (Figure 10). In this case, higher temperatures were necessary to expel the increasing amount of free acid and other degradation products trapped in the nylon phase on quenching. Once these species are expelled, crystallization follows at temperatures (T_c^c) which vary with the amount of PANI in the blend.

The associated enthalpies of cold crystallization (ΔH_c^c) of these blends are plotted as a function of composition in Figure 11. The data show an initial rise in ΔH_c^c followed by a plateau region at intermediate PANI concentration. At high PANI content, ΔH_c^c is seen to decrease. The low enthalpy of cold crystallization for pure nylon 6 indicates that significant melt crystallization had occurred during quenching in liquid nitrogen. With increasing PANI concentration, there is a progressive decrease in melt crystallization during the quenching process due to the presence of degradation products which inhibit melt crystallization. Consequently, the degree of cold crystallization increases with the amount of PANI component. Cold crystallization requires the expulsion of trapped species from within the crystallizing units. At high concentration of PANI component, a significant concentration of these species remain within an otherwise crystallizing nylon domain. This results in a decrease in cold crystallization as evident by lower ΔH_c^c values at high PANI component concentration.

Summary

We have used differential scanning calorimetric measurements to determine the level of component interaction in blends of nylon 6 or of nylon 12 with doped and undoped polyaniline. The composition-independent and counterion-independent glass transition temperature observed for these blends is indicative of the absence of polymer−polymer interaction on the molecular scale. Electron microscopy results demonstrated that even though the blends are phase-separated, the degree of polyaniline dispersion in the nylon matrix is dependent upon the nature of the counterion of the doping acid. Evidence was presented to show that the changes observed in other thermal transitions, such as melting and crystallization transitions and associated enthalpies, were due to effects of thermally induced dissociation and decomposition products from the polyaniline component.

References and Notes

(1) Cao, Y.; Smith, P.; Heeger, A. J. *Synth. Met.* **1992**, *48*, 91.
(2) Yang, C. Y.; Cao, Y.; Smith, P.; Heeger, A. J. *Synth. Met.* **1993**, *53*, 293.
(3) Cao, Y.; Smith, P.; Heeger, A. J. U.S. Patent 1993, 5232631.
(4) Stockton, W. B.; Rubner, M. F. *Mater. Res. Soc. Symp. Proc.* **1994**, *328*, 257.
(5) Ong, C. H.; Goh, S. H.; Chan, H. S. O. *Polymer* **1997**, *38*, 1065.
(6) Im, S. S.; Byun, S. W. *J. Appl. Polym. Sci.* **1994**, *51*, 1221.
(7) Abraham, D.; Bharathi, A.; Subramanyam, S. V. *Polymer* **1996**, *37*, 5295.
(8) Hopkins, A. R.; Rasmussen, P. G.; Basheer, R. A. *Macromolecules* **1996**, *29*, 7838.
(9) Annis, B. K.; Wignall, G. D.; Hopkins, A. R.; Rasmussen, P. G.; Basheer, R. A. *J. Polym. Sci. B, Polym. Phys.* **1997**, *35*, 2765.
(10) Wunderlich, B. *Macromol. Phys.* **1980**, *3*, 104.
(11) Kyotani, M. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 103.
(12) Ishikawa, T.; Nagai, S,.; Kasai, N. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 1413.
(13) Kettle, G. J. *Polymer* **1977**, *18*, 742.
(14) Hopkins, A. R.; Rasmussen, P. G.; Basheer, R. A.; Annis, B. K.; Wignall, G. D. In *The Effect of Dopant Counterion on the Conductivity and Morphology of Polyaniline/Nylon Blends*; Hsieh, B., Ed.; Adv. Chem. Ser.; American Chemical Society: Washington, DC, 1998.
(15) Flory, P. J. *Macromolecules* **1978**, *11*, 1138.
(16) Jonah, D. A.; Brostow, W.; Hess, M. *Macromolecules* **1993**, *26*, 76.
(17) Goh, S. H.; Chan, H. S. O.; Ong, C. H. *J. Appl. Polym. Sci.* **1998**, *68*, 1839.
(18) Byun, S. W.; Im, S. S. *Polymer* **1998**, *39*, 485.
(19) Yang, C. Y.; Reghu, M.; Heeger, A. J.; Cao, Y. *Synth. Met.* **1996**, *79*, 27.
(20) Magill, J. H. *Polymer* **1962**, *3*, 43.
(21) Yakhnin, E. D.; Egorova, Y. V.; Evko, E. I.; Taubmann, A. B.; Lukyanovich, V. M. *Vysokomol. Soedin. Ser.* **1970**, *A12*, 771.
(22) Eisenberg, A.; Shen, M. *Prog. Solid State Chem.* **1967**, *3*, 407.
(23) Buchanan, D. R.; Walters, J. P. *Textile Res. J.* **1977**, *47*, 398.
(24) Kozlowski, W. *J. Polym. Sci., Part C* **1972**, *38*, 47.

MA981935R