Investigation on the Interaction between Polyamide and Lithium Salts

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ABSTRACT: FTIR spectroscopy and thermal analysis were applied to study the nylon 6–lithium salt systems. The DTA results show that lithium ions cause a significant reduction of the melting point of nylon–lithium salt samples. In addition, lithium salts can also prevent the crystallization of molten nylon in the cooling process. Temperature-variable FTIR spectroscopy demonstrates that stronger hydrogen bonds form when nylon–lithium halide is molten. Such stronger hydrogen bonds in molten nylon lithium systems may account for the reduction of the melting point and delaying the crystallization of the amorphous nylon. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 2685–2690, 2000

Key words: nylon; lithium salt; FTIR; thermal analysis; hydrogen bonds

INTRODUCTION

Interaction between metal ions and polar groups of polymers provides a chance to modify the performance of polymer in various aspects. Ionomers, as a successful branch in this field, have attracted a wide attention.[1–5] On the other hand, extensive investigations have shown that amide groups possess considerable ability to coordinate with metal ions.[5–8] Such a coordinating effect is useful in improving the properties of polyamide. For instance, Ciferri, Ward and their coworks demonstrated that LiCl and LiBr could drastically re-

duce the crystallization rate of nylon. At the same time, the salt greatly increases the melt viscosity of the polymer due to a labile crosslinking effect resulting from polymer–salt interaction. In addition, after drawing and annealing, the Young's modulus of nylon can be improved significantly.[9–12] As a result, introducing lithium halide into nylon becomes one of the successful ways to produce high modulus nylon fiber.[13]

In this article, we use FTIR spectroscopy, a powerful tool to characterize the molecular interaction,[14] to study the nylon–lithium salt systems. The spectroscopic evidence has shown that the changes of the hydrogen bonds are closely related to the dramatically variation of the thermal behavior in nylon–lithium salt systems.

EXPERIMENTAL

Nylon 6, LiCl, and LiBr were dissolved in formic acid. After mixing nylon and LiCl/LiBr solutions
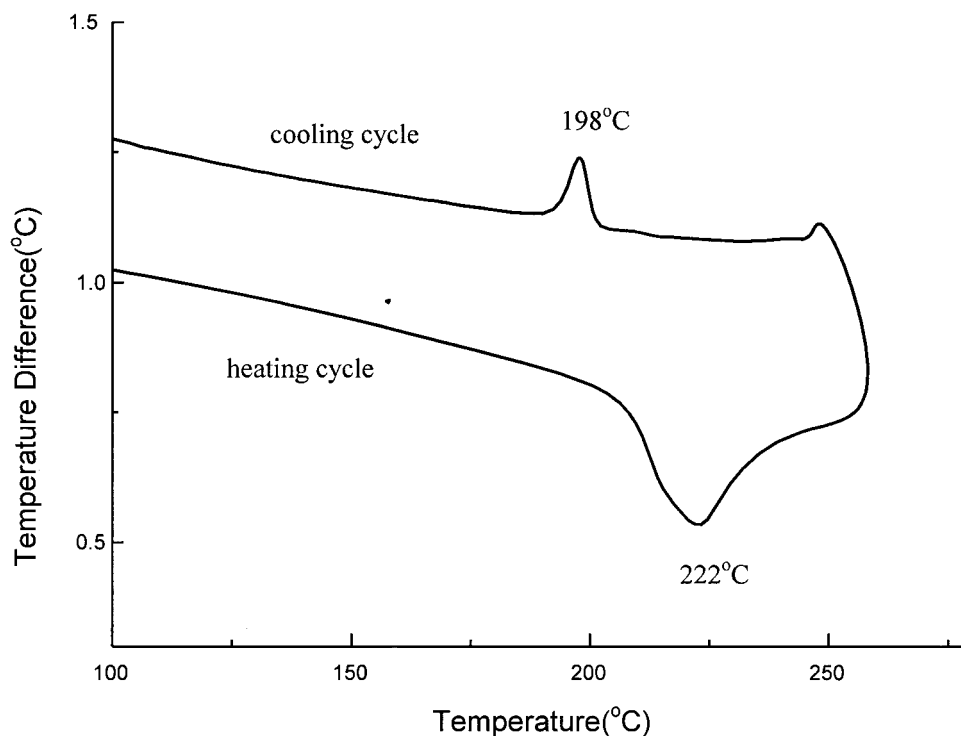
Figure 1 The DTA of pure nylon film, pure nylon melted at 222°C in the heating cycle, and crystallized at 198°C in the cooling cycle.

with various proportions, nylon 6–LiCl and nylon 6–LiBr films were obtained using spin-coating methods.

Thermal analysis of the nylon 6–LiCl and nylon 6–LiBr films was performed on an SDT 2960 DTA-TG thermal analysis instrument of the TA Corporation. A nitrogen flux was used as a purge gas for the furnace in the experiment. The measurement was composed of a heating cycle and a cooling cycle. In the heating cycle, the samples were kept in 100°C for 20 min to remove the adsorbed water and formic acid. After such a treatment, no obvious weight loss was observed before the DTA measurements. Then the samples were heated to 280°C at a heating rate of 10°C/min. In the cooling cycle, the molten samples were cooled to 100°C at a cooling rate of 5°C/min.

In addition, the change of crystalline contents in the heating process was also characterized by the variation of the intensities of depolarized light using a DPL II crystallization recorder.

Temperature-variable FTIR spectra of the samples were recorded on a Nicolet Magna 750 FTIR spectrometer with a Perkin-Elmer temperature-variable cell. To remove the adsorbed water and prevent the oxidation of the sample

in the heating process, the measurement was performed under vacuum. The experimental results show that neither the OH stretching band around 3400 cm^{-1} for water nor C=O stretching band around 1700 cm^{-1} for formic acid was found when the samples were heated to 70°C under vacuum.

RESULTS AND DISCUSSION

DTA Studies on Nylon 6–LiCl and Nylon 6–LiBr Systems

Figure 1 illustrates the DTA of pure nylon 6. The sample melts at 222°C in the heating cycle and crystallizes at ca. 198°C in the cooling cycle. However, significant variation on the thermal behavior is observed for nylon–lithium salt systems. Figures 2 and 3 show the DTA of nylon 6 + 10 wt % LiCl and nylon 6 + 20 wt % LiBr systems. The figures demonstrate that lithium ions cause two effects on the thermal behavior of nylon: (1) the melting point of nylon is greatly reduced. The nylon–LiCl and nylon–LiBr samples melt around 140–160°C. The depression of melting points amounts to 60–70°C compared with pure nylon.
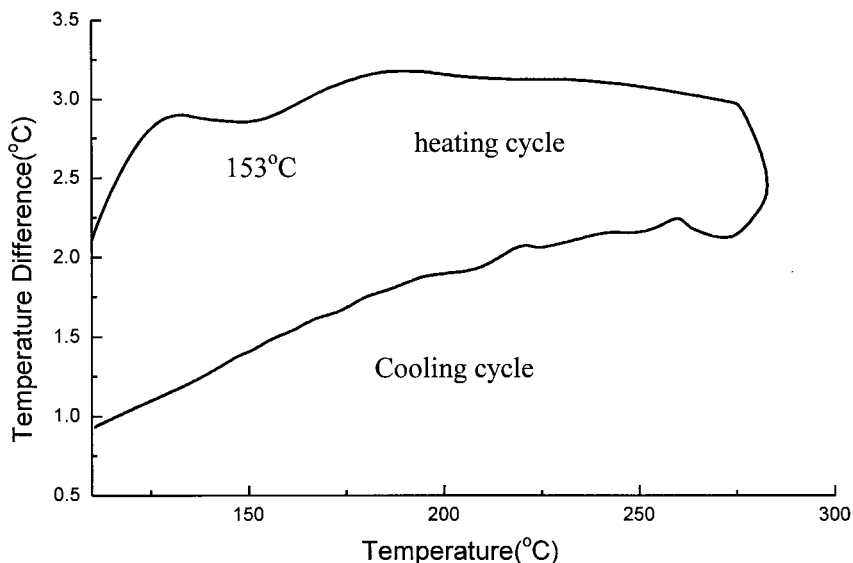
Figure 2   The DTA of nylon-6 + 10 wt % LiCl, the sample melted at ca. 153°C in the heating cycle and did not crystallize in the cooling cycle.

The reduction of melting point in the nylon–lithium halide systems gets support from the variation of intensities of depolarized light, as shown in Figure 4. The results indicate that the crystallites of nylon melt completely when the temperature reaches ca. 150°C. (2) Lithium ions prevent the nylon from crystallizing in nylon 6–LiCl and nylon 6–LiBr systems, because no crystallization peak is found in the cooling cycle.

FTIR Studies on Nylon 6–LiCl and Nylon 6–LiBr Systems

Figure 5 illustrates the temperature-variable FTIR spectra in the N—H stretching region for pure nylon 6. The sharp amide A band, which is assigned to the crystalline nylon,[15] moves from 3298 cm^{-1} to 3316 cm^{-1} when the temperature of nylon is elevated to its melting point. The band
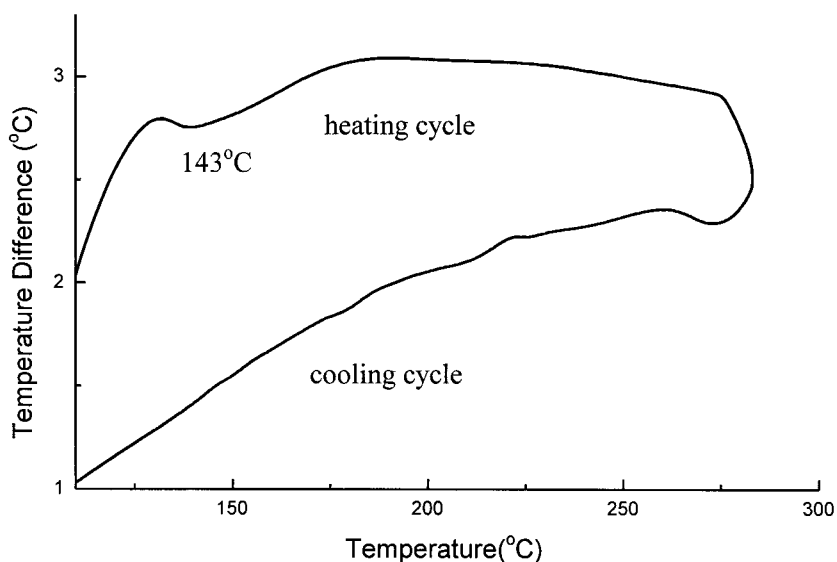

Figure 3   The DTA of nylon-6 + 20 wt % LiBr film, the melting point of the sample was around 143°C, and the molten sample did not crystallize in the cooling cycle.
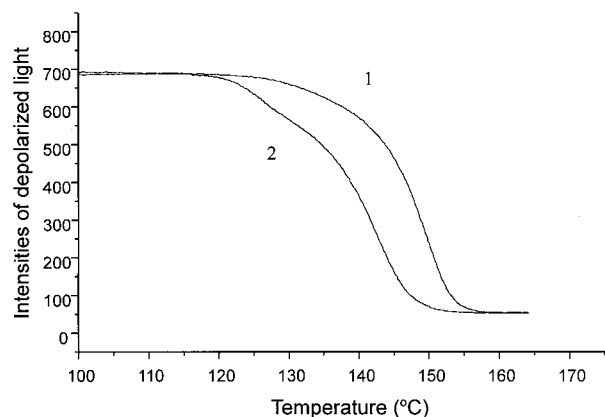
Figure 4 The variation of intensities of depolarized light after passing nylon 6–lithium salt films in heating processes. The results conform with the fact that the crystallites of nylon melt completely at ca. 150°C. (1) Nylon + 10 wt % LiCl film, (2) nylon + 20 wt % LiBr.

Figure 6 The temperature variable FTIR spectra of nylon 6 + 10 wt % LiCl film 1. 50°C, 2. 60°C, 3. 70°C, 4. 80°C, 5. 90°C, 6. 100°C, 7. 110°C, 8. 120°C, 9. 130°C, 10. 140°C.

becomes broad and weak at the same time. Similar phenomena were observed in nylon 11 and amorphous polyamide by Coleman et al.[16,17] These phenomena show the hydrogen bonds between N—H and C=O in pure nylon are weakened when nylon is heated to higher temperatures. On the other hand, for some nylon–metal ion system, such as the nylon–Ga^{3+} system, the hydrogen bonds break as Ga^{3+} coordinates with the carbonyl of the amide groups. Consequently, the NH stretching band exhibits a 70 cm^{-1} movement to higher frequency.[6,7]

However, dramatically different spectral behaviors are observed as far as nylon–lithium salt systems are concerned. Figures 6 and 7 show the temperature-variable FTIR spectra of nylon 6 + 10 wt % LiCl and nylon 6 + 20 wt % LiBr systems, respectively. As the temperature of the samples increases, the intensities of the crystalline band of amide A band decrease. At the same time, the intensities of several weak bands at the
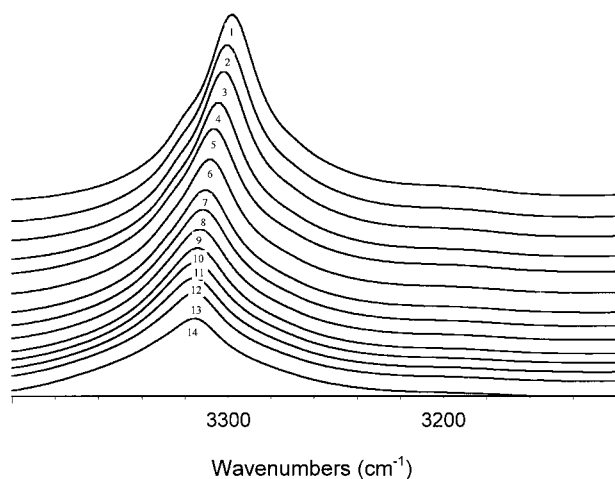

Figure 5 The temperature variable FTIR spectra of pure nylon 6 film. 1. 50°C, 2. 70°C, 3. 90°C, 4. 110°C, 5. 130°C, 6. 150°C, 7. 170°C, 8. 180°C, 9. 190°C, 10. 200°C, 11. 210°C, 12. 220°C, 13. 225°C, 14. 227.5°C.
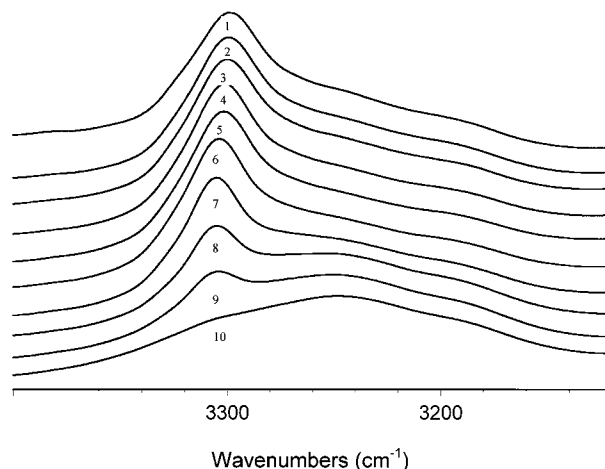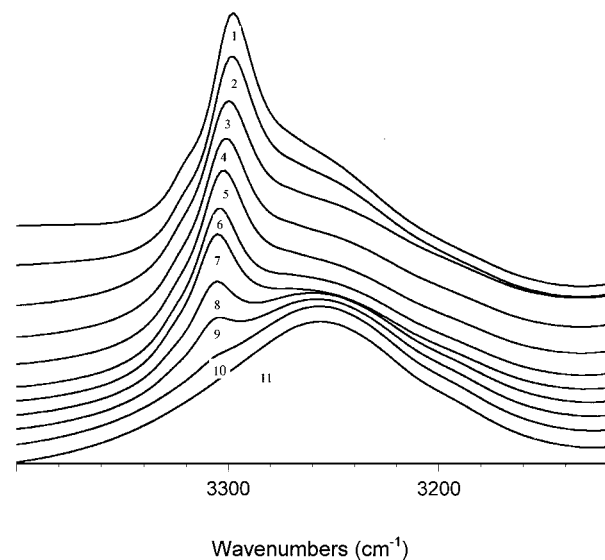

Figure 7 Temperature variable FTIR spectra of nylon 6 + 20 wt % LiBr film. 1. 50°C, 2. 60°C, 3. 70°C, 4. 80°C, 5. 90°C, 6. 100°C, 7. 110°C, 8. 120°C, 9. 125°C, 10. 130°C, 11. molten film.
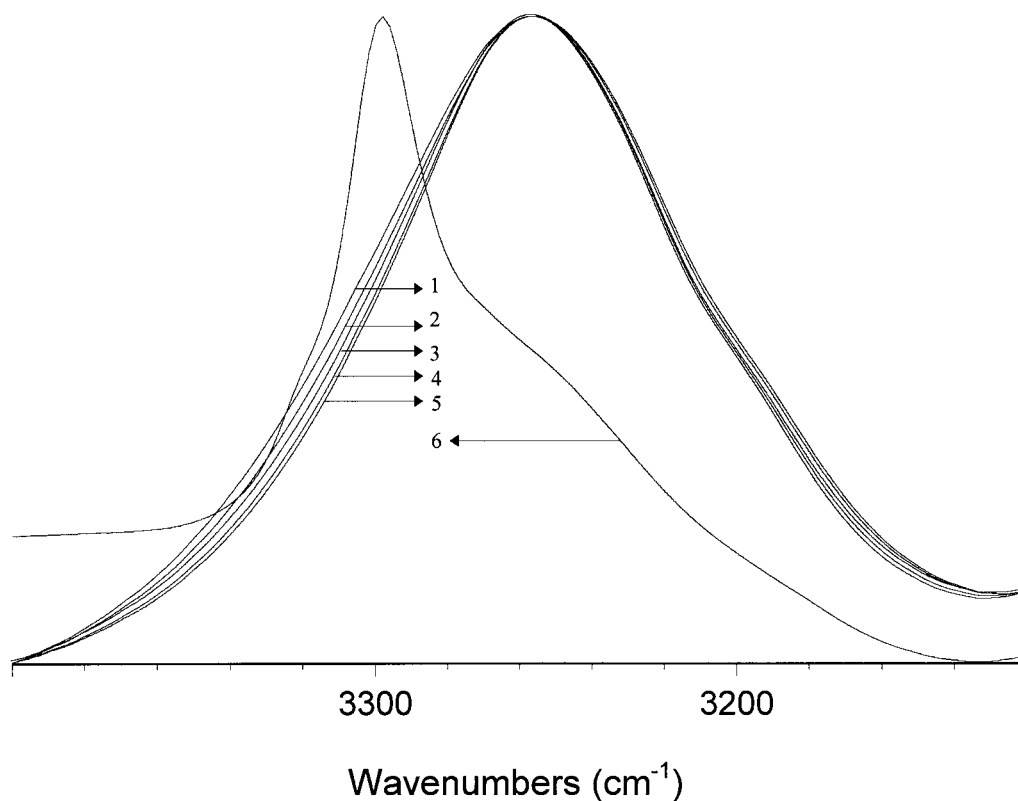
Figure 8 Little spectral variation of amide A band of nylon 6 + 20 wt % LiBr amorphous film in the cooling process, for comparison, the amide A band of the same sample before melting is also shown. 1. molten film, 120°C, 2. 110°C, 3. 90°C, 4. 70°C, 5. 50°C, 6. the sample at 50°C.

low wave number side of the amide A band increase. The relative intensities of the lower wave number bands become stronger and stronger. At last, they exceed the crystalline band at 3300 cm^{-1} when the sample is near their melting temperature. After the sample melted, the crystalline band at 3300 cm^{-1} disappeared and the amide A band became a wide band around 3250 cm^{-1}. The amide A band for melting nylon in the nylon–lithium system exhibits a 50-cm^{-1} band shift to a lower frequency compared with the crystalline band at 3300 cm^{-1}. Considering that the peak position of the amide A band is directly related to the strength of the hydrogen bonds,[18,19] the red shift of the band means that a stronger hydrogen bond is formed in the melting nylon–lithium salt samples. On the other hand, the amide A band of the molten films of nylon–lithium salt systems exhibit almost no variations in the cooling process (Fig. 8). Similar results are also observed in the nylon 6 + 20 wt % LiCl and nylon 6 + 10 wt % LiBr systems.

The above FTIR results are helpful in explaining the decreasing of the melting points of nylon–lithium salt system and the phenomena that nylon–lithium salt system does not crystallize in the cooling process. The melting point of nylon is determined by the variation of entropy and enthalpy in the melting process, as shown in eq. (1):

$$\Delta G = \Delta H - T\Delta S \tag{1}$$

Enthalpy variation plays an important role in the melting of nylon. A large amount of enthalpy is needed in the melting process to weaken or break the hydrogen bonds for pure nylon. As for nylon–LiCl/nylon–LiBr systems, new and stronger hydrogen bonds, which produce negative enthalpy, form as the hydrogen bond of the nylon crystal is weakened or broken in the heating process. Therefore, the total enthalpy for melting the nylon crystal is greatly reduced. Consequently, the melting points of nylon–LiCl/nylon–LiBr systems decrease accordingly. On the other hand,

because the hydrogen bonds in the molten nylon–LiCl/nylon–LiBr systems are more stable than those in the crystalline nylon, crystallization of nylon becomes more difficult for amorphous nylon–lithium salt systems.

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