

STUDY ON THE MECHANISM OF NYLON 6,6 DISSOLVING PROCESS USING $\text{CaCl}_2/\text{MeOH}$ AS THE SOLVENT*

SUN Benhui (孙本惠)

(Research Institute of Polymer Materials, Beijing Institute of Chemical Technology, Beijing 100029)

ABSTRACT

A discussion of the mechanism of nylon 6,6 dissolving process using $\text{CaCl}_2/\text{MeOH}$ as the solvent is presented. The calcium chloride forms a complex compound with nylon 6,6 by breaking the hydrogen bonds. The melting point of the CaCl_2 -nylon 6,6 complex was found to be reduced by 91K relative to the pure nylon 6,6 polymer. The role of methanol is somewhat similar to a catalyst. The results demonstrate that the complexation of a Lewis acid (CaCl_2) and a Lewis base (nylon 6,6) can be used to probe intermolecular interactions such as hydrogen bonding in polymers, to modify the polymer properties and mediate its solubility and processing.

INTRODUCTION

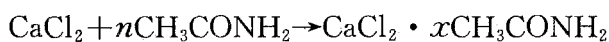
Asymmetric nylon 6,6 membranes can be made by a standard wet phase inversion process provided a suitable solvent can be found. As nylon 6,6 has a structure in which the N-H groups in the chain are hydrogen bonded to the C=O groups in adjacent chains (Figure 1), it has high crystallinity, a high melting point (523–545K)^[1], good mechanical properties, and chemical stability. Consequently, it is impossible to dissolve nylon 6,6 before its hydrogen bonds are severed, and it is difficult to find a suitable solvent to dissolve nylon 6,6.

In recent years, two kinds of solvents for nylon 6,6 were developed. One is formic acid^[2,3,4]. However, formic acid is unpleasant to work with and causes some degradation of the polyamide^[5,6]. The other is an alcohol/salt solution. This solvent system can be used to form porous membrane sheets of high molecular weight polymer without degradation and strength reduction as associated with the formic-acid-based membranes. For example, a methanol/ CaCl_2 solution is a desirable solvent for nylon 6,6.

Nylon 6,6 was observed to be insoluble in methanol, but soluble in a methanol / CaCl_2 solution. This shows that the salt is important in the

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polymer dissolving process. It is known that calcium chloride is a Lewis acid, and it can complex with amides (Lewis bases). For example, it can complex with acetamide and the complex number x may be 1, 3, 4 or 6 depending on the temperature^[7].



Roberts et al.^[8] reported the concept of using a Lewis acid (gallium chloride) complexation of a polymer (nylon 6) to modify polymer properties. The aim of this paper, therefore, is to report the findings of our study on the role of the salt and the mechanism of the nylon 6,6 dissolving process.

EXPERIMENTAL

Materials

The Nylon 6,6 studied was Celanese 1200-1 with $\overline{M}_w$ of 120,000 and $\overline{M}_n$ of 50,300. The calcium chloride was Fisher Certified ACS grade. The methanol was J. T. Baker Analyzed Reagent grade.

Solution preparation

Two different kinds of solutions were prepared.

Solution A: nylon polymer was added to methanol and heated to reflux for several hours, then CaCl_2 was added and the resulting mixture was heated to reflux for several hours more.

Solution B: nylon polymer was added to a solution of calcium chloride in methanol and heated to reflux until the nylon dissolved.

Membrane sample preparation

CaCl_2 -nylon 6,6 membrane: Membrane samples of CaCl_2 -nylon 6,6 for Fourier transform infrared (FTIR) and melting point measurement were prepared by casting the nylon 6,6/ CaCl_2 /methanol solution onto a glass substrates followed by a slow evaporation of the solvent in a fume hood and then in a vacuum oven at room temperature for 48 hours.

Nylon 6,6 membrane: A casting solution was prepared by dissolving

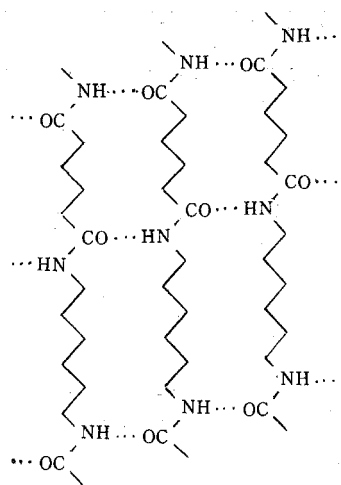


Fig. 1 Hydrogen bonded structure of nylon 6,6

nylon 6,6 in formic acid at about 400 K. The solution was then cast onto a glass substrate followed by a slow evaporation of the formic acid in a fume hood, then in a vacuum oven at room temperature for 48 hours.

Test for free Ca^{2+} in solution

Carbon dioxide gas was passed through solution A and solution B separately to test for the existence of free calcium cations.

Analysis of permeate of solution B

Solution B was separated by permeating through a PVC ultrafiltration membrane under the pressure of 18 psi and at room temperature. The permeate, a pure methanol sample, and a methanol/ CaCl_2 complex solution sample were cast separately onto a KBr substrate for infrared spectroscopy. Methanol sample were cast separately onto a KBr substrate for infrared spectroscopy. Infrared spectra were collected on a Beckman Infrared Spectrometer.

Melting point measurement

The melting points of the CaCl_2 -nylon 6,6 membrane sample and the nylon 6,6 sample were measured with a PERKIN-ELMER DSC-2 Differential Scanning Calorimeter using flowing nitrogen. Indium (m. p. 156.6°C) DSC Standard was used to calibrate the measured transition points. Samples in the range of 1.7 to 4.4 mg were sealed in DSC pans. The scan rate was 10 K/min.

FTIR measurement of membrane samples

The infrared spectra of the CaCl_2 -nylon 6,6 membrane sample and the nylon 6,6 membrane sample were collected on a BIORAD FTS-15/90 Fourier Transform Infrared Spectrometer at room temperature (22°C) under nitrogen purge.

RESULTS

Experimental phenomena of the dissolving process

Three different experimental phenomena of the dissolving process were observed. First, nylon 6,6 would not dissolve in methanol. Second, the nylon 6,6 in solution A partially dissolved. Third, when calcium chloride was dissolved in methanol, much heat was released. Finally, nylon 6,6 dissolved completely in the resulting $\text{MeOH}/\text{CaCl}_2$ solution.

Free Ca^{2+} in solution

Upon passing CO_2 through the solutions, a large amount of white precipitant (CaCO_3) formed in solution A, but no precipitant formed in solution B. This demonstrates that there were free calcium cations in solution A, and no free calcium cations in solution B.

Analysis of permeate of solution B

The infrared spectra of the permeate of solution B and of the pure methanol sample are shown in Figure 2 and Figure 3, respectively. Figure 4 shows the IR spectrum of the methanol- CaCl_2 complex. By comparing these IR spectra we find that the first two figures are the same (they have no 1640cm^{-1} peak). That is, the permeate of the solution B is methanol.

Melting point

DSC results from heating at 10 K/min. showed the melting point of the pure nylon 6,6 is 530.72 K and the melting point of the CaCl_2 —nylon 6,6 membrane sample is 439.35 K , which is about 91 K lower than that of the nylon 6,6 sample. Endotherm peaks indicated 13.48 cal/g and 323.8 cal/g , respectively.

Infrared spectra of membrane samples

A comparison of the FTIR spectra results for the CaCl_2 —nylon 6,6 membrane and nylon 6,6 membrane in Table 1 shows that the changes in the main bonds are those anticipated for the severing of the $\text{N-H}\cdots\text{O}=\text{C}$ hydrogen bonds and complexation at the carbonyl oxygen site of the amide group. The amide I mode, which is known^[9] to be dominated by the $\text{C}=\text{O}$ absorption bond, is shifted in the complex by 15 cm^{-1} to a lower frequency.

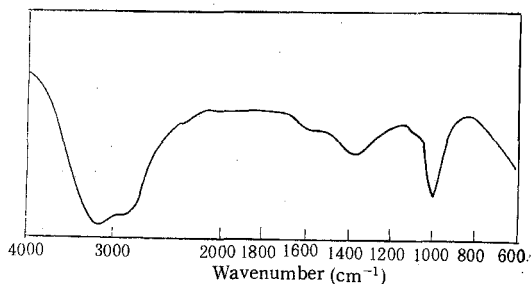


Fig. 2 IR spectrum of permeate of casting solution

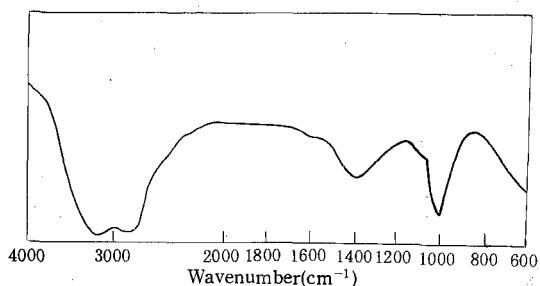
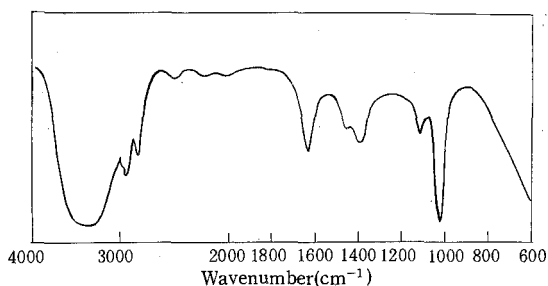


Fig. 3 IR spectrum of pure methanol

Fig. 4 IR spectrum of MeOH-CaCl₂ complex**Table 1** Assignment of FTIR spectra of nylon 6,6 and CaCl₂-nylon 6,6 sample at 22°C (cm⁻¹)

Sample	N-H (str.)	CH ₂ (asymmetric str.)	CH ₂ (symmetric str.)	Amide I (str.)	Amide II (def.)
Nylon 6,6	3300	2930	2870	1645	1550
CaCl ₂ • nylon 6,6	3300	2935	2870	1630	1535

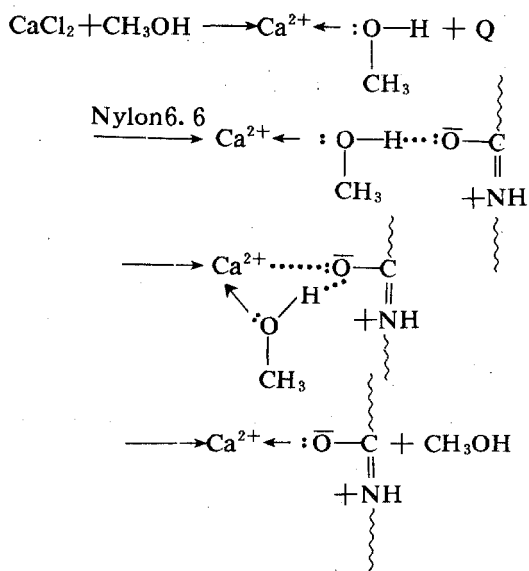
DISCUSSION

The possible mechanism of the nylon 6,6 dissolving process

Based on theoretical analysis and experimental phenomena, the nylon 6,6 dissolving process proposed is:

In the process of dissolving calcium chloride in methanol, a large amount of heat is released. This shows that complexation is occurring. It is necessary to heat the solution in order to sever the hydrogen bonds of methanol. In the next step, the CaCl₂—CH₃OH complex molecules come

close to the nylon 6,6 molecules owing to the intermolecular interactions between O-H groups and C=O groups. Because the complexing capability of the calcium cation with a carbonyl group is stronger than that with a hydroxyl group^[10], complex bonds between the calcium cation and the oxygen atom of a carbonyl group are gradually formed. Finally, a CaCl_2 -nylon 6,6 complex and free methanol are formed.



Proof of CaCl_2 -nylon 6,6 complex formation

The experimental results proved that no free calcium cations exist in solution B. That is to say, calcium cations must exist in a combined state. The IR analysis of the permeate of solution B shows that the permeant from solution B is methanol. This means that the methanol is free, and the calcium cations are combined with nylon 6,6 molecules. The melting point of the CaCl_2 -nylon 6,6 membrane sample is about 91K lower than that of the pure nylon 6,6 sample. This shows that the hydrogen bonds between the nylon 6,6 molecules were severed, the intermolecular interactions of the polymer were decreased, and the crystallinity of the nylon sample was decreased as well. The infrared spectrum shows that the C=O absorption bond has been shifted to a lower frequency. This proves the existence of the complex compound of CaCl_2 -nylon 6,6 (see next paragraph).

The effect of the CaCl_2 -nylon 6,6 complex on its IR spectrum

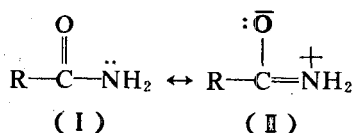
Table 1 shows that the C=O absorption bond is shifted in the complex

by 15 cm^{-1} to a lower frequency. This can be explained by Hooke's Law^[11]:

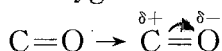
$$\gamma = 1/2\pi \{k(M_a + M_b)/M_a M_b\}^{1/2}$$

where γ is the appropriate stretching frequency, M_a and M_b are the masses of the two atoms in the chemical bond, and k is the force constant of the chemical bond. Single, double, and triple bonds exhibit force constants of about 5×10^5 , 1.0×10^6 , and 1.5×10^6 dynes/cm, respectively. The formula shows that the weaker the bond, the more electron releasing the group, the lower the group stretching frequency; the stronger the bond, the more withdrawing, the higher the frequency.

It is known that amide exists in two resonance forms:



Based on the IR spectrum and space considerations, the complexation is carried out in the form of formula (II). That is, when the carbonyl stretches, there is some charge redistribution so that the carbon becomes more positively charged and the oxygen more negatively charged^[12]:



As the tendency of the $\text{C}=\text{O}$ bond to exist in the single bond form increased, $\text{C}=\text{O}$ absorption bond shifts to a lower frequency.

The analysis of endotherm peaks

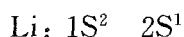
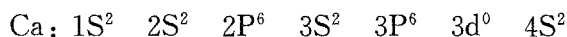
DSC results showed the endotherm peaks of the pure nylon 6,6 and CaCl_2 -nylon 6,6 membrane sample are 13.48 cal/g and 323.8 cal/g, respectively. This means that during the melting process, the intermolecular forces of pure nylon 6,6, mainly hydrogen bonding, were severed; however, both the intermolecular forces and the complex bonding of the CaCl_2 -nylon 6,6 complex compound were severed, and the bond dissociation enthalpy for complex bonds is much larger than that for hydrogen bonds. We know that the bond dissociation enthalpy for normal hydrogen bonds is ca. 3–10 Kcal/mol, for strong EPD (electron pair donor)/EPA (electron pair acceptor) complexes is 10–45 Kcal/mol, and for covalent single bonds is 50–100 Kcal/mol^[13]. Thus the DSC results of endotherm peaks also prove the existence of the CaCl_2 -nylon 6,6 complex.

The role of methanol

Although the Lewis acid (CaCl_2) can complex with the Lewis base (nylon 6,6), it is impossible to dissolve them directly. This is because both of them are solids, and calcium chloride is hydrophilic, but nylon 6,6 is hydrophobic. However, methanol is both hydrophilic and hydrophobic. Thus, it is easy to complex MeOH with calcium chloride in the proximity of nylon. Therefore, it plays the role of a bridge, or somewhat similar to a catalyst. As the complexing capability of the calcium cation with the carbonyl group is larger than that with the hydroxyl group, the CaCl_2 -nylon 6,6 complex is formed and the methanol freed at last.

Other salts

What kind of salts can possibly be the Lewis acids to complex with Lewis bases such as nylon 6,6? There are two main criteria. First, the cation formed by the salt must be able to receive at least one electron from the Lewis base; that is, it must have an empty electron orbitals or be able to form a hybrid orbitals, such as



Second, two properties of the anion of the salt affect complexation are important: the electronegativity and the space obstruction of the anion. If the electronegativity of the anion is strong, or if its space obstruction is large, the complex compound of the salt can not be formed. For instance, anions such as F^- and Br^- will not form complex compounds. From this point of view, it is easy to understand why some salts are successful while others are unsuccessful in the process of dissolving nylon 6,6. The successful salts are CaCl_2 , $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, Ca. salicylate, NaSCN , $\text{CaI}_2 \cdot 4\text{H}_2\text{O}$, LiCl etc. The unsuccessful salts include $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CaBr}_2 \cdot 2\text{H}_2\text{O}$, CaF_2 , MgCl_2 , $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ etc.

CONCLUSION

The role of calcium chloride in the nylon 6,6 dissolving process is to form a complex compound with nylon 6,6 in which the hydrogen bonds have been severed. The melting point of the CaCl_2 -nylon 6,6 complex was found to be reduced by 91 K relative to the pure polymer. During the dissolving process, the role of methanol is somewhat similar to that of a catalyst. The

results demonstrate that the complexation of a Lewis acid with a Lewis base can be used to probe intermolecular interactions such as hydrogen bonding in polymers, to modify the polymer properties, and mediate its solubility and processing.

Keywords:

Dissolving mechanism; $\text{CaCl}_2/\text{MeOH}$ solvent; Polyamide; Complex.

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