Macromolecules 1991, 24, 3142–3146

Site-Specific Reversible Scission of Hydrogen Bonds in Polymers. An Investigation of Polyamides and Their Lewis Acid–Base Complexes by Infrared Spectroscopy

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Received October 24, 1990; Revised Manuscript Received January 10, 1991

ABSTRACT: Lewis acid–base complexation in conjunction with Fourier transform infrared spectroscopy was used to study the scission and re-formation of N—H···O=C hydrogen bonds in seven aliphatic polyamides and one aromatic polyamide. The characteristic shifts of the N-H stretch frequency, the amide I mode, and the amide II mode in the vibrational spectra of several polyamides on $GaCl_3$ complexation were examined at room temperature (25 °C). Complete scission of the intermolecular hydrogen bonds in polyamides was achieved by the 1:1 Lewis acid complexation of the basic oxygen sites of the carbonyl groups in the polymers, thus "liberating" the N-H groups from hydrogen bonding. Facile decomplexation of the polyamide–Lewis acid complexes resulted in the reformation of the hydrogen bonds and, consequently, the characteristic solid-state structure and properties of the polyamides. Thus, the hydrogen bonds in polyamides function like a molecular zipper: Lewis acid–base complexation "unzips" and decomplexation "zips" the macromolecular chains. These results have important implications for the understanding of hydrogen bonding in polymers and its effects on structure and properties. The results also suggest a possible application of our approach of reversible hydrogen bond scission to ultradrawing of polymers with hydrogen bonding to highly oriented materials with high strength and high modulus.

Introduction

Hydrogen bonding represents the dominant intermolecular interaction in a large number of both natural and synthetic polymers and is therefore essential to understanding the equilibrium structure and properties of these macromolecules.[1-7] Many of the known three-dimensional chain structures of synthetic polymers and biological macromolecules are highly *ordered* structures stabilized by hydrogen bonding involving intermolecular, intramolecular, or both interactions. For example, the well-known β-sheet structures of linear aliphatic polyamides (nylons) are due to intermolecular N—H···O=C hydrogen bonds between amide groups in adjacent chains.[1,2] The polyamides, as a result, are highly crystalline fiber-forming materials that are not readily soluble in common organic solvents. The α-helix and β-sheet structures of proteins are also due to both intermolecular and intramolecular N—H···O=C hydrogen bonds between amide groups.[3,4]

Recently, temperature-dependent Fourier transform infrared (FTIR) studies of the polyamides have been aimed at quantifying the strength and the distribution of hydrogen bonds in these polymers. Estimation of the equilibrium constant for hydrogen-bonded versus non-hydrogen-bonded amide groups in nylon 66 and related model compounds, by integrating peak areas in IR spectra at various temperatures, was proposed by Garcia and Starkweather.[5] The needed thermodynamic data were extracted from the temperature-dependent IR spectra by using a van't Hoff plot. The inherent limitations of this approach were shown by Skrovanek et al.,[6,8] who proposed an alternative interpretation of the origin of observed IR peak intensities. These latter authors proposed a model for curve fitting of IR spectra peaks assuming a Gaussian distribution of hydrogen bond strengths and an arbitrary dependence of absorption coefficients on frequency. One of the important conclusions from all the recent FTIR temperature studies of the polyamides is that hydrogen bonding is still significantly evident at temperatures in the range of their melting points.

Our interest in the problem of hydrogen bonding in polyamides stems in part from the current studies in our laboratory on the Lewis acid–base complexation reactions of polymers. We view such Lewis acid–base complexation reactions of polymers as (1) an approach to modify polymer structure and properties by preparing their Lewis acid–base complexes, (2) an approach to mediate solubility and solution or melt processing of rigid-chain polymers, and (3) a means to probe intermolecular and intramolecular interactions, such as hydrogen bonding, in polymers. We have already demonstrated the former two concepts with regard to rigid-chain polymers such as poly (*p*-phenylenebenzobisthiazole) (PBZT) and poly(benzimidazobenzophenanthroline)s (BBL, BBB).[9] Here, we will explore the Lewis acid–base complexation reactions of polyamides as a way of probing the intermolecular N—H···O=C hydrogen bonds in the polymers.

It occurred to us that the polyamides such as **1**, **2**, and **3** should undergo complex-forming reactions with strong Lewis acids such as $GaCl_3$, BF_3, BCl_3, and $AlCl_3$ in view of the two Lewis base sites (-NH—CO-) in the polymers. If the Lewis acid complexes with the carbonyl oxygen instead of with amide nitrogen and 1:1 (Lewis acid:amide group) stoichiometric complexes of the polymers are prepared, complete scission of the hydrogen bonds should result. Decomplexation of the complexes, on the other hand, should result in re-formation of the hydrogen-bonded polyamide structure. Thus, the FTIR spectra of the Lewis acid/polyamide complexes and the pure polymers obtained by decomplexation should provide information about the scission and re-formation of the intermolecular N—H···O=C hydrogen bonds in polyamides. This paper reports our studies along this line. The specific aliphatic polyamides investigated are **1a** (nylon 6), **1b** (nylon 11), **1c** (nylon 12), **2a** (nylon 66), **2b** (nylon 69), **2c** (nylon 610), **2d** (nylon 612), and their $GaCl_3$ complexes. The amorphous aromatic polyamide **3**, poly[(trimethylhexamethylene)terephthalamide] (PTMHT), and its gallium(III) chloride complex were also investigated.

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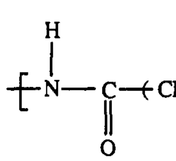
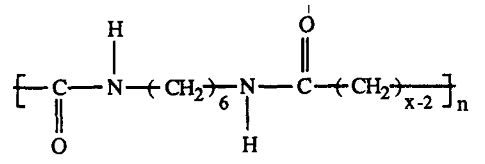


$$\left[\overset{\overset{\displaystyle H}{|}}{N}-\underset{\underset{\displaystyle O}{\|}}{C}-(CH_2)_{x-1}\right]_n$$

1a x = 6
1b x = 11
1c x = 12

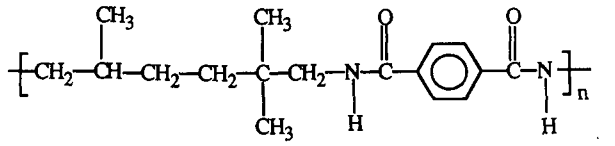
1



$$\left[\underset{\underset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle H}{|}}{N}-(CH_2)_6-\underset{\underset{\displaystyle H}{|}}{N}-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_{x-2}\right]_n$$

2a x = 6
2b x = 9
2c x = 10
2d x = 12

2



3

Experimental Section

The polyamide samples were obtained from Polysciences, Inc. (Warrington, PA), and Scientific Polymer Products (Ontario, NY): nylon 6 (**1a**, T_m = 220 °C, $M_w \approx$ 24 000); nylon 11 (**1b**, T_m = 189 °C); nylon 12 (**1c**, T_m = 177 °C); nylon 66 (**2a**, T_m = 260 °C, $M_w \approx$ 12 000–18 000); nylon 69 (**2b**, T_m = 213 °C); nylon 610 (**2c**, T_m = 220 °C); nylon 612 (**2d**, T_m = 219 °C). Samples of PTMHT (Scientific Polymer Products) had a sharp T_g of 153 °C and no observed melting endotherm. All samples were dried overnight in a vacuum oven at 60 °C to remove any moisture prior to use. Nitromethane (Aldrich, 99+%, bp 101 °C) and gallium(III) chloride (Aldrich, 99.99%, mp 78 °C) were used without further purification.

Lewis acid complexes of all the polyamides investigated were prepared by dissolving a stoichiometric amount of the polymers in a solution of the Lewis acid in nitromethane. All solutions were prepared in a Vacuum Atmosphere drybox filled with nitrogen. $GaCl_3$ complexes of the polyamides were prepared by adding a 1:1 ($GaCl_3$:amide group) stoichiometric amount of polymer to a solution of $GaCl_3$ in nitromethane. The mixtures were stirred when feasible and heated at 40–50 °C until complete polymer dissolution. Solution concentrations in the range of 5–7 wt % polyamide were found to be most suitable for thin film casting for preparing samples for FTIR spectroscopy.

Films of polyamide–$GaCl_3$ complexes for FTIR spectroscopy were prepared by casting the stoichiometric solutions onto NaCl substrates followed by evaporation of the solvent in vacuum at 65 °C overnight. Free standing films of the pure polyamides regenerated from solutions of the $GaCl_3$ complexes were prepared by shearing thin films of a solution between glass substrates and immersing the films in water or methanol to remove the Lewis acid. These films were left to soak in the precipitating nonsolvent liquid (water or methanol) overnight to ensure complete removal of the Lewis acid. The films were removed from the nonsolvent on a steel wire frame and dried 12–15 h under vacuum at 65 °C.

Infrared spectra were collected on a Nicolet 20 SXC Fourier transform infrared spectrometer at a resolution of 4 cm^{-1}. Sets of 32 scans were signal averaged, and the resulting spectra were stored on magnetic disk. Internal calibration of the frequency scale was done to an accuracy of 0.2 cm^{-1} by using a He–Ne laser. All spectra were taken at room temperature (25–27 °C) under nitrogen purge.

Results and Discussion

Lewis Acid–Base Complexes of Polyamides. All the polyamides investigated formed 1:1 ($GaCl_3$:amide group) complexes with Lewis acids. The stoichiometry was determined by quantitative addition of the components to form the complexes in solution and subsequent thermogravimetric analysis of the dried solid samples. The complexes were stable in solution and in the solid state. The Lewis acid complexes of polyamides have distinctive and definite physical properties that are different from the pristine polyamides. For example, $GaCl_3$ complexes of all the polyamides are transparent amorphous materials that are soluble in organic solvents (e.g. nitromethane) compared to the pure polyamides that are opaque, crystalline, and insoluble in nitromethane. After decomplexation by precipitation in water or methanol, the pure polyamides with their characteristic structure and properties are completely recovered. The detailed properties of the Lewis acid complexes of the polyamides investigated here, compared to the pure polymers, will be reported elsewhere.[10,11] In this paper, we will concentrate on the infrared spectra results and describe and interpret the spectral changes on going from the pure (essentially 100% hydrogen bonded) polyamides to the Lewis acid complexes where there is no hydrogen bonding.

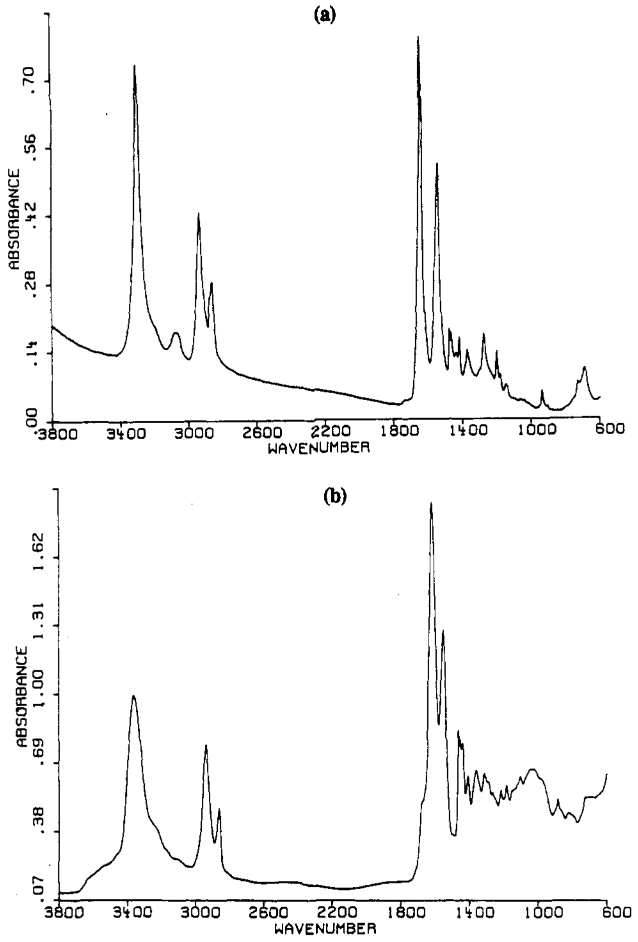


Figure 1. FTIR absorption spectra of (a) nylon 66 and (b) the 1:1 nylon 66–$GaCl_3$ complex.

Infrared Spectra of Polyamides and Their Lewis Acid Complexes. Figure 1a shows the FTIR spectrum of nylon 66 recovered from its $GaCl_3$ complex. The spectrum is identical with that of the pristine polymer.[12] Figure 1b shows the spectrum of the 1:1 $GaCl_3$ complex of nylon 66. The band assignments of the spectra of Figure 1 are shown in Table I. The band assignments of the FTIR spectra of the other polyamides and their 1:1 $GaCl_3$ complexes are also collected in Table I. The following analysis of the observed changes in the FTIR spectra of polyamides due to Lewis acid complexation is organized according to the major vibrational bands: N–H stretching, amide I mode, amide II mode, and CH_2 stretching.

Table I
Band Assignments of the FTIR Spectra of Polyamides and Their 1:1 $GaCl_3$ Complexes (Values in cm^{-1})

sample	N-H str.	amide I	amide II	b	CH_2 str.[c]	CH_2 str.[d]
nylon 6[a]	3293	1641	1558	3095	2857	2930
$GaCl_3$-nylon 6	3363	1616	1549		2866	2946
nylon 11[a]	3298	1637	1551	3089	2851	2921
$GaCl_3$-nylon 11	3358	1616	1551		2856	2929
nylon 12[a]	3290	1637	1558	3086	2850	2920
$GaCl_3$-nylon 12	3355	1615	1552		2855	2929
nylon 66[a]	3303	1638	1540	3077	2860	2934
$GaCl_3$-nylon 66	3366	1617	1553		2863	2940
nylon 69[a]	3297	1635	1549	3084	2851	2922
$GaCl_3$-nylon 69	3362	1616	1551		2860	2937
nylon 610[a]	3302	1638	1541	3077	2852	2926
$GaCl_3$-nylon 610	3362	1618	1552		2859	2935
nylon 612[a]	3306	1638	1541	3078	2852	2923
$GaCl_3$-nylon 612	3365	1615	1552		2857	2931
PTMHT[a]	3310	1640	1545	3072	2871	2930 2957[e]
$GaCl_3$-PTMHT	3352	1610	1548		2874	2934 2960[e]

[a] Regenerated from its $GaCl_3$ complex. [b] First overtone of amide II mode. [c] Symmetric CH_2 stretch. [d] Assymetric CH_2 stretch. [e] Aromatic CH stretch.

N-H Stretching. The N-H stretching region of the polyamides spans the range of approximately 3100 to 3500 cm^{-1}. From the data of Table I, the observed N-H stretching frequency of the pure polyamides is ~3300 cm^{-1}, varying from 3290 cm^{-1} in nylon 12 to 3306 cm^{-1} in nylon 612 and 3310 cm^{-1} in the aromatic polyamide PTMHT. The observed N-H stretching frequencies in Table I are similar to values reported for polyamides at room temperature (30 °C) and are characteristic of the hydrogen-bonded polyamides.[5-7,12] These values are also considerably lower than the expected N-H stretching frequency of ~3400 cm^{-1} for non-hydrogen-bonded polyamides.

The observed N-H stretching frequency in the 1:1 $GaCl_3$ complexes of the polyamides, shown in Table I, varies from 3352 cm^{-1} in $GaCl_3$-PTMHT to 3366 cm^{-1} in $GaCl_3$-nylon 66. This represents a significant increase of the N-H absorption frequency in the complexes compared to the pure polyamides. The magnitude of the N-H absorption frequency shift to a higher energy on Lewis acid complexation of the polyamides is between 59 and 70 cm^{-1}.

An explanation of the N-H stretching frequency increase in the complexes relative to the pure polyamides is that Lewis acid complexation severs the hydrogen bonds in polyamides as illustrated in Figure 2. In pure polyamides, intermolecular hydrogen bonding occurs, as illustrated in Figure 2a, between amide groups in adjacent chains. The competition between the N-H hydrogen of the amides and Lewis acid for the more basic carbonyl oxygen sites favors Lewis acid coordination to the oxygen sites and the consequent complete severance of the hydrogen bonds because the Lewis acid is a stronger electron acceptor than N-H. Therefore, the resulting Lewis acid complex of the polyamide contains "free" N-H groups and "complexed" C=O groups as shown in Figure 2b. In assigning the N-H groups of the polyamide complexes as "free", however, it must be recognized that the N-H bonds in the complexes will be longer than those expected for a polyamide in its vapor state—i.e., a pure uncomplexed polyamide with all hydrogen bonds severed—due to the strong electron-withdrawing effect of the Lewis acid (structure I). Consequently, the complexes can be expected to have N-H stretching frequencies lower than the ~3400 cm^{-1} expected for the non-hydrogen-bonded polyamides.[13] On the other hand, a significant increase in the N-H absorption frequency in the complexes can be expected compared to the N-H in N—H···O=C hydrogen-bonded polyamides.[13,14]

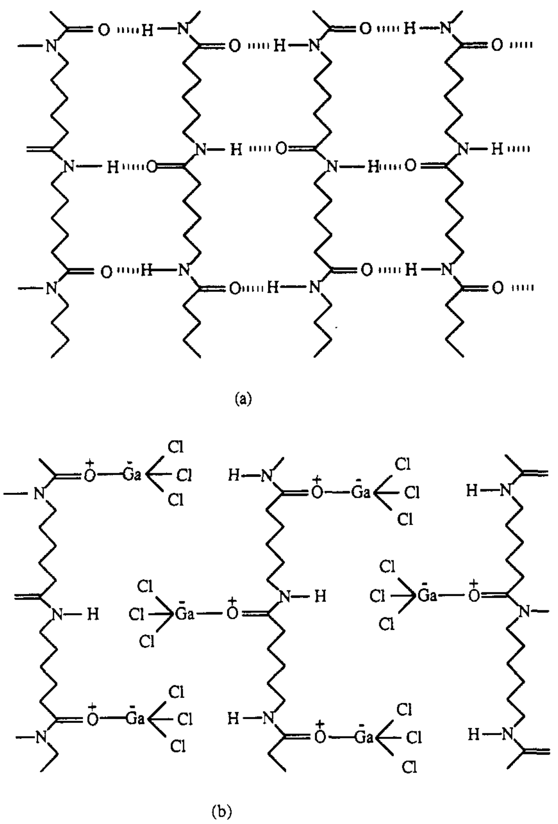
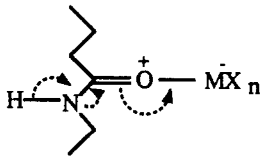


Figure 2. (a) Hydrogen-bonded ("zipped") sheet structure in nylon 6 and (b) non-hydrogen-bonded ("unzipped") structure of the nylon 6–$GaCl_3$ complex.



I

The magnitude of the observed N-H stretching frequency shift (59–70 cm^{-1}) is in good agreement with the reported N-H stretching frequency shift from 3300 to 3367 cm^{-1} when *N*-methylacetamide is complexed with BCl_3.[13] The magnitude of the observed frequency shifts upon severing the hydrogen bonds by complexation can also be compared with thermally induced hydrogen bond scission in polyamides. Skrovanek et al. have reported an increase from 3310 to 3332 cm^{-1} on heating an amorphous polyamide from 30 to 210 °C[6b] and a shift from 3300 to 3332 cm^{-1} on heating nylon 11 from 30 to 210 °C (which is above the ~189 °C melting point of nylon 11).[6c] These shifts were attributed to increases, 5–21.5% in the case of nylon 11, in the concentration of non-hydrogen-bonded N-H groups and the gross weakening of the remaining hydrogen bonds. Our observed N-H frequency shifts on complexation are about a factor of 2–3 larger than observed on heating and hence can be viewed as the limiting case of complete scission of the hydrogen bonds.

A decrease in the N-H stretching intensity and an increase in bandwidth are observed on Lewis acid complexation of polyamides. The typical changes observed in all the polyamides are exemplified by the spectra of nylon 66 and $GaCl_3$-nylon 66 in Figure 1. Although quantitative analysis of these changes in band intensity and bandwidth is unrealistic in the absence of absolute absorption coefficients, a comparison of the N–H stretching bands to the CH_2 stretching bands, which are unaffected by complexation, shows that the observed changes in the N–H stretching intensity and bandwidth are characteristic of the complexation. The trends in N–H stretching intensity and bandwidth on complexation are also in agreement with trends seen for the gradual hydrogen bond weakening with increasing temperature.[6] Our observed band intensity and bandwidth in the Lewis acid complexes represent the limiting case of zero hydrogen bond strength. The observed decrease in intensity of the N–H band due to scission of hydrogen bonds has also been theoretically predicted.[3b]

Amide I Mode. The amide I mode in polyamides is known to be dominated by the C=O stretching band. In polyglycine I, for example, C=O stretching accounts for 77% of the potential energy of amide I mode, with smaller contributions from the C—N stretch (14%) and the C—C—N deformation (12%).[3] Since the C=O stretching is dominated by the electrical properties of the highly electronegative oxygen atom, and since the Lewis acid has a stronger electron-withdrawing effect on the oxygen than the N—H···O=C hydrogen bond, we expect to see characteristic FTIR spectra changes of the amide I mode on complexation.

The observed stretching frequencies of the amide I mode of the polyamides and their 1:1 $GaCl_3$ complexes are shown in Table I. The frequency of the amide I mode in the pure (hydrogen-bonded) polyamides is ~1640 cm^{-1}, varying from 1635 cm^{-1} in nylon 69 to 1641 cm^{-1} in nylon 6. In contrast, the frequency of this mode in the complexes is shifted by 19–30 cm^{-1} to a lower energy.

The observed shift of the amide I mode to a lower frequency in the complexes is what one expects from Lewis acid complexation at the carbonyl oxygen sites. As mentioned previously, Lewis acid complexation has a stronger electron-withdrawing effect on the carbonyl oxygen than does hydrogen bonding. Hence, a decrease in the C=O bond strength in the complexes should shift the amide I mode to a lower frequency as observed in the data. This result is the exact opposite to the effect of weakening the hydrogen bonds by increasing the temperature. In the case of heating induced weakening or severing of the hydrogen bonds, it has been shown that the amide I absorption frequency increases due to strengthening of the C=O bonds.[5,6b,6c] However, compared to the changes in the N–H stretching mode, the frequency shift in the amide I mode was found to be less dramatic. An increase in intensity of the amide I band relative to the CH_2 stretch region was also observed on complexation.

Amide II Mode. The amide II mode is a mixed mode with contribution from the N–H in-plane bend and smaller contributions from the C–N stretch, C_α–C stretch, and N–C_α stretch. The absence of hydrogen bonding is expected to cause a decrease in the N–H in-plane bending frequency;[14] however, the shift is expected to be of much smaller magnitude than the N–H stretch. Similarly, the effects of severing the hydrogen bonds on the other contributions to the amide II mode are expected to be even smaller if at all evident.

The observed frequency of the amide II mode in the hydrogen-bonded polyamides, as shown in Table I, is in the range of 1540–1558 cm^{-1}. No significant shift of the frequency of this mode was observed in the complexes in that the shifts are of the order of the spectral resolution (4 cm^{-1}). The reason why an expected small decrease in the amide II absorption frequency was not observed may be due to a number of factors. The increased overlap of the amide I and amide II modes in the complex due to a clear shift of the amide I mode to a lower frequency in the complex could cause a shift in the observed frequency of amide II mode in the complex. Although the N–H in-plane bend contribution to this mode is the largest, it is not dominant (it contributes 43% to the potential energy in the case of polyglycine I),[3] and hence the overall effect of elimination of hydrogen bonding on this mode may be too small compared to the spectral resolution.

In the pure hydrogen-bonded polyamides, a small absorption band is observed at ~3072–3095 cm^{-1} (Table I) between the strong bands due to CH_2 and N–H stretches in the 2500–3300-cm^{-1} region. The most reasonable assignment of this band is that it is the first overtone of the amide II mode, enhanced in intensity due to Fermi resonance with the N–H stretching vibration. This band was absent in the spectra of the $GaCl_3$–polyamide complexes (see, for example, Figure 1). The absence of this band in the polyamide complexes is consistent with a decrease in intensity enhancement due to the shift of the N–H stretching band to a high frequency while the undetectable amide II overtone remains essentially at the same frequency or shifts only very slightly.

CH_2 Stretching. It is worthy of note that symmetric and asymmetric CH_2 stretching vibrations in the 2850–2930-cm^{-1} region are largely unaffected by the complexation, as expected, since they play no part in either the complexation or hydrogen bonding. Essentially no intensity or bandwidth changes were observed; in cases where some frequency shifts were seen, they were of the order of the spectral resolution and, therefore, negligible. This further confirms the site specificity of the Lewis acid–base complexation reaction of the polyamides.

Site-Specific Hydrogen Bond Scission and Reformation. The picture of the hydrogen bonding in polyamides that emerges from our analysis of the vibrational spectra of polyamides and their Lewis acid–base complexes is that of a zipper. Lewis acid complexation at specific C=O sites on the polyamides unzips the macromolecular chains as illustrated in Figure 2b. In this non-hydrogen-bonded (unzipped) state, the polyamide complexes are amorphous transparent materials with a sharp T_g in the range −5 to 10 °C and no melting transitions.[10,11] After decomplexation by precipitation with water or methanol, the regenerated hydrogen-bonded ("zipped") polyamides, illustrated in Figure 2a, regain all their characteristic structure and physical properties.[10,11]

Conclusions

In summary, we have effected complete scission of the N—H···O=C hydrogen bonds in polyamides by a room-temperature site-specific Lewis acid complexation at the basic carbonyl oxygen sites of the amide groups. Facile decomplexation of the polyamide–Lewis acid complexes effected re-formation of the hydrogen bonds. Thus, hydrogen bonding in polyamides can be viewed as functioning like a molecular zipper, and the site-specific reversible Lewis acid–base complexation reactions of the polyamides provide a way of unzipping and zipping it. Such a probing of the hydrogen bonding in polyamides shows the dramatic effects of hydrogen bonding on the structure and properties of polyamides.[15]

It has recently been shown that the same hydrogen bonding that makes polyamides important engineering thermoplastics because of the mechanical strength it imparts also represents the fundamental barrier to ultradrawing of polyamides to high draw ratios and high strength and high modulus using techniques, such as tensile drawing or gel spinning, which have been successful for polyethylene.[16] These authors also suggested that future progress in producing highly oriented polyamides through tensile drawing requires new ways, other than addition of plasticizers which has not been successful in the past, to suppress hydrogen bonding during processing. Clearly, our approach of Lewis acid-base complexation of polyamides provides a way to temporarily suppress the effects of hydrogen bonding, while processing, allowing deformation and orientation to the desired degree, and then to restore hydrogen bonding to the highly oriented material where it will impart strength and stiffness.

Acknowledgment. We thank the Amoco Foundation for financial support. We also thank K. Marshall and S. D. Jacobs for the use of the FTIR facility at the University of Rochester's Laboratory for Laser Energetics.

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(15) In this paper, we investigated and discussed the limiting cases of pure polyamides that are hydrogen bonded and 1:1 Lewis acid–base complexes that have no hydrogen bonding. A reviewer asked about the N–H region of the IR spectra of intermediate cases of nonstoichiometric complexes with partial hydrogen bonding. In such a sample, one would expect to see two N–H stretching bands, one due to H-bonded N–H (pure polyamide) and the other due to non-H-bonded N–H (complex). We observed such two peaks in some partially regenerated polyamide films when regeneration was not complete due to insufficient time in water or methanol (as confirmed by thermogravimetric analysis).

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Registry No. 1a, 25038-54-4; **1b** (SRU), 25035-04-5; **1b** (homopolymer), 25587-80-8; **1c** (SRU), 24937-16-4; **1c** (homopolymer), 25038-74-8; **2a** (SRU), 32131-17-2; **2b** (SRU), 28757-63-3; **2b** (copolymer), 27136-65-8; **2c** (SRU), 9008-66-6; **2c** (copolymer), 9011-52-3; **2d** (SRU), 24936-74-1; **2d** (copolymer), 26098-55-5; PTMHT (SRU), 9071-17-4; PTMHT (copolymer), 53834-90-5.