Computational Characterization of Nylon 4, a Biobased and Biodegradable Polyamide Superior to Nylon 6

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Supporting Information

ABSTRACT: This study is an attempt to develop a theoretical methodology to elucidate or predict the structural characteristics and the physical properties of an isolated polymeric chain and its crystalline state precisely and quantitatively. To be more specific, conformational characteristics of a biobased and biodegradable polyamide, nylon 4, in the free state have been revealed by not only ab initio molecular orbital calculations on its model compound but also nuclear magnetic resonance experiments for the model and nylon 4. Furthermore, the crystal structure and solid-state properties of nylon 4 have been elucidated by density functional theory calculations with a dispersion force correction under periodic boundary conditions. In the free state, the nylon 4 chain forms intramolecular N–H–O=C hydrogen bonds, which force the polymeric chain into distorted conformations including a number of gauche bonds, whereas nylon 4 crystallizes in the fully extended all-trans structure (α form) that is stabilized by intermolecular N–H–O=C hydrogen bonds. The intermolecular interaction energy (ΔE") in the crystal was accurately calculated via a counterpoise (CP) method contrived here to correct the basis set superposition error, and the ultimate crystalline modulus (Eγ) in the chain axis (b axis) direction at 0 K was also evaluated theoretically. The results were compared with those obtained from the α and γ crystalline forms of nylon 6, and, consequently, the superiority of nylon 4 to nylon 6 in thermal stability and mechanical properties was indicated: the ΔE" and Eγ values are, respectively, −214 cal g⁻¹ and 334 GPa (nylon 4), −191 cal g⁻¹ and 316 GPa (α form of nylon 6), and −184 cal g⁻¹ and 120 GPa (γ form of nylon 6). In conclusion, nylon 4 is expected to be put to practical use as a tough environmentally friendly polyamide.

INTRODUCTION

In order to suppress global warming, we are increasingly required to replace chemical production based on fossil resources with manufacture from carbon-neutral feedstock. Nylon 6 is produced by ring-opening polymerization of ε-caprolactam, and its monomeric unit includes six carbon atoms originating from the starting material, benzene, phenol, cyclohexane, or 1-cyclohexanol. If the carbon sources were produced from plants, nylon 6 would become a carbon-neutral material. Nylon 6 was suggested to be degraded by a white rot fungi strain IZU-154, Phanerochaete chrysosporium, and Trametes versicolor through oxidation processes; however, the degradation is so slow that nylon 6 is far from biodegradable.

Nylon 4 is produced from 2-pyrrolidone, which has recently come to be prepared by fermentation of biomass using Escherichia coli from biobased γ-glutamic acid via γ-aminobutyric acid; therefore, nylon 4 can be considered to be biobased and carbon-neutral. Furthermore, it was found that nylon 4 is hydrolyzed to γ-aminobutyric acid by Pseudomonas sp. ND-11 widely inhabiting activated sludge and finally decomposed into CO₂, H₂O, and NO₃⁻. Besides, this polyamide is degraded in vivo.

Nylon 6 is superior in mechanical strength, rigidity, thermal stability, and chemical residence. These favorable properties are partly due to interchain N–H–O=C hydrogen bonds. Nylon 4 also forms so strong interchain hydrogen bonds as to exhibit melting points of 260–265 °C higher than that (225 °C) of nylon 6. This means that, compared with nylon 6, nylon 4 has an advantage of superior thermal resistance and a disadvantage of higher energy costs in annealing and molding processes. Despite the drawback, nylon 4 is expected to become a biobased and biodegradable substitute for nylon 6.

In expectation of future utilization of nylon 4, we have elucidated its structural characteristics and physical properties by computational chemistry and nuclear magnetic resonance (NMR) experiments as follows: (chain characteristics) conformational analysis via molecular orbital (MO) calculations and NMR experiments on its small model compound, N-acetyl-γ-aminobutyric acid N'-methylamide (designated herein as ABAMA, Figure 1) and nylon 4; (crystal structure and properties) density functional theory (DFT) calculations.
on the α crystalline form of nylon 4 under periodic boundary conditions to optimize the crystal structure, evaluate the interchain interaction energy via correction for the basis set superposition error (BSSE), and calculate the crystalline moduli. The solid-state properties of the superposition error (BSSE), and calculate the crystalline interchain interaction energy via correction for the basis set

**RESULTS AND DISCUSSION**

**MO Calculations.** It is well established that small model compounds with the same bond sequence as that of a given polymer can represent conformational characteristics of the polymer; therefore, we have usually employed such model compounds instead of polymers themselves. Here, we have adopted ABAMA as a model for nylon 4.

As for the molecular geometry of ABAMA, the following assumptions may be allowed: the C(==O)−NH atoms lie on a plane, the C−N bond is not rotatable, and the methyl terminal has a C₃ symmetry. Therefore, only internal rotations around bonds 3–6 have been considered here (Figure 1), and hence 81 (=3³) staggered conformers (trans, gauche⁺, and gauche⁻) may be possible under the rotational isomeric state (RIS) approximation. However, inasmuch as the all-trans form of ABAMA has a C₃ symmetry, the gauche⁺ and gauche⁻ conformations of each bond are equivalent in energy, and hence the number of its independent conformers is reduced to 41. Although the 41 conformers underwent the geometrical optimization at the B3LYP/6-311+G(2d,p) level, only 15 conformers reached the local energy minimum (Table 1). Not all dihedral angles of the 15 conformers stay within the standard values of well-defined rotamers such as trans, gauche, and cis conformations. Dihedral angles of the CH₂−C(==O) bond (bond 6) in particular are distributed widely and those of the HN−CH₂ bond (bond 3) are also scattered, whereas those of bonds 4 and 5 are found to be normal. In the γ crystal of nylon 6, the adjacent bonds of the amide group adopt a skew conformation. In fact, the B3LYP optimization with a dispersion force correction (abbreviated as B3LYP-D) for the configuration C(==O) bond rendered dihedral angles of the HN−CH₂ bonds ±111.8° and ±117.5°, respectively. Therefore, these two bonds of aliphatic polyamides seem to be readily variable, and their rotational flexibility allows the polyamides to have a conformation. In the α form, the interchain hydrogen bonds are suggested to be more efficient than in the γ form, whereas,

![Figure 1. (a) Nylon 4 and (b) its model compound, ABAMA with designations of carbon atoms (α, β, and ω) of nylon 4 and hydrogen atoms (A, B, B’, C, C’, D, and D’) and bond numbers (1–8) of ABAMA. (c) Nylon 6.](image)

| k   | dihedral angle, ° | conformation | ΔG° kcal mol⁻¹ |
|-----|------------------|--------------|---------------|
|     | bond             | bond         | medium |     |
| 1⁻  | 180.0            | 180.0        | 180.0       | 180.0     | t | 0.00 |
| 2   | −175.4           | −66.6        | 91.1       | 149.2     | t | −0.31 |
| 3   | −91.4            | 177.7        | 172.2      | 125.9     | g⁺ | −4.65 |
| 4   | −74.7            | 160.8        | −71.6      | −6.6      | t | −2.51 |
| 5   | −88.7            | 179.3        | 67.9       | −153.1    | g⁺ | −3.80 |
| 6   | −84.1            | −61.7        | −172.3     | −117.9    | t | −3.30 |
| 7   | −96.8            | −66.7        | 175.9      | 120.8     | g⁻ | −1.78 |
| 8   | −79.8            | −59.1        | −65.3      | 160.6     | g⁺ | −0.98 |
| 9   | −97.3            | −48.5        | −49.3      | −103.1    | g⁻ | −3.01 |
| 10  | −99.7            | −70.8        | 73.6       | −121.0    | g⁺ | −4.31 |
| 11  | −106.8           | 64.6         | −172.1     | −138.6    | g⁺ | −1.95 |
| 12  | 103.8            | −67.0        | −177.2     | −158.9    | g⁻ | −2.97 |
| 13  | −104.2           | 64.0         | −81.9      | 132.6     | t | −3.11 |
| 14  | −99.6            | 69.6         | 74.2       | −100.2    | g⁻ | −5.25 |
| 15  |                  |              |           |           |     | −5.65 |

The dihedral angle is defined here according to the IUPAC recommendation: trans (t) ≈ 180 ± Δ; gauche⁺ (g⁺) ≈ −60 ± Δ; gauche⁻ (g⁻) ≈ +60 ± Δ, where Δ stands for the allowance. The dihedral angles of bond 6 are distributed too widely to be classified into a few RISs. At the MP2/6-311+G(2d,p)//B3LYP/6-311+G(2d,p) level. Relative to ΔG° of the all-trans conformation. For the bond numbers, see Figure 1. Dimethyl sulfoxide. The molecular geometry was optimized with the dihedral angles fixed at 180° so that the all-trans conformation would be the control for ΔG° and ¹³C NMR chemical shifts.
in the γ form, the optimum packing of the methylene units appears to dominate over the hydrogen bond. Therefore, nyons 4 and 6 prefer the α form, whereas nyons n (n ≥ 8) show the γ preference.

Figure 2 illustrates some conformations with low ΔGk values, showing the formation of N−H···O=C close contacts, that is, intramolecular hydrogen bonds. Here, ΔGk represents the free energy difference of conformer k from that of the all-trans form. For the conformer number k, see Table 1. The ΔGk values including solvation of 2,2,2-trifluoroethanol (TFE) and H···O distances were evaluated to be, respectively, −3.92 kcal mol⁻¹ and 2.00 Å (k = 15), −3.59 kcal mol⁻¹ and 1.94 Å (k = 3), and −2.95 kcal mol⁻¹ and 2.65 Å (k = 14). Therefore, it is obvious that the low ΔGk’s are due to the intramolecular hydrogen bonds.

The trans fractions (p₁’s) of bonds 3−5 were calculated with the ΔGk data according to the conformational classification shown in Table 1. All the p₁ values (see Table 3) are so small as to indicate that ABAMA strongly prefers distorted shapes rich in gauche conformations (Figure 2). Because the p₁ values tend to increase with medium polarity, the intramolecular hydrogen bonds would be weakened or cleaved by the polar solvents.

NMR Experiments. Vicinal Coupling Constants. Figure 3 shows the ¹H NMR spectra observed from three kinds of methylene protons, BB’, CC’, and DD’ (see Figure 1), of ABAMA and nylon 4. The gNMR simulations for ABAMA exactly reproduced the observed spectra to yield the chemical shifts and spin−spin coupling constants. Of the NMR parameters, only vicinal coupling constants, used in the conformational analysis, are listed in Table 2.

The vicinal ¹H−¹H coupling constant (JXY) between protons X and Y can be expressed as a function of trans (p₁) and gauche (p₂) fractions of the centrally intervening bond as follows: between protons A and B (B’) about bond 3

\[ J_{AB} = J_{AB'} = \frac{I_{C1} + I_{C2}}{2} p_1 + \frac{I_C + I_E}{2} p_2 \]

between protons B (B’) and C (C’) about bond 4

\[ J_{BC} = J_{B'C'} = I_{C} p_1 + \frac{I_C + I_E}{2} p_2 \]

and between protons C (C’) and D (D’) about bond 5

\[ J_{BC} = J_{B'C'} = I_{C} p_1 + \frac{I_C + I_E}{2} p_2 \]

Figure 2. Stable conformers of ABAMA with the electrostatic potential surface: (a) k = 15, c'g'g' (‘g’); (b) k = 3, c'g' (‘t’); (c) k = 14, g'c'g’ (‘t’). k is the conformer number (see Table 1), and approximate conformations of bond 6 are written within parentheses. The dotted lines represent intramolecular N−H···O=C hydrogen bonds.

Figure 3. Observed (above) and calculated (below) ¹H NMR spectra of three kinds of methylene protons (from left to right, BB’, CC’, and DD’, for the proton designations, see Figure 1): (a) ABAMA dissolved in chloroform-đ at 45 °C; (b) ABAMA in TFE at 25 °C; (c) nylon 4 in TFE at 25 °C. The number-average and weight-average molecular weights of the nylon 4 sample were determined to be 10.3 and 67.7 kDa, respectively. The molecular weight distribution is shown in Figure S1 (Supporting Information).
that the small values (Table 3); in general, the agreement seems to be fully sets A, B, C, and E show good agreement with the theoretical those of sets D and F are somewhat larger, whereas those of

The proton symbols and bond numbers are defined in Figure 1. The coefficients (J_C's J_D, J_E's, and J_s' of the individual equations, illustrated in Figure 4, were obtained as follows: (set A) from the Karplus equation for the same bond sequence as that of ABAMA; (sets B, D, and F) from MO calculations for ABAMA itself at the B3LYP/6-311++G-(3df,3pd)//B3LYP/6-311+G(2d,p) level; (sets C and E) from experimental coupling constants of a ring compound, 2-(3df,3pd)//B3LYP/6-311+G(2d,p) level; (sets C and E)

By definition, the following relation must always be fulfilled:

\[ p_1 + p_8 = 1 \]  

(6)

The proton symbols and bond numbers are defined in Figure 1. The coefficients (J_C's J_D, J_E's, and J_s' of the individual equations, illustrated in Figure 4, were obtained as follows: (set A) from the Karplus equation for the same bond sequence as that of ABAMA; (sets B, D, and F) from MO calculations for ABAMA itself at the B3LYP/6-311++G-(3df,3pd)//B3LYP/6-311+G(2d,p) level; (sets C and E) from experimental coupling constants of a ring compound, 2-methylpiperidine or cyclohexane, which has a bond sequence similar to that of ABAMA. The numerical values of the coefficients are written in the footnotes of Table 3. Substitution of the observed \( J_{XY} \) values into the above equations yields \( p_1 \) and \( p_8 \) of the individual bonds, and only the \( p_1 \) values are listed in Table 3 because of eq 6.

Compared with the \( p_1 \) values derived from the MO calculations, those of sets D and F are somewhat larger, whereas those of sets A, B, C, and E show good agreement with the theoretical values (Table 3); in general, the agreement seems to be fully acceptable. As discussed above, the MO calculations suggest that the small \( p_1 \) values result from the intramolecular N–H···O=C hydrogen bonds. Therefore, the NMR data also indicate formation of the hydrogen bonds in the solutions.

Inasmuch as both MO and NMR data here suggest that ABAMA forms the strong intramolecular N–H···O=C hydrogen bond, it is probable that the isolated nylon 4 chain also includes the hydrogen bonding. To prove this conjecture, we measured the \(^1\)H NMR spectra of nylon 4 itself and attempted to reproduce the observed spectra using the same geminal and vicinal coupling constants as derived from ABAMA. In Figure 3c, as an example, the measured and calculated spectra of nylon 4 in TFE at 25 °C are compared. It can be seen that both spectra are essentially identical. This fact indicates that nylon 4 has the \( J_{XY} \) and \( p_1 \) values (i.e., conformational distribution) close to those of ABAMA and hence supports the abovementioned conjecture. All spectra observed from nylon 4 dissolved in TFE at different temperatures were reproduced exactly.

\(^{13}\)C NMR Chemical Shifts. Ando et al.\(^{23}\) measured solid-state \(^{13}\)C NMR of nylon 4 via the cross-polarization/magic-angle spinning (MAS), \(^{13}\)C pulse saturation transfer/MAS, and \(^{13}\)C low-power decoupling/MAS techniques, determined the \(^{13}\)C chemical shifts of the crystalline and noncrystalline chains separately, and plotted the chemical shift differences (\( \Delta \delta \)’s, \( i \) carbon species) between the crystalline and amorphous carbons against the carbon position as shown in Figure 5. The \( ^{13}\)C chemical shift differences of nylon 4 between in the crystallite and in a 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) solution were also investigated. As seen from Figure 5, both \( \Delta \delta \)’s depend largely on the carbon position in the backbone, and the two plots (open triangle and square) oscillate similarly. It was suggested that the experimental data would be interpreted in terms of the so-called \( \gamma \) and \( \delta \) substituent effects. The former and latter effects were shown to result from shielding or de-shielding caused by chemical species (atoms) separated from the observed carbon atom by three and four bonds, respectively, thus depending on conformations of the in-between bonds.\(^{26}\) On the basis of these effects, conformational analyses of polymers have been carried out: the \( \delta \) and \( \gamma \) effect parameters are appropriately assumed and weight-averaged over the possible conformations to yield \(^{13}\)C chemical experimental values.\(^{27,28}\) However, it is too difficult to carry out

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### Table 2. Observed Vicinal \(^1\)H–\(^1\)H Coupling Constants of ABAMA\(^{\text{a,b}}\)

| solvent          | temp  \( ^{\circ}\)C | \( J_{ab} \) | \( J_{bc} \) | \( J_{bc'} \) | \( J_{cd} \) | \( J_{cd'} \) |
|------------------|--------------------|----------|----------|----------|----------|----------|
| chloroform-\( d \) | 15                 | 5.85     | 7.88     | 4.94     | 8.07     | 5.18     |
|                  | 25                 | 5.86     | 7.86     | 4.98     | 8.05     | 5.21     |
|                  | 35                 | 5.88     | 7.81     | 5.05     | 8.04     | 5.24     |
|                  | 45                 | 5.89     | 7.79     | 5.10     | 8.02     | 5.26     |
|                  | 55                 | 5.90     | 7.76     | 5.18     | 7.99     | 5.27     |
| TFE              | 15                 | 5.84     | 8.37     | 5.58     | 8.53     | 6.49     |
|                  | 25                 | 5.85     | 8.32     | 5.61     | 8.51     | 6.50     |
|                  | 35                 | 5.86     | 8.29     | 5.63     | 8.45     | 6.53     |
|                  | 45                 | 5.88     | 8.28     | 5.65     | 8.32     | 6.58     |
|                  | 55                 | 5.88     | 8.24     | 5.68     | 8.26     | 6.62     |
| methanol-\( d \)  | 15                 | 8.44     | 6.55     | 6.88     | 6.46     |
|                  | 25                 | 8.39     | 5.66     | 6.62     | 6.49     |
|                  | 35                 | 8.32     | 5.69     | 8.58     | 6.50     |
|                  | 45                 | 8.30     | 5.70     | 8.48     | 6.52     |
|                  | 55                 | 8.24     | 5.71     | 8.38     | 6.53     |
| dimethyl-\( d \)  | 25                 | 8.52     | 5.60     | 8.59     | 6.51     |
|                  | 35                 | 8.55     | 5.62     | 8.54     | 6.54     |
|                  | 45                 | 8.48     | 5.65     | 8.49     | 6.57     |
|                  | 55                 | 8.42     | 5.67     | 8.46     | 6.59     |
|                  | 100                | 8.02     | 5.91     | 8.07     | 6.82     |

\( ^{a}\)In Hz. \( ^{b}\)Not available probably because the NH proton was replaced with deuterium of the solvent.

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\[
J_{CD} = J_{C'D'} = J_{P1} + \frac{J_T + J_G}{2} p_8
\]

(4)

and

\[
J_{C'D} = J_{CD'} = J_{P1} + \frac{J_T + J_G'}{2} p_8
\]

(5)

\[^{\text{4}}\]In Hz. \[^{\text{5}}\]Not available probably because the NH proton was replaced with deuterium of the solvent.

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The numbers \( p_1 \) and \( p_8 \) are plotted in Figure 3c. As an example, the measured and calculated spectra of nylon 4 in TFE at 25 °C are compared. It can be seen that both spectra are essentially identical. This fact indicates that nylon 4 has the \( J_{XY} \) and \( p_1 \) values (i.e., conformational distribution) close to those of ABAMA and hence supports the abovementioned conjecture. All spectra observed from nylon 4 dissolved in TFE at different temperatures were reproduced exactly.

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\[^{\text{13}}\]C NMR Chemical Shifts. Ando et al.\(^{23}\) measured solid-state \(^{13}\)C NMR of nylon 4 via the cross-polarization/magic-angle spinning (MAS), \(^{13}\)C pulse saturation transfer/MAS, and \(^{13}\)C low-power decoupling/MAS techniques, determined the \(^{13}\)C chemical shifts of the crystalline and noncrystalline chains separately, and plotted the chemical shift differences (\( \Delta \delta \)’s, \( i \) carbon species) between the crystalline and amorphous carbons against the carbon position as shown in Figure 5. The \( ^{13}\)C chemical shift differences of nylon 4 between in the crystallite and in a 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) solution were also investigated. As seen from Figure 5, both \( \Delta \delta \)’s depend largely on the carbon position in the backbone, and the two plots (open triangle and square) oscillate similarly. It was suggested that the experimental data would be interpreted in terms of the so-called \( \gamma \) and \( \delta \) substituent effects. The former and latter effects were shown to result from shielding or de-shielding caused by chemical species (atoms) separated from the observed carbon atom by three and four bonds, respectively, thus depending on conformations of the in-between bonds.\(^{26}\) On the basis of these effects, conformational analyses of polymers have been carried out: the \( \delta \) and \( \gamma \) effect parameters are appropriately assumed and weight-averaged over the possible conformations to yield \(^{13}\)C chemical experimental values.\(^{27,28}\) However, it is too difficult to carry out...
Table 3. Trans Fractions of the HN–CH$_2$ (Bond 3), NCH$_2$–CH$_2$ (Bond 4), and CH$_2$–CH$_2$C(=O) (Bond 5) Bonds of ABAMA, Determined from MO Calculations and NMR Experiments

| medium          | temp (°C) | 3: HN–CH$_2$ | 4: NCH$_2$–CH$_2$ | 5: CH$_2$–CH$_2$C(=O) |
|-----------------|-----------|--------------|--------------------|------------------------|
|                 |           | MO           | set A              | set B                  | set C              | set D                  | set E                      | set F                      |
| gas             | 15        | 0.09         | 0.03               | 0.01                  |                      |                      |                          |                          |
|                 | 25        | 0.10         | 0.04               | 0.02                  |                      |                      |                          |                          |
|                 | 35        | 0.10         | 0.04               | 0.02                  |                      |                      |                          |                          |
|                 | 45        | 0.10         | 0.04               | 0.02                  |                      |                      |                          |                          |
|                 | 55        | 0.11         | 0.05               | 0.02                  |                      |                      |                          |                          |
| chloroform      | 15        | 0.22         | 0.08               | 0.06                  |                      |                      |                          |                          |
|                 | 25        | 0.22         | 0.08               | 0.06                  |                      |                      |                          |                          |
|                 | 35        | 0.24         | 0.09               | 0.07                  |                      |                      |                          |                          |
|                 | 45        | 0.21         | 0.09               | 0.08                  |                      |                      |                          |                          |
|                 | 55        | 0.21         | 0.10               | 0.08                  |                      |                      |                          |                          |
| TFE             | 15        | 0.25         | 0.10               | 0.11                  |                      |                      |                          |                          |
|                 | 25        | 0.25         | 0.10               | 0.12                  |                      |                      |                          |                          |
|                 | 35        | 0.24         | 0.11               | 0.12                  |                      |                      |                          |                          |
|                 | 45        | 0.24         | 0.11               | 0.13                  |                      |                      |                          |                          |
|                 | 55        | 0.24         | 0.12               | 0.14                  |                      |                      |                          |                          |
| dimethyl sulfoxide | 25       | 0.25         | 0.11               | 0.12                  |                      |                      |                          |                          |
|                 | 35        | 0.24         | 0.11               | 0.13                  |                      |                      |                          |                          |
|                 | 45        | 0.24         | 0.12               | 0.14                  |                      |                      |                          |                          |
|                 | 55        | 0.24         | 0.12               | 0.14                  |                      |                      |                          |                          |
| chloroform-d    | 15        | 0.21         | 0.19               | 0.10                  | 0.24                  | 0.11                 | 0.12                   | 0.29                     |
|                 | 25        | 0.21         | 0.19               | 0.10                  | 0.25                  | 0.11                 | 0.13                   | 0.29                     |
|                 | 35        | 0.20         | 0.18               | 0.11                  | 0.26                  | 0.11                 | 0.13                   | 0.29                     |
|                 | 45        | 0.20         | 0.18               | 0.11                  | 0.26                  | 0.11                 | 0.13                   | 0.30                     |
|                 | 55        | 0.19         | 0.18               | 0.12                  | 0.27                  | 0.12                 | 0.13                   | 0.30                     |
| TFE             | 15        | 0.22         | 0.19               | 0.12                  | 0.27                  | 0.17                 | 0.19                   | 0.35                     |
|                 | 25        | 0.21         | 0.19               | 0.12                  | 0.27                  | 0.18                 | 0.19                   | 0.35                     |
|                 | 35        | 0.21         | 0.19               | 0.13                  | 0.28                  | 0.18                 | 0.20                   | 0.36                     |
|                 | 45        | 0.20         | 0.18               | 0.13                  | 0.28                  | 0.19                 | 0.21                   | 0.37                     |
|                 | 55        | 0.20         | 0.18               | 0.13                  | 0.28                  | 0.20                 | 0.22                   | 0.37                     |
| methanol-d$_4$  | 15        | 0.21         | 0.19               | 0.10                  | 0.24                  | 0.11                 | 0.12                   | 0.29                     |
|                 | 25        | 0.21         | 0.19               | 0.10                  | 0.25                  | 0.11                 | 0.13                   | 0.29                     |
|                 | 35        | 0.20         | 0.18               | 0.11                  | 0.26                  | 0.11                 | 0.13                   | 0.29                     |
|                 | 45        | 0.20         | 0.18               | 0.11                  | 0.26                  | 0.11                 | 0.13                   | 0.30                     |
|                 | 55        | 0.19         | 0.18               | 0.12                  | 0.27                  | 0.12                 | 0.13                   | 0.30                     |
| dimethyl-d$_4$ sulfoxide | 25 | 0.20         | 0.18               | 0.13                  | 0.28                  | 0.19                 | 0.19                   | 0.35                     |
|                 | 35        | 0.20         | 0.18               | 0.13                  | 0.28                  | 0.19                 | 0.19                   | 0.35                     |
|                 | 45        | 0.20         | 0.18               | 0.13                  | 0.28                  | 0.19                 | 0.20                   | 0.36                     |
|                 | 55        | 0.14         | 0.28               | 0.18                  | 0.20                 | 0.18                  | 0.20                   | 0.36                     |

“By the coefficients calculated from the Karplus equation proposed by Ludvigsen et al.”

“By the coefficients calculated from MO calculations for ABAMA itself at the B3LYP/6-311++G(3df,3pd)//B3LYP/6-311+G(2d,p) level: $J_{C1} = 1.52$, $J_{C2} = 3.54$, $J_{C3} = 8.83$, and $J_{C4} = 4.41$ Hz. By coupling constants of 2-methylpiperidine: for example, for chloroform-d, $J_{C1} = 12.00$, $J_{C2} = 3.06$, $J_{C3} = 12.00$, $J_{C4} = 4.05$, $J_{C5} = 2.34$, and $J_{C6} = 2.80$ Hz (for the details, see the literature).”

“By the coefficients calculated from MO calculations for ABAMA itself at the B3LYP/6-311++G(3df,3pd)//B3LYP/6-311+G(2d,p) level: $J_{C1} = 11.33$, $J_{C2} = 4.18$, $J_{C3} = 11.80$, $J_{C4} = 2.53$, $J_{C5} = 3.49$, and $J_{C6} = 1.42$ Hz. By coupling constants of cyclohexane: $J_{C1} = 13.12$, $I_{C2} = 3.65$, $J_{C3} = 13.12$, $I_{C4} = 3.65$, $J_{C5} = 2.96$, and $I_{C6} = 3.65$ Hz.”

“By the coefficients calculated from MO calculations for ABAMA itself at the B3LYP/6-311++G(3df,3pd)//B3LYP/6-311+G(2d,p) level: $J_{C1} = 11.75$, $I_{C2} = 3.71$, $J_{C3} = 12.01$, $I_{C4} = 1.95$, $I_{C5} = 5.73$, and $I_{C6} = 1.85$ Hz.”

Not available because the corresponding vicinal coupling constant was not observed.

Conformational analysis of nylon 4 and ABAMA in this manner, because, as discussed above, dihedral angles of bonds 3 and 6 are variable to a large extent; therefore, it is impossible to simulate the $^{13}$C chemical shifts with a small number of $\delta$ and $\gamma$ effect parameters.

Instead, we calculated the chemical shift differences ($\Delta \delta$) of ABAMA between in the all-trans conformation and in the free state. The chemical shift $\langle \delta \rangle$ of carbon $i$ of ABAMA in the free state can be calculated as the weight average over all the possible conformations

$$
\langle \delta \rangle = \frac{\sum \delta_i \exp \left( -\frac{\Delta \delta_i}{RT} \right)}{\sum \exp \left( -\frac{\Delta \delta_i}{RT} \right)}
$$

where $\delta_i$ is the $^{13}$C chemical shift of carbon $i$ of conformer $k$, $\Delta G_k$ is given in Table 1, $R$ is the gas constant, and $T$ is the
and solutions). Both vicinal $^1$H coupling constants and $^{13}$C chemical shifts show that the free nylon 4 chain tends to form the intramolecular hydrogen bonds.

The lattice constants optimized at the B3LYP-D/6-31G(d,p) level are as follows: $\alpha$ form of nylon 4, $a = 9.56$ (9.56) Å, $b = 17.48$ (17.24) Å, $c = 7.48$ (8.01) Å, $\beta = 68.0^\circ$ (67.5$^\circ$); $\gamma$ form of nylon 6, $a = 8.89$ (9.33) Å, $b = 16.96$ (16.88) Å, $c = 4.80$ (4.78) Å, $\beta = 125.4^\circ$ (121$^\circ$).

Figure 5. $^{13}$C NMR chemical shift differences of ABAMA and nylon 4: (●) ABAMA in the gas phase, from eq 8; (▲) ABAMA in TFE, from eq 8; (△) nylon 4 in the amorphous phase, from $\Delta\delta = \delta_{\text{crystalline}} - \delta_{\text{amorphous}}$; (□) nylon 4 in the HFIP solution, from $\Delta\delta = \delta_{\text{crystalline}} - \delta_{\text{solution}}$. $i$ indicates the carbon species (C=O, “CH$_2$,”CH$_2$, and “CH$_3$ see Figure 1a).

Figure 6. Structure of the $\alpha$ form of nylon 4, optimized at the B3LYP-D/6-31G(d,p) level ($R = 0.253$ defined in eq 10); (above) top and (below) side views. The hydrogen bond geometry (N–H···O=C) of nylon 4 was calculated by the PLATON program; $N=H–O=C$ 1.02 Å; $N=H–O=C$ 1.81 Å; $N=O–C$ 2.819 Å; $N=H–O=C$ 168$^\circ$. The crystalline moduli in the $a$, $b$ (chain axis), and $c$ axis directions were evaluated to be 53.6, 334, and 16.8 GPa, respectively.

Structure of the $\alpha$ Crystalline Form of Nylon 4, Optimized by the B3LYP-D Calculation. The lattice constants optimized at the B3LYP-D/6-31G(d,p) level are as follows: $\alpha$ form of nylon 4, $a = 9.50$ (9.29) Å, $b = 12.36$ (12.24) Å, $c = 7.39$ (7.97) Å, $\beta = 111.6^\circ$ (114.5$^\circ$); $\gamma$ form of nylon 6, $a = 9.56$ (9.56) Å, $b = 17.48$ (17.24) Å, $c = 7.48$ (8.01) Å, $\beta = 68.0^\circ$ (67.5$^\circ$); $\gamma$ form of nylon 6, $a = 8.89$ (9.33) Å, $b = 16.96$ (16.88) Å, $c = 4.80$ (4.78) Å, $\beta = 125.4^\circ$ (121$^\circ$). Here, the experimental data are written in the parentheses. $\Delta\delta$ The agreement between theory and experiment is satisfactory. Milani et al. also optimized the $\alpha$ and $\gamma$ structures of nylon 6 at the same level and derived slightly different lattice constants from ours; however, the discrepancies may stay within allowances of the structural optimization. Figure 6 shows the optimized crystal cell of the nylon 4.
of the crystal structure by Fredericks et al. resulted in calculated structure factors, respectively. The original analysis be estimated from basis set and hence is termed B, calculated with basis sets {AB} of both molecules, and this basis, the interaction energy (from b to d), the BSSE would approach a certain value, BSSE(∞) (see Figure 8).

Figure 7. Schematic illustration of the CP method proposed herein to correct the BSSE of polymer crystals: (above) side and (below) top views. (a) Target chain of infinite length. (b–d) Target chain surrounded by ghost chains of infinite length. As the number (n_g) of ghost chains increases (from b to d), the BSSE would approach a certain value, BSSE(∞) (see Figure 8).

\[ R = \frac{\sum |F_{\text{obs}}| - F_{\text{calc}}|}{\sum F_{\text{obs}}} \]  

(10)

was obtained as 0.253. Here, \( F_{\text{obs}} \) and \( F_{\text{calc}} \) are the observed and calculated structure factors, respectively. The original analysis of the crystal structure by Fredericks et al. resulted in \( R = 0.273 \). Thus, the present DFT-D calculations yielded somewhat better agreement with the observation.

**Intermolecular Interaction Energies of Crystals of Nylons 4 and 6.** The intermolecular interaction energy (\( \Delta E \)) between molecules A and B may be simply estimated from

\[ \Delta E = E_{\text{AB}} - E_{\text{A}} - E_{\text{B}} \]  

(11)

where \( E_{\text{AB}} \) is the energy of the complex of molecules A and B, \( E_{\text{A}} \) and \( E_{\text{B}} \) calculated with basis sets \{AB\} of both molecules, and \( E_{\text{A}} \) \( (E_{\text{B}}) \) is the energy of molecule A (B) calculated with the basis set \{A\} \{B\}. However, it is well known that the \( \Delta E \) value includes the so-called BSSE. To eliminate the BSSE, the counterpoise (CP) method has often been employed. On this basis, the interaction energy (\( \Delta E_{\text{CP}} \)) is derived from

\[ \Delta E_{\text{CP}} = E_{\text{AB}} - E_{\text{A}} - E_{\text{B}} \]  

(12)

Here, for example, \( E_{\text{A}} \) is the energy of molecule A, calculated with basis sets \{AB\}; molecule B supplies only its basis set and hence is termed ghost. Therefore, the BSSE may be estimated from

\[ \text{BSSE}_{\text{g}} = E_{\text{SC}} - E_{\text{A}} - E_{\text{B}} \]  

(13)

For three-dimensional crystals in which polymeric chains of infinite length are packed densely, we have devised a suitable CP method (Figure 7). The BSSE per repeating unit may be denoted as

\[ \text{BSSE}_{\text{g}} = E_{\text{SC}} - E_{\text{A}} - E_{\text{B}} \]  

(14)

Therefore, the interaction energy per repeating unit, based on the CP method, can be calculated from

\[ \Delta E_{\text{CP}}(n_g) = \left( \frac{E_{\text{Crystal}}}{Z} - E_{\text{SC}} \right) - \text{BSSE}(n_g) \]  

(15)

where \( E_{\text{Crystal}} \) is the total energy of the crystal including Z repeating unit, and \( E_{\text{SC}} \) is the SC energy with the dispersion force correction. The \( E_{\text{CP}}(n_g) \), \( E_{\text{SC}} \), and \( E_{\text{SC}} \) terms are evaluated per repeating unit. In principle, the \( E_{\text{CP}}(n_g) \) value must become more reliable (freer from the BSSE) with increasing domain size, that is, the number (\( n_g \)) of ghost chains (see Figure 7). Ultimately, the most reliable BSSE can be derived from

\[ \text{BSSE}_{\text{g}} = \lim_{n_g \to \infty} \text{BSSE}(n_g) \]  

(16)

From BSSE\( (n_g) \), we can obtain the ideal interaction energy, \( E_{\text{CP}}(\infty) \). In this study, the \( E_{\text{CP}}(\infty) \) and \( E_{\text{SC}} \) energies were calculated at the B3LYP/6-31G(d,p) and B3LYP/pob-TZVP levels, and the \( E_{\text{Crystal}} \) and \( E_{\text{SC}} \) energies were evaluated at the same levels with the dispersion force correction (B3LYP-D/6-31G(d,p) and B3LYP-D/pob-TZVP).

Figure 8 shows the BSSE\( (n_g) \) versus \( n_g \) plot for the \( \alpha \) form of nylon 4, in which the magnitude of BSSE\( (n_g) \) increases with \( n_g \) and finally converges on a horizontal line: BSSE\( (n_g) = -6.06 \text{ kcal mol}^{-1} \) (B3LYP/6-31G(d,p)) or -5.24 kcal mol\(^{-1}\) (B3LYP/pob-TZVP). The \( \Delta E_{\text{CP}}(\infty) \) energy was derived from the BSSE\( (\infty) \) with eq 15 as shown in Table 4. For more detailed numerical data, see Table S5 (Supporting Information). Similarly, the \( \Delta E_{\text{CP}}(\infty) \) energies of nylon 6 were evaluated. Because nylon 4 is different from nylon 6 in monomer size, the \( \Delta E_{\text{CP}}(\infty) \) value was recalculated in two units: kcal per mol of the skeletal bond; cal g\(^{-1}\). The scaled values suggest that nylon 4 would be more thermally stable than nylon 6. Actually, the melting point of nylon 4 has been observed in the range of 260–265 °C, whereas the equilibrium melting point (\( T_m \)) of nylon 6 was determined to be 225 °C. However, it should be noted that the
Appendix A (Supporting Information) are the sti
thermodynamically stable than the
γ
approach
A
fi
mol
forms, corrected for the BSSE by our CP method, is 0.09 kcal
largest modulus that the polymer can exhibit.43 Shown in
comprise crystalline and amorphous regions, the crystalline
may be the most important characteristics especially from a

Figure 8. BSSE of the α form of nylon 4 as a function of the number
(n_g) of ghost chains. As n_g increase, the BSSEs at the B3LYP/6-
31G(d,p) (filled circle) and B3LYP/pob_TZVP (filled square) levels
approach −6.06 and −5.24 kcal mol\(^{-1}\) (horizontal dotted lines),
respectively. A function of \(A + B \exp(-n_g/C)\) (dotted curve)
was fitted to the calculated data, where \(A, B,\) and \(C\) are adjustable
parameters and \(A\) corresponds to BSSE(∞).

\[\Delta E_{CP}(∞) = \Delta H_{\text{therm}} - \Delta S_{\text{therm}}\]

It is known that, for nylon 6, the α form is more
thermodynamically stable than the γ form.16,17,37,41,42 The
energy difference (\(E_{\alpha} - E_{\gamma}\)) between the two crystalline
forms, corrected for the BSSE by our CP method, is 0.09 kcal
mol\(^{-1}\) (6-31G(d,p)) or −0.59 kcal mol\(^{-1}\) (pob_TZVP), and
other studies17,41,42 have also calculated the \(E_{\alpha,\gamma}\) values
of nylon 6 to be −0.29, −0.323, and −0.50 kcal mol\(^{-1}\).

Crystal Elasticity. As for polymers, mechanical properties
may be the most important characteristics especially from a
practical point of view. Inasmuch as semicrystalline polymers
comprise crystalline and amorphous regions, the crystalline
modulus in the chain axis direction at 0 K is, in principle,
the largest modulus that the polymer can exhibit.53 Shown in
Appendix A (Supporting Information) are the stiffness and
compliance tensors calculated for the α form of nylon 4 and
the α and γ forms of nylon 6. The compliance tensor yields
Young’s moduli (\(E_{\alpha}, E_{\beta},\) and \(E_{\gamma}\)) in the a, b (chain axis),
and c directions of the crystal. In Table 5, the calculated
modulus at 0 K are compared with other theoretical and experimental
data. Most of the experimental values were determined from X-ray
diffraction measurements at room temperature. Therefore, it is
natural that the crystalline moduli calculated here are larger than the experimental
values, because the crystalline modulus depends on the temperature
(cf. \(E_{\gamma}\)'s (100 and 270 GPa) of the α form of nylon 6 at 18 and

\[E_{\alpha} \sim E_{\beta} \sim (\gamma) > E_{\gamma}\]

Table 5. Crystalline Moduli of Nylons 4 and 6

| literature | crystalline modulus, GPa | temp, °C |
|------------|--------------------------|----------|
| theoretical (this study) | nylon 4, α Form | 53.6 | 16.8 | −273 |
| Dasgupta41 1996 | 243 |
| Peeters45 2002 | 389 |
| theoretical (this study) | nylon 6, α Form | 44.5 | 19.4 | −273 |
| Manley46 1973 | 244 | 263 |
| Tashiro47 1981 | 312 |
| Dasgupta41 1996 | 235 |
| Peeters45 2002 | 334 |
| experimental | Sakura50 1964 | 25 |
| Manley46 1973 | 183 |
| Miyasaka44 1980 | 100 | 18 |
| Tashiro47 1981 | 19 |
| Peeters45 2002 | 44.5 | 316 | 19.4 |

Table 4. Interaction Energies (\(\Delta E_{CP}(∞)\)) at the B3LYP-D Level of Theory, Corrected by the CP Method for the BSSEs of
Nylons 4 and 6

| crystal form | basis set | \(E_{\text{Cryst}}/Z - E_{\text{SC}+\text{D}}\) | BSSE(∞) | \(\Delta E_{CP}(∞)\) |
|-------------|-----------|-----------------|---------|-----------------|
| nylon 4 α   | 6-31G(d,p) | −23.96          | −6.06   | −17.90          |
|              | pob_TZVP  | −23.49          | −5.24   | −18.25          |
| nylon 6 α   | 6-31G(d,p) | −28.63          | −7.38   | −21.25          |
|              | pob_TZVP  | −29.32          | −7.67   | −21.65          |
| nylon 6 γ   | 6-31G(d,p) | −27.60          | −7.10   | −20.50          |
|              | pob_TZVP  | −28.98          | −8.20   | −20.78          |

**CONCLUSIONS**

The MO calculations on the model compound, ABAMA, well
reproduced not only the bond conformations determined from

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NMR vicinal $^1$H–$^1$H coupling constants but also the conformational dependence of $^{13}$C NMR chemical shifts of nylon 4 existing in the amorphous and solution environments. These facts show that the nylon 4 chain in itself tends to lie in distorted conformations rich in gauche states because of intramolecular $\text{N}–\text{H}–\text{O}≡\text{C}$ hydrogen bonds. The DFT calculations at the B3LYP/6-31G(d,p) level including the dispersion force correction under the three-dimensional periodic boundary condition reproduced the experimental crystal structures of nyons 4 and 6. A CP method for correcting the BSSE of polymer crystals has been devised and applied to the three crystalline forms to yield the following interaction energies: $-214$ cal g$^{-1}$ ($\alpha$ form of nylon 4); $-191$ cal g$^{-1}$ ($\alpha$ form of nylon 6); and $-184$ cal g$^{-1}$ ($\gamma$ form of nylon 6). Therefore, nylon 4 is suggested to be more thermally stable than nylon 6. The B3LYP-D calculations also yielded the crystalline moduli parallel to the crystalline $a$, $b$, and $c$ axes. As the maximum stiffness, Young’s moduli in the chain axis ($b$ axis) direction of the crystals at 0 K were predicted: 334 GPa ($\alpha$ form of nylon 4); 316 GPa ($\alpha$ form of nylon 6); and 120 GPa ($\gamma$ form of nylon 6). These data suggest that nylon 4 is also superior to nylon 6 in stiffness. Because of the potential carbon neutrality and biodegradability, nylon 4 will be used for strong environmentally friendly materials and, probably, also biomedical materials left in human bodies, such as sutures for surgery, whereas its biodegradability would be disadvantageous for the use of durable materials kept long in the environment, for example, fishing lines and nets. In conclusion, nylon 4 will be partly substituted for nylon 6 and open up the possibility of new functional materials. The computational characterization developed here can also be applied to other polymers, furthermore, for molecular design of new polymers.

## METHODS

**Materials.** *Synthesis of Model Compound, ABAMA.* The model compound, ABAMA, was, in principle, prepared by reference to previous studies.52,53 Aqueous solution of methylamine (40%, 40 mL) was added to ethyl 4-aminobutyrate hydrochloride (2.5 g, 15 mmol), stirred at 0 °C for 15 min, and then condensed on a rotary evaporator. The residue was dissolved in a small amount of methanol and added dropwise to petroleum ether to yield a white precipitate. The precipitate was filtered, dissolved in methanol, and dropped into tetrahydrofuran including 7% methylamine to yield a white solid. After removal of the precipitate, the filtrate was condensed and dried under reduced pressure to yield a yellow oily product, which was identified as ABAMA by $^1$H and $^{13}$C NMR and electrospray ionization mass spectrometry (ESI MS).

$^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 1.85 (quin, 2H, CH$_2$CH$_2$CH$_2$), 2.00 (s, 3H, CH$_3$C≡O), 2.26 (t, 2H, CH$_2$CH$_2$C≡O), 2.83 (d, 3H, NHCH$_3$), 3.31 (q, 2H, NHCH$_2$), 6.34 (br s, 2H, NH); $^{13}$C NMR (CDCl$_3$, $\delta$): 23.2 (CH$_2$C≡O), 25.6 (CH$_2$CH$_2$CH$_2$), 26.4 (NHCH$_3$), 33.8 (CH$_2$CH$_2$C≡O), 39.2 (NHCH$_3$), 171.2 (CH$_3$C≡O), 173.9 (CH$_2$CH$_2$C≡O); ESI MS m/z: 159.1122 [M + H$^+$], calc for C$_4$H$_7$O$_2$N$_2$: 159.1128. m/z: 157.0976 [M – H$^-$], calc for C$_4$H$_7$O$_2$N$_2$: 157.0983.

**Nylon 4.** The nylon 4 sample was supplied by the Biomedical Research Institute of Advanced Industrial Science and Technology (AIST).4,8,9,11 The molecular weight distribution was measured by TOSOH Analysis and Research Center Co., Ltd. on a TOSOH HLC-8220GPC system equipped with two TOSOH TSKgel Super AWM-H columns and a refractive index detector under the following conditions: eluting solvent, HFIP including sodium trifluoroacetate (10 mM); polymer concentration, 1 mg mL$^{-1}$; column temperature, 40 °C; flow rate, 0.3 mL min$^{-1}$; injection volume, 20 μL; molecular weight calibration, poly(methyl methacrylate) standards. The number-average and weight-average molecular weights were evaluated to be 10.3 and 67.7 kDa, respectively. The size-exclusion chromatographic (SEC) differential curve is shown in Figure S1 (Supporting Information).

**1H NMR Measurements.** $^1$H NMR spectra of ABAMA were recorded at 400 MHz on a JEOL JNM-ECX400 spectrometer equipped with a variable temperature control unit in the Center for Analytical Instrumentation of Chiba University. The typical conditions were as follows: scan, 32; 90° pulse width, 12 μs; acquisition time, 6.6 s; recycle delay, 5.0 s; temperature range, 15 or 25 °C; temperature interval, 10 °C. The free induction decay was zero-filled before the Fourier transform so as to yield enough digital resolution for the subsequent spectrum simulation.

The model compound was dissolved at a concentration of 50 mM in chloroform-$d$, methanol-$d_4$, or dimethyl-$d_6$ sulfoxide, injected into a 5 mm NMR sample tube, and underwent the measurement. However, the TFE solution was prepared differently: ABAMA was dissolved in nondeuterated TFE and injected into a 3 mm glass tube (coaxial insert), the tube was inserted into a normal 5 mm one, and the space between them was filled before the Fourier transform so as to yield enough chemical shifts and $^1$H–$^1$H coupling constants. $^1$H NMR of nylon 4 was measured and analyzed similarly.

**MO Calculations of the Model Compound.** MO calculations of ABAMA were carried out with the Gaussian 09 program19 installed on an HPC Silent-SCC T2 workstation. For each conformer, the molecular geometry was fully optimized at the B3LYP/6-311+G(2d,p) level under tight convergence, thermochemical energies at 25 °C and 1 atm were computed by the frequency calculation at the same level, and an accurate electronic energy was calculated at the MP2/6-311+G(2d,p) level. The Gibbs-free energy ($\Delta G_0$) of conformer $k$ was evaluated from the MP2 electronic and B3LYP thermochemical energies, being expressed herein as the
difference from that of the all-trans conformer. The solvation effects on the MP2 electronic energy were also evaluated by the polarizable continuum model using the integral equation formalism variant (IEF-PCM).65

**DFT Calculations on Crystal Structures under Periodic Boundary Conditions.** DFT calculations under the periodic boundary condition were carried out with the CRYSTAL14 program installed in an HPC 5000-XBW216TS-Silent workstation. The initial data (i.e., lattice constants and atomic positions) for the structural optimization of the α forms6 of nylon 4 and the α6,68 and γ16 forms of nylon 6 were taken from the crystal structures determined by X-ray diffraction, and the total energy was minimized under the following conditions: DFT, B3LYP with a dispersion force correction (B3LYP-D) described below; basis set, 6-31G(d,p); space group, P21 (α form) or P2_1/a (γ form); self-consistent field (SCF) convergence threshold, 10^{-7}; truncation criteria for bielectronic integrals, 10^{-7}, 10^{-7}, 10^{-7}, and 10^{-7}; and 10^{-14}; integration grid, 75 radial and 974 angular points; Fock/Kohn–Sham matrix mixing, 80% (with the modified Brody method),67 shrinking factor, 4.

**Dispersion Force Correction.** As often pointed out, the dispersion force correction (B3LYP-D) described below; basis set, 6-31G(d,p); space group, P21 (α form) or P2_1/a (γ form); self-consistent field (SCF) convergence threshold, 10^{-7}; truncation criteria for bielectronic integrals, 10^{-7}, 10^{-7}, 10^{-7}, and 10^{-7}; and 10^{-14}; integration grid, 75 radial and 974 angular points; Fock/Kohn–Sham matrix mixing, 80% (with the modified Brody method),67 shrinking factor, 4.

The steric and van der Waals radii (R_{stic} and R_{vdW}) of atoms i and j represent the numbers (1–6) of the Voigt notation, ε is the rank-2 symmetric tensor of pure strain, and E_{Crystal} and V are the total energy and volume per crystal cell, respectively.

The compliance tensor, S, is the inverse matrix of C, and the S tensor of the monoclinic lattice is expressed as

\[
S = \frac{1}{V} \frac{\partial^2 E_{Crystal}}{\partial u \partial v}
\]

where u and v represent the numbers (1–6) of the Voigt notation, ε is the rank-2 symmetric tensor of pure strain, and E_{Crystal} and V are the total energy and volume per crystal cell, respectively.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b00915.

SEC differential curve of nylon 4; ^{13}C NMR chemical shifts of ABAMA, calculated at the B3LYP/6-31+ +G(3df,3pd) level; fractional coordinates of the α form of nylon 4, optimized at the B3LYP-D/6-31G(d,p) level; optimized and experimental Cartesian coordinates of the
α form of nylon 4; observed and calculated structure factors of the α form of nylon 4; crystal energies, SC energies, BSSEs, and interaction energies of nylons 4 and 6; stiffness and compliance tensors of the α form of nylon 4 and the α and γ forms of nylon 6 (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Nylon. List of Synthetic Polymers, Polyamide, Thermoplastic, Peptide Bond, Condensation Polymer, Fiber, Nylon 6-6, Nylon 6, Ballistic Nylon, Ripstop Nylon, Nylon-Eating Bacteria, Surhone, L. M., Timpledon, M. T., Marselen, S. F., Eds.; Betascript Publishing: VDM Publishing House: Beau Bassin, Mauritius, 2010.

(2) Deguchi, T.; Kakezawa, M.; Nishida, T. Nylon biodegradation by lignin-degrading fungi. Appl. Environ. Microbiol. 1997, 63, 329–331.

(3) Deguchi, T.; Kitakoa, Y.; Kakezawa, M.; Nishida, T. Purification and characterization of a nylon-degrading enzyme. Appl. Microbiol. 1998, 64, 1366–1371.

(4) Yamano, N.; Kawasaki, N.; Takeda, S.; Nakayama, A. Production of 2-pyrrolidone from biobased glutamate by using Escherichia coli. J. Polym. Environ. 2013, 21, 528–533.

(5) Hashimoto, K.; Hamano, T.; Okada, M. Degradation of several polyamides in soils. J. Appl. Polym. Sci. 1994, 54, 1579–1583.

(6) Hashimoto, K.; Sudo, M.; Ohta, K.; Sugimura, T.; Yamada, H.; Aoki, T. Biodegradation of nylon4 and its blend with nylon6. J. Appl. Polym. Sci. 2002, 86, 2307–2311.

(7) Hashimoto, K.; Sudo, M.; Sugimura, T.; Inagaki, Y. Synthesis of novel block copolymers containing polyamide4 segments and control of their biodegradability. J. Appl. Polym. Sci. 2004, 92, 3492–3498.

(8) Kawasaki, N.; Nakayama, A.; Yamano, N.; Takeda, S.; Kawata, Y.; Yamamoto, N.; Aiba, S. Synthesis, thermal and mechanical properties and biodegradation of branched polyamide 4. Polym. Degrad. Stabil. 2005, 46, 9987–9993.

(9) Yamano, N.; Nakayama, A.; Kawasaki, N.; Yamamoto, N.; Aiba, S. Mechanism and characterization of polyamide 4 degradation by Pseudomonas sp. J. Polym. Environ. 2008, 16, 141–146.

(10) Tachibana, K.; Hashimoto, K.; Yoshikawa, M.; Okawa, H. Isolation and characterization of microorganisms degrading nylon 4 in the composted soil. Polym. Degrad. Stab. 2010, 95, 912–917.

(11) Yamano, N.; Kawasaki, N.; Ida, S.; Nakayama, Y.; Nakayama, A. Biodegradation of polyamide 4 in vivo. Polym. Degrad. Stab. 2017, 137, 281–288.

(12) Galanty, P. G. In Polymer Data Handbook; Mark, J. E., Ed.; Oxford University Press: New York, USA, 1999; pp 180–185.

(13) Dachs, K.; Schwartz, E. Pyrrolidone, capryllactam and laurolactam as new monomers for polyamide fibers. Angew. Chem., Int. Ed. 1962, 1, 430–435.

(14) Mandelkern, L. Crystallization of Polymers Volume 1. Equilibrium Concepts, 2nd ed.; Cambridge University Press: Cambridge, U.K., 2002; Chapter 6.

(15) Flory, P. J. Statistical Mechanics of Chain Molecules; Wiley & Sons: New York, USA, 1969.

(16) Arimoto, H.; Ishibashi, M.; Hirai, M.; Chatani, Y. Crystal structure of the γ-form of nylon 6. J. Polym. Sci., Part A: Gen. Pap. 1965, 3, 317–326.

(17) Galimberti, D.; Quarti, C.; Milan, A. Polyorphism of even nylons revisited through periodic quantum chemical calculations. Polymer 2015, 67, 167–173.

(18) IUPAC. Compendium of Chemical Terminology (the “Gold Book”), 2nd ed.; McNaught, A. D., Wilkinson, A., Eds.; Blackwell Scientific Publications: Oxford, U.K., 1997.

(19) Budzelaar, P. H. gNMR, version 5.0; IvorySoft & Adept Scientific plc: Letchworth, U.K., 2004.

(20) Ludvigsen, S.; Andersen, K. V.; Poulsen, F. M. Accurate measurements of coupling constants from two-dimensional nuclear magnetic resonance spectra of proteins and determination of α-angles. J. Mol. Biol. 1991, 217, 731–736.

(21) Sasanuma, Y.; Hattori, S.; Imazu, S.; Ikeda, S.; Kaizuka, T.; Iijima, T.; Sawanobori, M.; Azam, M. A.; Law, R. V.; Steinke, J. H. G. Conformational analysis of poly(ethylene imine) and its model compounds: Rotational and intermolecular isomerizations and intramolecular and intermolecular hydrogen bonds. Macromolecules 2004, 37, 9169–9183.

(22) Garbisch, E. W.; Griffith, M. G. Proton couplings in cyclohexane. J. Am. Chem. Soc. 1968, 90, 6543–6544.

(23) Kubo, K.; Ando, I.; Shiibashi, T.; Yamamoto, T.; Komoto, T. Conformations and 13C NMR chemical shifts of some polyamides in the solid state as studied by high-resolution 13C NMR spectroscopy. J. Polym. Sci., Polym. Phys. Ed. 1991, 29, 57–66.

(24) Pillala, K.; Kleinpeter, E. Carbon-13 NMR Chemical Shifts in Structural and Stereochemical Analysis; VCH Publishers: New York, USA, 1994.

(25) Tonelli, A. E. NMR Spectroscopy and Polymer Microstructure: The Conformational Connection; Wiley-VCH Publishers: New York, USA, 1989.

(26) Bovey, F. A.; Mirau, P. A. NMR of Polymers; Academic Press: New York, USA, 1996.

(27) Sasanuma, Y.; Iwata, T.; Kato, Y.; Kato, H.; Yarita, T.; Kinugasa, S.; Law, R. V. Carbon-13 NMR chemical shifts of dimeric model compounds of poly(propylene oxide): A proof of existence of the (C−H−O) attraction. J. Phys. Chem. A 2001, 105, 3277–3283.

(28) Sasanuma, Y. In Annual Reports on NMR Spectroscopy; Webb, G. A., Ed.; Academic Press: New York, USA, 2003; Vol. 49, pp 213–280.

(29) Flory, P. J. Principles of Polymer Chemistry; Cornell University Press: Ithaca, NY, 1953; pp 601–602.

(30) Flory, P. J. Theoretical predictions on the configurations of polymer chains in the amorphous state. J. Macromol. Sci., Part B: Phys. 1976, 12, 1–11.

(31) Flory, P. J. Conformations of macromolecules in condensed phases. Pure Appl. Chem. 1984, 56, 305–312.

(32) Flory, P. J.; Williams, A. D. Configurational statistics of polyamide chains. J. Polym. Sci., Part A-2: Polym. Phys. 1967, 5, 399–415.

(33) Saunders, P. R. The unperturbed dimensions of nylon 66. J. Polym. Sci., Part A: Gen. Pap. 1964, 2, 3765–3770.

(34) Sasanuma, Y. Conformational characteristics, configurational properties, and thermodynamic characteristics of poly(ethylene terephthalate) and poly(ethylene-2,6-naphthalate). Macromolecules 2009, 42, 2854–2862.

(35) Fredericks, R. J.; Doyne, T. H.; Sprague, R. S. Crystallographic studies of nylon 4. I. Determination of the crystal structure of the α
polymorph of nylon 4. J. Polym. Sci., Part A-2: Polym. Phys. 1966, 4, 899–911.

(36) Holmes, D. R.; Bunn, C. W.; Smith, D. J. The crystal structure of polyacrylamide: Nylon 6. J. Polym. Sci. 1955, 17, 159–177.

(37) Quarti, C.; Milani, A.; Civalieri, B.; Orlando, R.; Castiglioni, C. Ab initio calculation of the crystalline structure and IR spectrum of polymers: Nylon 6 polymorphs. J. Phys. Chem. B 2012, 116, 8299–8311.

(38) Spek, A. L. Structure validation in chemical crystallography. Acta Crystallogr., Sect. D: Struct. Biol. 2009, 65, 148–155.

(39) Boys, S. F.; Bernardi, F. The calculation of small molecular interactions by the differences of separate total energies. Some procedures with reduced errors. Mol. Phys. 1970, 19, 553–566.

(40) van Duinenveldt, F. B.; van Duinenveldt-van de Rijdt, J. G. C. M.; van Lente, J. H. State of the art in counterpoise theory. Chem. Rev. 1994, 94, 1873–1885.

(41) Dasgupta, S.; Hammond, W. B.; Goddard, W. A. Crystal structures and properties of nylon polymers from theory. J. Am. Chem. Soc. 1996, 118, 12291–12301.

(42) Berndad, P.; Alemán, C.; Pugallig, J. Relative stability between the α and γ forms of even nylons based on group contributions. Eur. Polym. J. 1999, 35, 835–847.

(43) Kurita, T.; Fukuda, Y.; Takahashi, M.; Sasanuma, Y. Crystalline moduli of polymers, evaluated from density functional theory calculations under periodic boundary conditions. ACS Omega 2018, 3, 4824–4835.

(44) Miyasaka, K.; Isomoto, T.; Koganeya, H.; Uehara, K.; Ishikawa, K.; Ogata, N. Nylon-6 α-phase crystal: Chain repeat distance and modulus in the chain direction at low temperature. J. Polym. Sci., Polym. Phys. Ed. 1980, 18, 1047–1052.

(45) Peeters, A.; van Alsenoy, C.; Bartha, F.; Bogár, F.; Zhang, M.-L.; van Doren, V. Ab initio calculations of the Young’s modulus of α-polymides. Int. J. Quantum Chem. 2003, 87, 303–310.

(46) Manley, T. R.; Martin, C. G. The elastic modulus of nylons. Polymer 1973, 14, 632–638.

(47) Tashiro, K.; Tadokoro, H. Calculation of three-dimensional elastic constants of polymer crystals. 3. α and γ Forms of nylon 6. Macromolecules 1981, 14, 781–785.

(48) Peeters, A.; van Alsenoy, C.; Bartha, F.; Bogár, F.; Zhang, M.-L.; van Doren, V. Ab initio investigation of the Young’s modulus of polyamide-6. Int. J. Quantum Chem. 2003, 91, 32–38.

(49) Sakurada, I.; Kajii, K. Relation between the crystal structure of polymers and the elastic modulus of polymer crystals in the direction perpendicular to the chain axis. Die Makromolekulare Chem. 1975, 1, 599–620.

(50) Kajii, K.; Sakurada, I. Determination of the elastic modulus of polyamide crystals along the chain axis by X-ray diffraction, 1 The α-form of nylon 6. Die Makromolekulare Chem. 1978, 179, 209–217.

(51) Sakurada, I.; Ito, T.; Nakamae, K. Elastic moduli of crystal lattices of polymers (special issue of polymer chemistry, 1). Bull. Inst. Chem. Res., Kyoto Univ. 1964, 42, 77–92.

(52) Conley, J. D.; Kohon, H. Functionalized DL-amino acid derivatives. Potent new agents for the treatment of epilepsy. J. Med. Chem. 1987, 30, 567–574.

(53) Dado, G. P.; Gellman, S. H. Intramolecular hydrogen bonding in derivatives of β-alanine and γ-amino butyric acid; model studies for the folding of unnatural polypeptide backbones. J. Am. Chem. Soc. 1994, 116, 1054–1062.

(54) Frisch, M. J.; et al. Gaussian 09, Revision B01; Gaussian Inc.: Wallingford CT, USA, 2009.

(55) Cancés, E.; Mennucci, B.; Tomasi, J. A new integral equation formalism for the polarizable continuum model: Theoretical background and applications to isotropic and anisotropic dielectrics. J. Chem. Phys. 1997, 107, 3032–3041.

(56) Dovesi, R.; Orlando, R.; Erba, A.; Zicovich-Wilson, C. M.; Civalieri, B.; Casassa, S.; Maschio, L.; Ferrabone, M.; De La Pierre, M.; D’Arco, P.; Noël, Y.; Causa, M.; Rérat, M.; Kirtman, B. CRYSTAL14: A program for the ab initio investigation of crystalline solids. Int. J. Quantum Chem. 2014, 114, 1287–1317.