A Solid State NMR Study on Crystalline Forms of Nylon 6

AKANE OKADA, MASAYA KAWASUMI, ICHIRO TAJIMA,
TOSHIO KURAUCHI, and OSAMI KAMIGAITO, *Toyota Central
Research and Development Laboratories, Inc., Nagakute, Aichi,
480-11, Japan*

Synopsis

High-resolution ^{13}C-NMR spectra were studied for two different crystalline structures of nylon 6 in the solid state by the cross polarization/magic angle spinning (CP/MAS) method. Two crystalline structures, α-form and γ-form, gave different chemical shifts for methylene carbons. The results showed that the hydrogen bonds between intermolecular chains are stronger in the γ-form than in the α-form. This strongly supports the results of the X-ray study of nylon 6 by Malta et al. Our results also showed that intramolecular delocalization of positive charges occurs in the γ-form through hyperconjugation in which the dihedral angle between the π bond and neighboring σ bonds is 30° while no such effect can be expected in the α-form in which the angle is 0°.

INTRODUCTION

Nylon 6 is one of the most important engineering plastics in the automobile industry (for a review, see Ref. 1). The hydrogen bonds between the nylon 6 main chains are thought to be responsible for the high performance of this polymer. The scission of the bonds by water, solvents, salts, and other chemicals would cause undesirable changes or degradations. However, chemical structures of plastics in use are not completely understood.

Many X-ray studies of nylon 6[2-10] were made, and it was cleared that crystal structure of nylon 6 are sorted into two types, α-form and γ-form. The α-form is of a planar zigzag structure, and the γ-form is of a helix structure as illustrated in Figure 1.[5] However, there is discrepancy and disagreement[2,3] among above studies concerning the distance between adjacent chains, and consequently the strength of the hydrogen bond in each crystalline structure seems not to be determined. For that, solid-state NMR seems to be helpful.[11-13] We observed the first ^{13}C CP/MAS NMR spectra of both forms of nylon 6 to get further information on bondings and structures. All peaks were assigned for both spectra. The difference of the spectra was attributed to strengths of intermolecular hydrogen bonds and intramolecular hyperconjugation. The object of this paper is to point out the importance of hyperconjugation in NMR spectra of polymers.

EXPERIMENTAL

Specimen. Nylon 6 was prepared by a standard hydrolytic polymerization.[1] It was of the α-form. The specimen was molten at 250°C and then rapidly
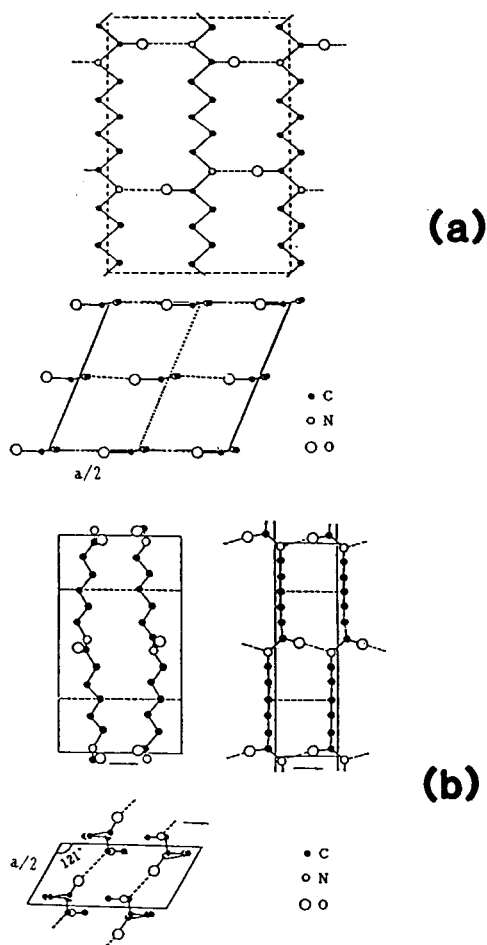
Fig. 1. Crystal structures of nylon 6: (a) α-form; (b) γ-form.[5] (●) C; (∘) N; (○) O.

quenched into a liquid nitrogen bath, giving γ-form. The crystalline structure was determined with the X-ray diffraction method. A Rigaku SX X-ray diffractometer was used for that. Profiles of diffracted X-ray from the specimen used for NMR measurement were shown in Figure 2, in which Co-Kα radiation was used.

^{13}C-NMR. CP/MAS spectra were observed with a Bruker MSL 300 WB spectrometer operating at 75.49 MHz for ^{13}C nuclei and at a magnetic field strength of 7.0 T. The specimen was rotated at 2500–4500 rpm at room temperature. The sweep range was 300 ppm. Glycine carbonyl signal (176.03 ppm) was used as the standard of chemical shifts. The pulse width was 6 μs, and the pulse repetition time was 6 s. Data points were 8000, and the spectra were accumulated 500 times. Contact time was used at 1 ms.

RESULTS AND DISCUSSIONS

^{13}C CP/MAS NMR spectra of the α-form and γ-form of nylon 6 are shown in Figure 3. The patterns of the spectra differ largely from each other, indicating that the electronic circumstances are different for both crystals.
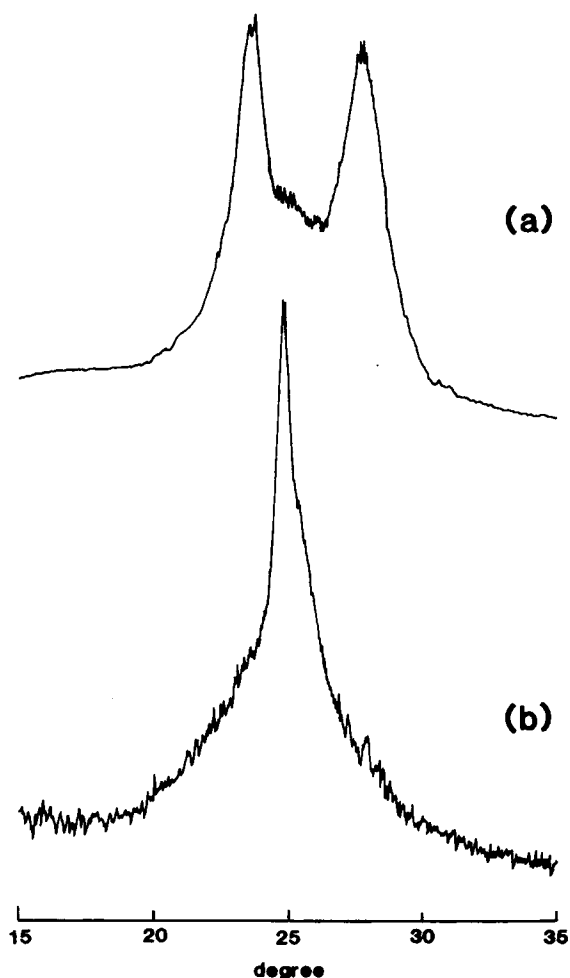
Fig. 2.   X-ray diffraction diagrams of nylon 6: (a) α-form; (b) γ-form.

All peaks were well resolved and were assigned according to a solution, NMR spectra of nylon 6, on the assumption that the relative order of peaks should be unchanged in the solid and the solution because chemical bond sequences of elements and groups are unchanged.

[13]C chemical shifts are summarized in Table I. The difference of the chemical shifts between two crystals, $\Delta\delta c$, was defined as follows:

$$\Delta\delta c = \delta c(\gamma) - \delta c(\alpha) \tag{1}$$

where $\delta c(\gamma)$ and $\delta c(\alpha)$ are, respectively, the chemical shifts of the γ- and α-crystal. The positions of carbons were indicated in the chemical formula with Table I. As shown in Table I, the chemical shifts of the γ-form were downfield at C_3 and C_5 by 3.9 ppm, and at C_2 by 1.0 ppm from those of the α-form. The chemical shift of the γ-form was upfield at C_6 by 3.2 ppm from that of the α-form.

It is well known that the α-form has a planar zigzag structure in which the hydrogen bonds are formed between antiparallel chains and that the γ-form
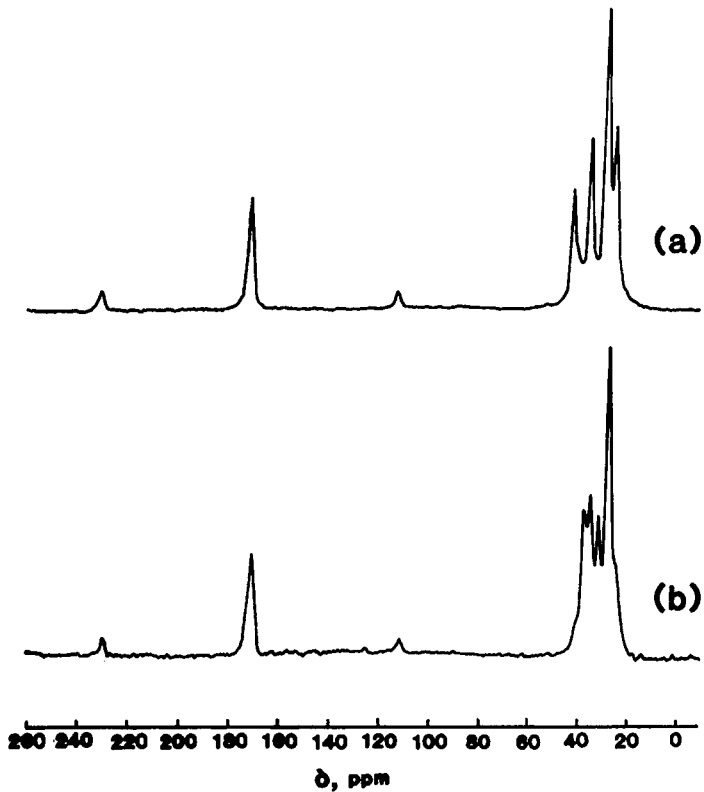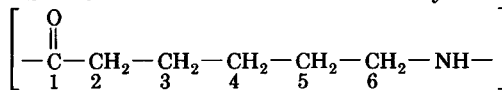
Fig. 3.   Solid-state ^{13}C-NMR spectra of nylon 6: (a) α-form; (b) γ-form.

TABLE I
Solid-State ^{13}C-NMR Chemical Shifts of Nylon 6

$$\left[\begin{array}{c} O \\ \parallel \\ -C-CH_2-CH_2-CH_2-CH_2-CH_2-NH- \\ 1 \quad\; 2 \qquad 3 \qquad 4 \qquad 5 \qquad 6 \end{array} \right]$$

Specimen	C_1	C_2	C_3	C_4	C_5	C_6
α-Form	171.1	34.4	24.3	28.1	28.1	41.1
γ-Form	171.0	35.4	28.2	28.2	32.0	37.9
$\Delta\delta c^a$	-0.1	$+1.0$	$+3.9$	$+0.1$	$+3.9$	-3.2
Solution[b]	176.4	34.6	24.4	25.0	27.2	39.2

[a]$\Delta\delta c = \delta c(\gamma) - \delta c(\alpha)$.
[b]Cited from "Carbon-13 NMR of Monomers and Polymers," Sadler Res. Lab., 1981, D388C.

has a helix structure in which the hydrogen bonds are formed between parallel chains.

γ-Form of nylon 6 has a chemical formula 1 through intermolecular hydrogen bonds.

1
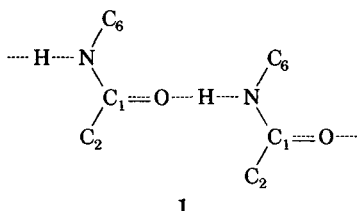
The chemical formula of α-form is similar to that of γ-form whereas the hydrogen bonds are formed between antiparallel chains in α-form.

The hydrogen bonded formula 1 may be described as prototropy between 2 and 3:

(2)
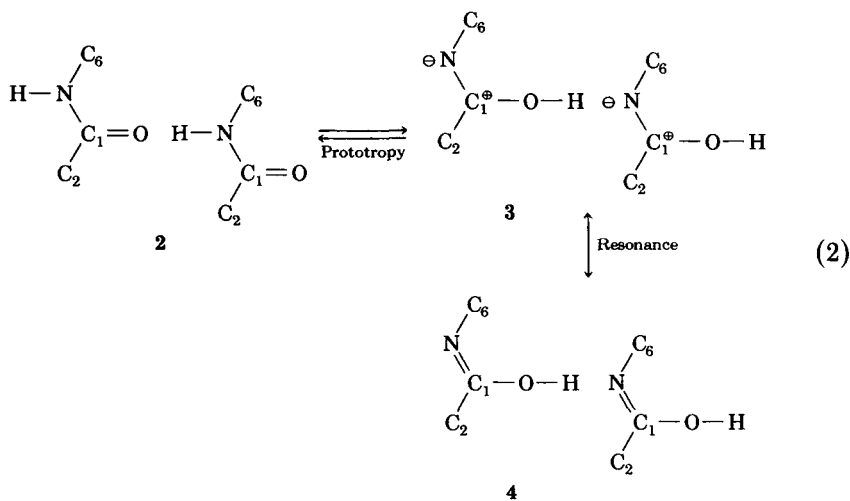
In structure 3, the positive charge on C_1 induces partial positive charge on C_2 and the negative charge on N atom induces partial negative charge on C_6 through inductive effects. The fact that $\Delta\delta c$ at C_2 is 1.0 ppm and $\Delta\delta c$ at C_6 is -3.2 ppm means that C_2 is more deshielded and C_6 is more shielded in γ-form than in α-form. Thus, the contribution of the zwitterion structure 3 is more important in γ-form than in α-form. In conclusion, the hydrogen bond between the chains must be stronger in γ-form than in α-form.

Malta et al.[2] examined the structure of α-form more exactly by the X-ray diffractometry. They reported that the lattice constant a, which is twice of the distance between the hydrogen-bonded chains, is larger than those in earlier works[3] and that a of α-form is larger than that of γ-form.[3,9] Further, they showed that the hydrogen bond length is longer than that in earlier works[3,7] and also than that of γ-form.[9] Their results are listed in Table II with those of earlier works on the α- and γ-form. They also emphasized that the hydrogen bond is very weak in α-form.

TABLE II
Unit Cell Data of Nylon 6

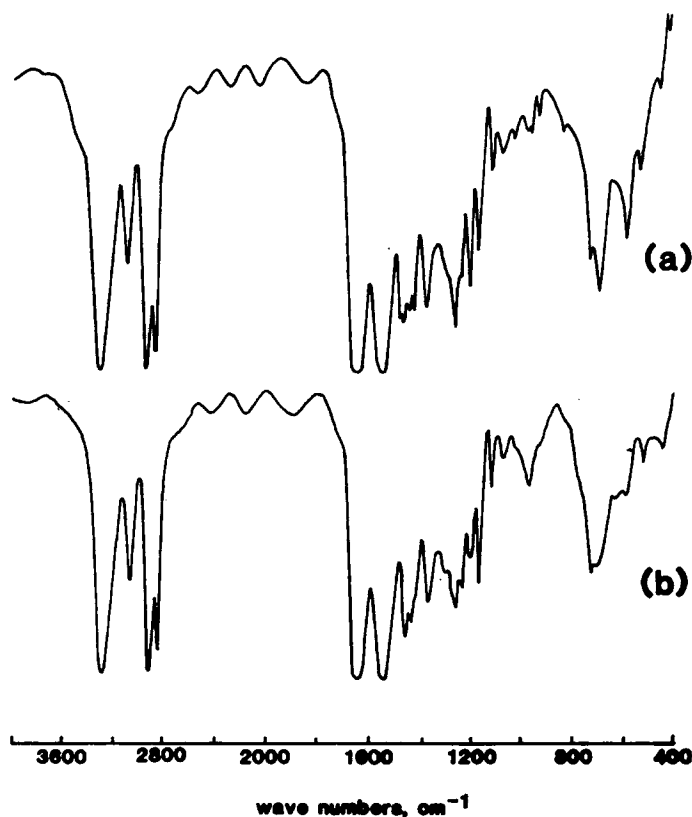| Specimen	Author	Lattice constant[a] a (Å)	Hydrogen bond length (Å)
α-Form	Malta	9.71	2.98
	Holmes	9.56	2.81
γ-Form	Arimoto	9.56	2.83

[a] $a/2$ = distance between hydrogen-bonded chains.

Fig. 4.   FT-IR spectra of nylon 6: (a) α-form; (b) γ-form.

Our NMR study supports Malta's X-ray results. The hydrogen bond of the γ-form was shown to be stronger than that of α-form from the IR spectroscopy.[8,10] We measured FT-IR spectra of both crystals of nylon 6 as shown in Figure 4. The band assigned to CO–NH vibration was found at 976 cm^{-1} for the γ-form and at 930 cm^{-1} for the α-form. The fact indicates that the contribution of structure 4 is higher in γ-form, namely, the hydrogen bond strength is higher in γ-form than in α-form.

Now stereoelectronic effects caused by hydrogen bonds should be discussed. Due to the resonance structures 3 and 4, partial positive charge is produced on
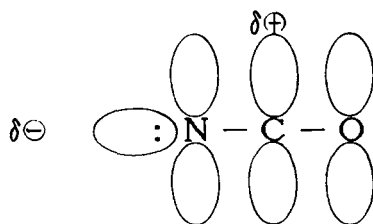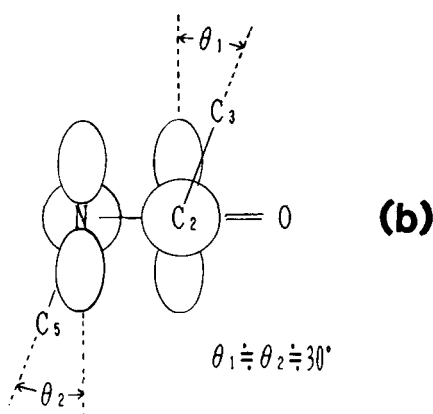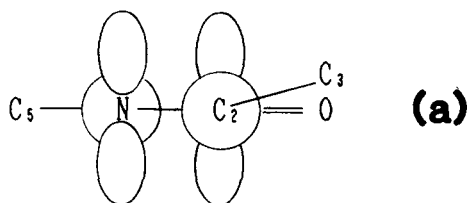
Fig. 5.   Polarization of amide of hydrogen-bonded nylon 6.

Fig. 6.   Conformations and hyperconjugative effects in nylon 6: (a) α-form; (b) γ-form.

π orbitals perpendicular to the plane formed by N—C—O, and partial negative charge is produced on the lone pair of N atoms on the plane, as illustrated in Figure 5.

In α-form all the carbon atoms are on the same plane of N—C—O, so that the interaction between the positive π orbital and methylene carbons at C_3 and C_5 is negligible. In γ-form the dihedral angles θ between the π orbital and the $\sigma(C_2—C_3)$ bond and that between the π orbital and the $\sigma(C_6—C_5)$ bond are about 30°, judging from the X-ray study (Fig. 6). The conformation is very advantageous for hyperconjugation or $\sigma-\pi$ conjugation. Therefore, it is expected that in γ-form the positive π orbital withdraws electrons from C_3 and C_5 carbons and therefore downfield shifts occur at C_3 and C_5. In fact, it was found that $\Delta\delta c$ at C_3 and C_5 is +3.9 ppm.

Fig. 7. Hyperconjugation of 1-adamatyl cation.[14]

The deshielding effect is higher at the β-position (C_3) than at the α-position (C_2) to the formal cation center (C_1). Similar effects were reported on the ^{1}H-NMR and ^{13}C-NMR of 1-adamatyl cation in a super acid by Olah et al. (Fig. 7).[14] They also attributed such a big deshielding at C_3 to hyperconjugation.

Hyperconjugation is a well-defined concept[15,16] in ESR,[17-19] UPS,[20] CT,[21,22] and UV[23] spectroscopy. Recently importance of hyperconjugation on NMR spectroscopy was pointed out by Botkin et al.,[24] Ernst et al.,[25] Brown and Periasamy,[26] Siehl and Walter,[27] and Olah et al.[14] However, their studies do not concern the hyperconjugation in solid-state NMR spectroscopy, with which our study is concerned, but, from their success in dealing with it, our study must be reasonable concerning the use of the concept.

It is not always necessary to take stereoelectronic effects into consideration for solution NMR since σ bonds can rotate freely. However, hyperconjugation is important for identifications of compounds and explanations of spectra for solid-state NMR particularly for NMR of polymers, since conformations are fixed in the solid states.

We conclude as follows:

1. High-resolution solid-state ^{13}C-NMR spectra were studied for α-form and γ-form of nylon 6.

2. The difference of the spectra was explained in terms of intermolecular hydrogen bonds and intramolecular hyperconjugation.

3. Our NMR study agrees well with recent X-ray results and IR studies.

4. We think that hyperconjugation is an important concept to understand structure of polymers and also to elucidate NMR chemical shifts.

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