FT-IR Spectroscopic Investigation on the Interaction Between Nylon 66 and Lithium Salts

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ABSTRACT: FT-IR spectroscopy has been utilized to study nylon 66/lithium salt systems. The results show that coordination between nylon 66 and lithium ions brings about significant variation in the FT-IR spectra: (1) a stronger hydrogen bond is formed in the systems; (2) the interaction induces obvious conformational changes of the nylon 66 chains. A coordination model has been proposed to rationalize the observed spectral phenomena. The interaction between amide groups and lithium ions is a feasible approach to modify the performance of nylon 66. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 91: 2869–2875, 2004

Key words: nylon 66; lithium salts; FT-IR; metal–polymer composites; coordination

INTRODUCTION

Interaction between metal ions and polar groups of polymers provides a new chance to improve the performance of polymer and to develop a variety of functional materials.[1–4] Extensive investigations have shown that amide groups possess considerable ability to coordinate with metal ions.[5–12] Nylons, a family of polymers with broad application in plastics and fiber, possess amide groups in their backbones. Many efforts have thus been made to promote or to modify the performance of nylon using metal salts. In the 1960s, it was found that stressed nylon bands would break when a concentrated solution of zinc chloride or lithium chloride was poured onto them.[13,14] This phenomenon invoked extensive investigation on the interactions between metal ions and the amide groups of nylon.[15–17] For instance, the hydrogen bonding networks of nylon were broken in nylon–$GaCl_3$ systems, and therefore $GaCl_3$ may open a new approach to process nylon.[6,7] Ciferri, Ward, and coworkers have demonstrated that LiCl and/or LiBr can drastically reduce the crystallization rate of nylon. At the same time, lithium salts greatly increased the melt viscosity of the polymer due to a labile cross-linking effect resulting from polymer–salt interaction. In addition, after drawing and annealing, Young's modulus for nylon fiber can be improved significantly. As a result, introduction of lithium halide into nylon has been proposed to improve the initial modulus of nylon fiber.[18–21]

Systematic investigations on the interaction of nylon 6/metal ions systems have also been performed in our laboratories.[10,11,22–24] FT-IR spectroscopy, FT-Raman spectroscopy, thermal analysis, X-ray diffraction, EXAFS, TEM, and near-field scanning optical microscopy (NSOM) were utilized to study the interactions between nylon 6 and various metal ions. The results demonstrated that introduction of lithium salt into this nylon brought about dramatic reductions of the crystallinity and melting point of nylon 6. Moreover, FT-IR spectra indicated that the amide A and amide I bands exhibited different spectral behavior upon introduction of metal ions into the nylon systems. Phase separation and the formation of ionic aggregates were observed using TEM and NSOM techniques. Additionally, electronic Raman bands of neodymium around 2000 cm^{-1}, corresponding to the f–f transition between $^4I_{9/2}$ and $^4I_{11/2}$ manifolds were also used to study[11] the variation of coordinated structures of ionic clusters in nylon matrices. The results showed that the coordinated structure around neodymium ions varied with the composition and the experimental conditions used to prepare the composites.

In this article, we report on the investigation of the interaction between nylon 66 and lithium salts. Although nylon 66 is quite similar to nylon 6 (Scheme 1),

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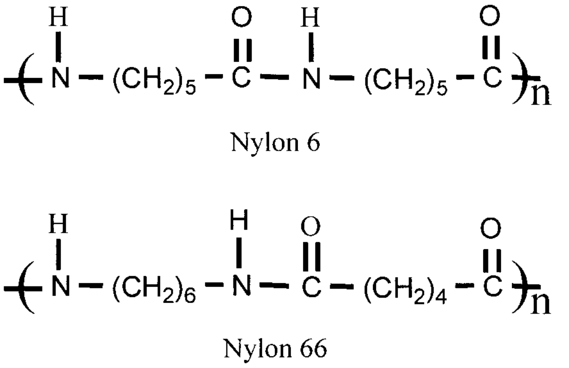


$\left(\overset{H}{\overset{|}{N}}-(CH_2)_5-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-(CH_2)_5-\overset{O}{\overset{\|}{C}}\right)_n$

Nylon 6

$\left(\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\right)_n$

Nylon 66

Scheme 1 Molecular structures of nylon 6 and nylon 66.

the experimental results demonstrate that the behavior of nylon 66/lithium salt systems is rather different from that of nylon 6/lithium salt systems reported in our previous article. FT-IR spectroscopy, an important tool to characterize the structure and interaction of molecular systems,[25] has been applied to study the interaction between nylon 66 and metal ions. The results led us to propose a coordinated model to explain the observed spectral changes.

EXPERIMENTAL

Nylon 66 is a commercial product from DuPont Co. (Wilmington, DE). LiCl and LiBr (AR grade) were purchased from Beijing Chemical Plant (Beijing, China). Both nylon 66 and lithium salts were dissolved in formic acid. After nylon and LiCl/LiBr solutions were mixed at various proportions, nylon 66/LiCl and nylon 66/LiBr films were obtained using the spin-coating method.

FT-IR spectra of the samples were recorded on a Nicolet Magna 750 FT-IR spectrometer at a resolution of 4 cm^{-1}, and 32 scans were averaged. To remove the adsorbed water, the measurements were performed under vacuum. As the temperature of the samples approached 70°C, the OH stretching bands of water around 3400 cm^{-1} were no longer observed. The FT-IR spectra of the nylon 66/lithium salts systems were recorded under these conditions.

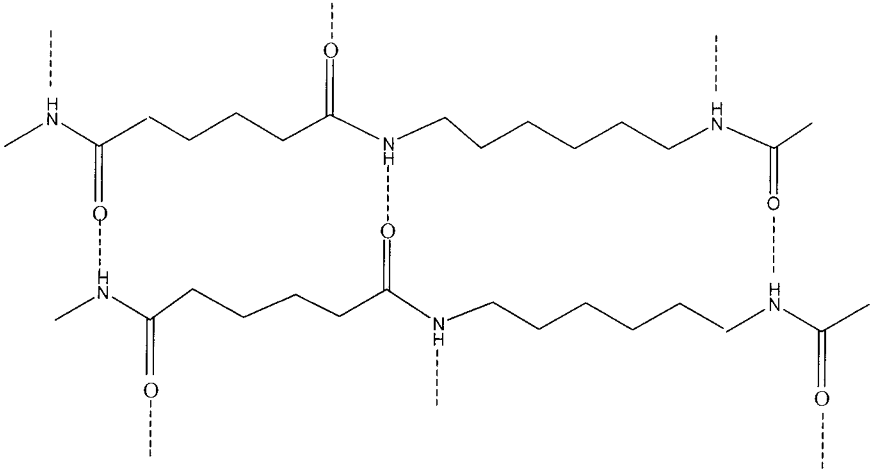
RESULTS AND DISCUSSION

By comparison with the FT-IR spectrum of pure nylon 66, significant variations are found in amide A, amide I, and vibrational bands of methylene groups in nylon 66/lithium salt systems.

Amide A

The amide A band at about 3300 cm^{-1} can be assigned to the N—H stretching of the amide group in nylon [26]. In most cases, the N—H groups of nylon form hydrogen bonds with C═O groups from the vicinal nylon chain as shown in Scheme 2. The amide A band of nylon is regarded to be not conformationally sensitive since its peak position remains invariant even if nylon adopts different crystalline phase.[27] However, the variation of the amide A band is useful to study the variation of the hydrogen bond in polyamide systems. For example, the amide A band undergoes a blue shift (blue shift means that the bands move along the direction toward higher frequency) upon melting.[28–30] A significant blue shift of the amide A band was observed when $GaCl_3$ was added into polyamide systems as a Lewis acid.[6,7]

The amide A band in pure nylon 66 is a sharp peak located around 3300 cm^{-1}.[31–33] The N—H stretching bands of nylon 66/lithium salts systems are shown in Table I and Figure 1. The peak becomes broad, and its



Scheme 2 Hydrogen bond formation in nylon 66.

TABLE I
IR Peak Positions (cm^{-1}) of Amide A Band in Nylon 66 and Its Lithium Salt Composites

Sample	Amide A
Nylon 66	3300
Nylon 66 + 10 wt % LiBr	3267
Nylon 66 + 10 wt % LiCl	3255
Nylon 66 + 20 wt % LiCl	3253

peak position varies from 3267 to 3253 cm^{-1}, i.e., the amide A band of nylon 66/lithium salt systems exhibits a red shift (red shift means that the bands move along the direction toward lower frequency) of 30–50 cm^{-1} as lithium ions are introduced into nylon 66 matrix. Since the peak position of amide A is directly related to the strength of the hydrogen bonds,[34–37] the red shift of the band implies that stronger hydrogen bonds form in the mixture.

Similar results were reported in our previous work. The amide A band of nylon 6 exhibited a red shift upon coordinating with lithium ions. However, significant differences can be found between nylon 6/lithium salt and nylon 66/lithium salt systems. Crystalline nylon 6 still existed in the nylon 6/lithium salts system when the samples were prepared by spin-coating method, since a sharp amide A band for crystalline nylon can be observed around 3300 cm^{-1}. A melting procedure is necessary to achieve the red shift of the amide A band of nylon 6/lithium salt systems. As far as the nylon 66/lithium salt systems are concerned, the predominant feature of amide A band is a broad band around 3250 cm^{-1} when the sample film was prepared using spin-coating method. The sharp crystalline nylon band at 3300 cm^{-1} is buried under the broad envelope of the amide A band and barely observed, i.e., the coordination between lithium ion and amide group prevents the formation of crystallite similar to pure nylon 66.

Amide I

The amide I band involves mainly the C═O stretching displacements of the polyamide backbone with contributions from the CN and NH motions.[38] The amide I mode is conformationally sensitive and thus widely used to characterize the variation of the secondary structures such as α-helix, β-sheet, and random coil in protein and polypeptides.[39–41] In the present work, we also find that the amide I band exhibits significant variation as lithium ion is introduced into the nylon 66 matrix.

As shown in Figure 2, the amide I band of pure nylon 66 is located at around 1636 cm^{-1}, indicating that the packing mode of nylon 66 chains is similar to the β-sheet structure of proteins. As lithium ion is introduced into the polymeric matrix, a great variation in the amide I band can be observed. The amide I band is roughly composed of two overlapping bands. The main peak is located at ca. 1650 cm^{-1}, and the other one is around 1620 cm^{-1}. Two reasons may account for the above spectral variation: the first is the conformational changes of the nylon 66 chains; the second is the result of the coordination between the carbonyl groups and lithium ions. In our previous work, we studied the interaction between lithium ion and poly-

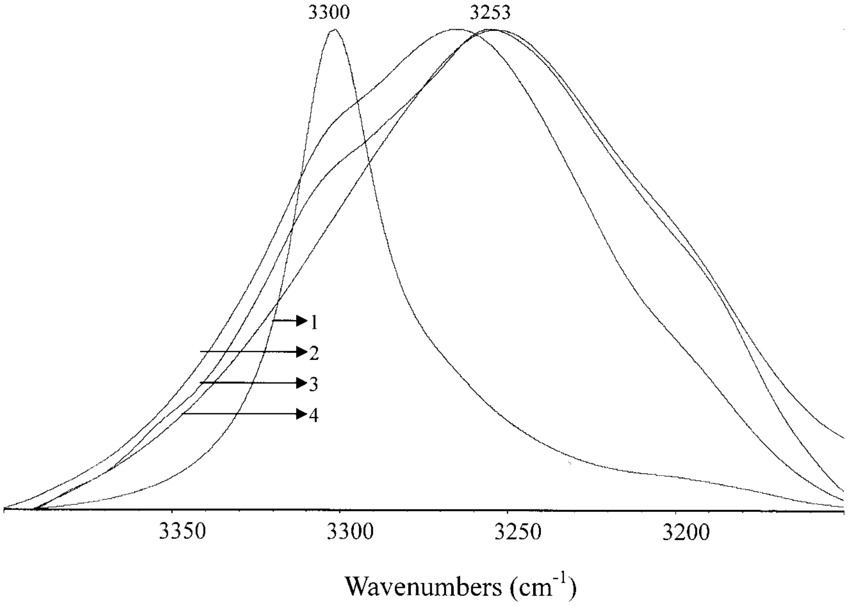


Figure 1 The amide A bands of nylon 66 and its composites with lithium salts. 1—pure nylon 66; 2—nylon 66 + 10wt% LiBr; 3—nylon 66 + 10wt% LiC1; 4—nylon 66 + 20wt% LiC1.

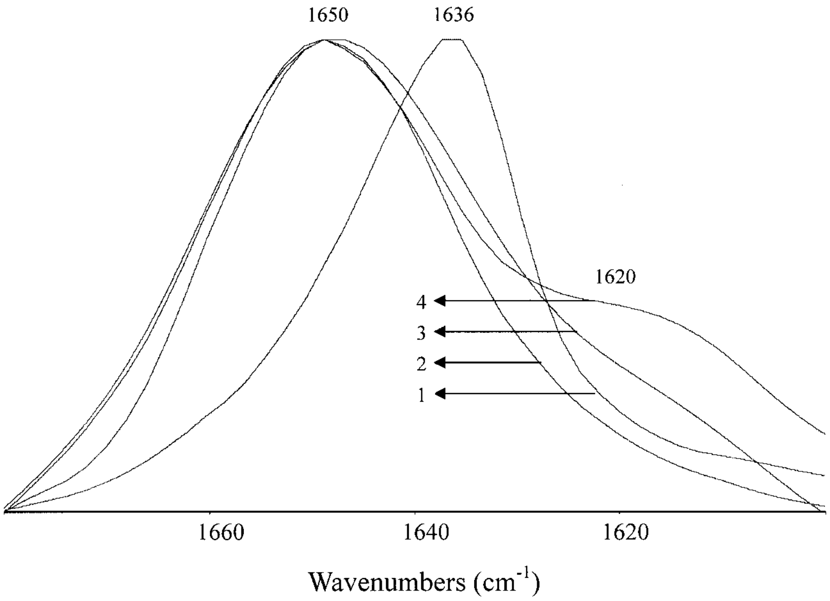


Figure 2 The amide I bands of nylon 66 and its composites with lithium salts. 1—pure nylon 66; 2—nylon 66 + 10wt% LiBr; 3—nylon 66 + 10wt% LiC1; 4—nylon 66 + 20wt% LiC1.

vinylpyrrolidone (PVP),[12] an amorphous polymer with amide group on its side chain: one of the consequences of the interaction between amide groups and metal ions was a 20-cm^{-1} red shift of the amide I band in comparison with pure PVP.

In comparison with the 1636-cm^{-1} band of pure nylon 66, the 1650-cm^{-1} band is a result of blue shift rather than red shift. Therefore, the 1650-cm^{-1} band cannot be considered as the direct result of coordination between a lithium ion and an amide group but rather as a change of the secondary structure of nylon chains, i.e., lithium ions induce remarkable changes of the secondary structure of nylon 66. According to the literature on the secondary structure of protein, we suggest that the conformation and hydrogen bonding arrangement of nylon 66/lithium salt systems is similar to α-helix or random coil in protein. This result is different from our previous study on nylon 6/lithium salt systems, where lithium ions brought about insignificant variation of the amide I bands in both solid and melt states. As far as the 1620-cm^{-1} band is concerned, its relative intensity, in comparison with the 1650 cm^{-1}, seems to be related to the concentration of lithium ion (Table II).

The above results show that the amide groups exist at least in two kinds of states in the nylon 66/lithium salt systems. Such differences may be attributed to the differences in coordination states. The molar ratio between amide group and lithium ion ranges from 1.7 to 7 (Table II). We suggest that some of the amide groups coordinate with lithium ions while some may not. This hypothesis is supported by our previous work.[11,23] We found that ionic clusters may occur in nylon/metal ion systems. This effect reduced the opportunity of coordination between metal ions and amide groups.

CH_2 Stretching and Scissoring

From the variation of the amide I band, we find that the conformation of the nylon 66 chain changes as lithium ion is introduced. Such conformational change may also influence the spectral behavior of methylene groups. Figure 3 illustrates the C—H stretching band between 3000 and 2700 cm^{-1}. Four bands at 2945, 2933, 2875, and 2858 cm^{-1} can be observed for pure nylon 66. However, the bandwidths of 2933 and 2875 cm^{-1} increase remarkably and the bands at 2945 and 2875 cm^{-1} are no longer observed when lithium salt is added.

The CH_2 scissoring bands of nylon 66 and its composites are shown in Figure 4. The most prominent feature of nylon 66 is two sharp bands at 1474 and 1417 cm^{-1}, which are assigned to CH_2 (adjacent to N—H and C═O) scissoring vibrations in trans conformation.[42–45] In the nylon 66/lithium salt systems,

TABLE II
Molar Ratios of Amide Group/Lithium Ion in Nylon 66/Lithium salts

Sample	Amide group/Lithium ion
Nylon 66	0
Nylon 66 + 10 wt % LiBr	7:1
Nylon 66 + 10 wt % LiCl	3.4:1
Nylon 66 + 20 wt % LiCl	1.7:1

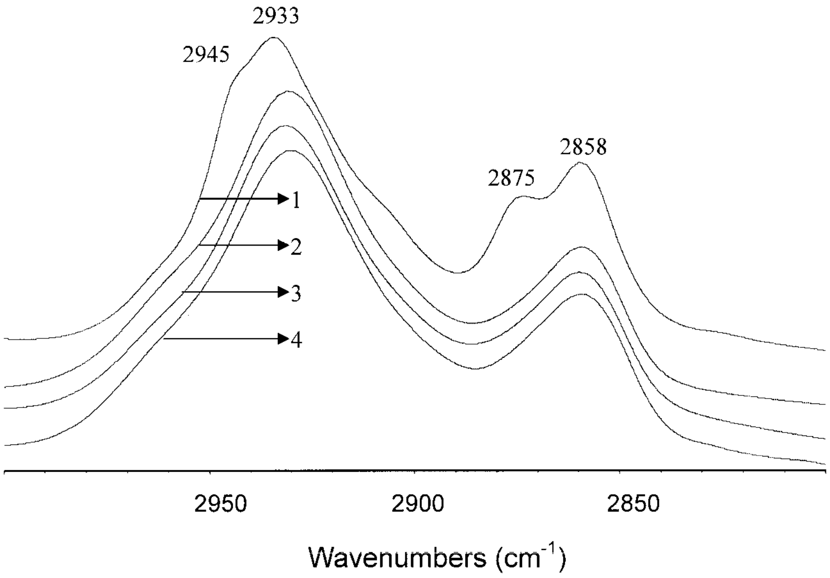


Figure 3 The C-H stretching bands of nylon 66 and its composites with lithium salts. 1—pure nylon 66; 2—nylon 66 + 10wt% LiBr; 3—nylon 66 + 10wt% LiC1; 4—nylon 66 + 20wt% LiC1.

these bands vanish and a series of broad bands become dominant at 1458–1437 cm^{-1}.

According to references 42, 44, and 45, the disappearance of the 1417- and 1474-cm^{-1} bands demonstrates that the amides are rotated out of the alkane plane, and the all-trans conformation is destroyed. This result provides further evidence to support that the conformation of the polymer chain changes when lithium ion is introduced.

Hypothesis model

The spectral behavior of nylon 66 exhibits marked changes as lithium ions are involved. We suggest that lithium ion coordinates with the amide group and accounts for the phenomena. Here, we propose a coordinating model depicted in Scheme 3. This mode is helpful to explain the following phenomena:

1. The amide A band undergoes a red shift rather than a blue shift in nylon 66/lithium salt systems, indicating that the hydrogen bond becomes stronger as lithium ions coordinate with amide groups. There is no evidence to support the dissociation of hydrogen bonding between N—H and C═O groups. In our model, the hydrogen bond and the coordinate bond coexist. Thus, it is not necessary to break the hydrogen

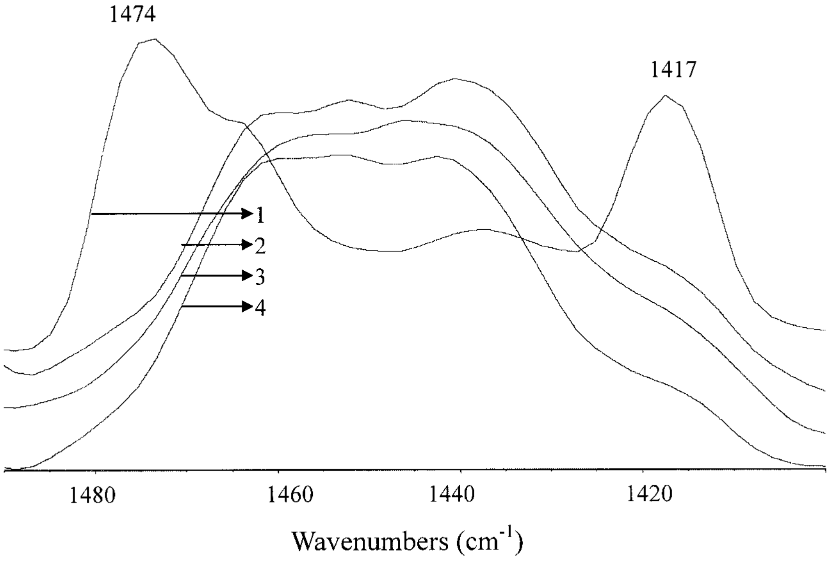
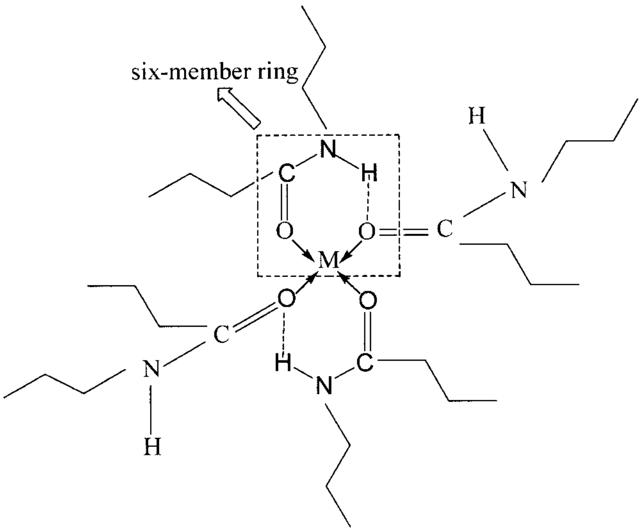


Figure 4 The CH_2 scissoring bands of nylon 66 and its composites with lithium salts. 1—pure nylon 66; 2—nylon 66 + 10wt% LiBr; 3—nylon 66 + 10wt% LiC1; 4—nylon 66 + 20wt% LiC1.



Scheme 3 Coordination model for the interaction between nylon 66 and lithium ion.

bond when the coordinated bond is formed. Moreover, a six-member ring, in which the hydrogen bond is involved, can be formed among lithium ion and amide groups. The stable six-member rings may favor a stronger hydrogen bond.

2. In pure nylon 66, the polymer chains are aligned parallel and a β-sheet like structure is dominant. Such a secondary structure is mainly determined by the hydrogen bond among the adjacent polymer chains. The interaction between lithium ion and amide group destroys such a hydrogen-bonding mode. Lithium ion, which plays a crosslinking role, coordinates with amide groups from different sites and/or from different polymer chains and makes the parallel-aligned structure unstable. Consequently, the nylon 66 chain adopts a new conformation in which the conformation and the hydrogen bond arrangement of the amide group may be similar to that of α-helix or coil in protein. Such conformational changes are reflected in the spectral behavior of amide I and vibrational bands of methylene groups.

CONCLUSION

In summary, FT-IR spectroscopic study demonstrates that strong interaction occurs between lithium ion and nylon 66. Such interaction brings about significant variation in the FT-IR spectra of nylon 66/lithium salt systems. First, coordination between lithium ions and amide groups of nylon 66 produces stronger hydrogen bonds. Second, the interaction induces obvious conformational change of the nylon 66 chains. A coordination model has been proposed to rationalize the observed spectral phenomena. Coordination between nylon 66 and lithium salt offers a reversible way to process nylon 66 by tailoring its physical-chemical properties.

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