ELSEVIER

Polymer 43 (2002) 1447–1451

polymer

www.elsevier.com/locate/polymer

Change in the structure of poly(tetramethylene succinate) under tensile stress monitored with solid state ^{13}C NMR

Tsunenori Kameda, Masatoshi Kobayashi, Juming Yao, Tetsuo Asakura*

Department of Biotechnology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan

Received 16 July 2001; accepted 20 September 2001

Abstract

A new solid-state NMR experimental equipment was developed to monitor the structural change of polymer and protein fibers under active uniaxial deformation. The equipment was applied to monitoring change in the structure of a biodegradable aliphatic polyester fiber, poly(tetramethylene succinate) (PTMS; $[-O(CH_2)_4OCO-(CH_2)_2CO-]_n$), as a function of tensile stress. The crystal transition from α to β forms for PTMS was induced by stress and monitored by the change of the methylene region in the ^{13}C NMR spectra. The ^{13}C chemical shielding constant for the model compound of poly(tetramethylene succinate) was calculated using the GIAO–CHF (gauge invariant atomic orbitals–coupled Hartree–Fock) with ab initio 6-311G** basis set. This calculation acceptably explains the experimental results. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(tetramethylene succinate); ^{13}C Solid state NMR; NMR Observation under tensile stress

1. Introduction

Understanding the mechanisms of deformation of semicrystalline polymers is of primary importance in their design and improvement [1]. There are many techniques which can probe the changes in the polymer as it is being deformed. Atomic force microscopy and wide angle X-ray spectroscopy as well as small-angle X-ray spectroscopy have been used to obtain orientation and morphological information in both amorphous and crystalline regions [2,3]. NMR is also used to obtain the molecular motions of the polymers or the low-molecular weight molecules absorbed in the polymers, especially in the amorphous regions, after deformation or in an active state of deformation [4–8].

PTMS (Fig. 1) is known as biodegradable aliphatic polyester which has received a great attention from industry, particularly from the ecological viewpoint [9,10]. The mechanical properties depend strongly on their crystal structure as well as on the crystallinity of the polymer. Two crystal modifications, α and β forms were reported by X-ray diffraction and FT-IR analyses [10]. The transition between α and β forms occurred reversibly under the application or removal of strain and the β form appeared under strain. The difference in the fiber periods of the two crystalline forms was attributed mainly to the conformational difference in the tetramethylene unit, i.e. ($T_7GTG'T$) of the α form and (T_{10}) of the β form, where T, G and G' denoted *trans*, *gauche* and another *gauche*, respectively [10].

The determination of polymer structure at the atomic level is possible by analyzing the orientation-dependent NMR interactions such as dipole–dipole, quadrupole and chemical shielding anisotropy [11–13]. We reported the structures of silk fibers [14–19] and several polymers [20–26] in analyzing the oriented polymers or protein fibers with the use of the chemical shift tensor in solid state NMR. Especially, the torsion angles of glycine and alanine residues of *Bombyx mori* and *Samia cynthia ricini* silk fibers were determined with high precision [15–18].

In this paper, the crystal transition induced by tensile stress for PTMS has been monitored through the change in the chemical shift tensor with new solid-state ^{13}C NMR probe in an active state of deformation. The ab initio ^{13}C chemical shift calculation was also performed for the peak assignment in the ^{13}C solid state NMR spectra of oriented PTMS fibers which are set parallel to the external magnetic field.

2. Experimental section

2.1. Materials

The PTMS fibers with diameter of 0.33 mm used in this

---

* Corresponding author. Tel./fax: +81-42-383-7733.
E-mail address: asakura@cc.tuat.ac.jp (T. Asakura).

PII: S0032-3861(01)00700-5

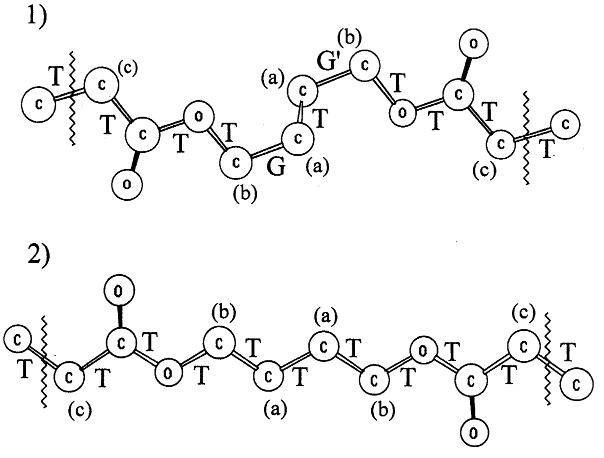

Fig. 1. Schematic diagram of segments of PTMS with α form; (1) and β form; (2). The methylene carbons were noted as CH_2(a) and CH_2(b). *T*, *G* and *G'* denoted *trans*, *gauche* and anothers *gauche*, respectively.

study are commercialized and utilized under the trade name of Field Mate that was supplied from TORAY Co. Ltd. From our solution NMR measurement ($^1H-^{13}C$ COSY NMR) of the sample, more than 80% is composed by PTMS.

2.2. Solid-state NMR

All of ^{13}C solid-state NMR experiments were performed with a Chemagnetics 400 Infinity NMR spectrometer. ^{13}C CP/MAS and static spectra for PTMS powder sample were obtained at 100.0 MHz following matched, $^1H-^{13}C$ cross polarization contacts of 50 kHz. Contact time of 2.0 ms were used. Samples were spun at a speed of 5000 Hz for MAS NMR. A 80 kHz rf field strength of the two-pulse phase-modulated (TPPM) pulse train for proton decoupling [27] was applied during the acquisition period. The probe with a 10-mm saddle coil and double tuning system for cross-polarization was home-made. $^1H-^{13}C$ cross polarization contacts of 33 kHz and contact time of 2.0 ms was used. A 28 kHz rf field strength was used for CW proton decoupling. The repetition time was 3.0 s. The probe allows free passage of a vertically suspended continuous fiber bundle through the entire probe body (Fig. 2).

Tension on the fiber bundle was applied through the use of the variable speed motor located away from the NMR magnet allowed the sample to be fully deformed and it was capable of producing tensile stress of up to 250 kgf. The approximately 90 fibers were bundled and the total length of the bundle was 250 mm.

2.3. Chemical shielding calculations

The chemical shielding calculations using the GIAO–CHF (gauge invariant atomic orbitals–coupled Hartree–Fock) with ab initio 6-311G** basis set were carried out. For the calculation, we adopted $CHO(CH_2)_2OCO(CH_2)_4OCO(CH_2)_2CHO$ as a PTMS model compound. The structures of two crystal modifications, α and β forms reported by X-ray diffraction method by Ichikawa et al. were used as shown in Fig. 1 [10]. In the application of a stress in the direction of fiber axis for PTMS, the direction of molecular chain axis (**M**) was parallel to the external magnetic field (**B**) in neglecting of the orientational distribution of molecules. Therefore, if θ_1, θ_2, θ_3 are the three angles made between each of the principal axes for principal values σ_{11}, σ_{22} and σ_{33} and **M**, the chemical shielding component, $\sigma_{\mathbf{M}}$, for the molecular chain axis direction is written by [28]:

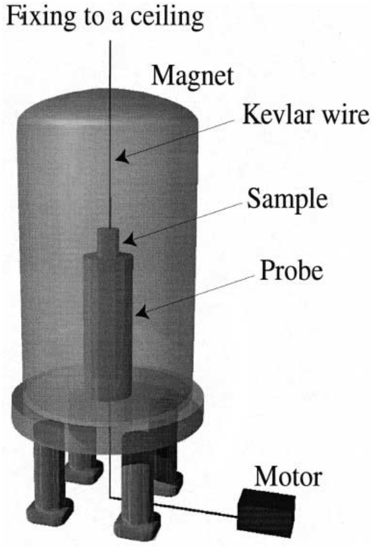

Fig. 2. Schematic diagram of developed NMR equipment to monitor change in the NMR spectra of polymers under tensile stress.

$$\sigma_{\mathbf{M}} = \sigma_{11}\cos^2\theta_1 + \sigma_{22}\cos^2\theta_2 + \sigma_{33}\cos^2\theta_3 \qquad (1)$$

3. Results and discussion

Fig. 3 shows the ^{13}C CP/MAS spectrum of PTMS with α form. These assignments were readily made by comparison with the calculated isotropic chemical shifts as listed in Table 1. The CH_2 carbon peaks were labeled (a)–(c) as shown in Fig. 1. Fig. 4 shows ^{13}C CP spectra of the PTMS fiber bundle without magic angle spinning as a function of tension, together with the ^{13}C CP static powder patterns (A) and (B). The chemical shift anisotropy of the carbonyl carbon is large and the principal chemical shift tensor values are determined from Fig. 4(B). The asymmetric broad peaks in the methylene carbon region also indicate the presence of the chemical shift anisotropy.

In Fig. 4(C), no significant tension was essentially applied to the sample: (tension of 6.3 kgf was applied to keep the fiber bundle to be well-aligned state). In this condition, PTMS polymer takes α form. The carbonyl carbon peak appears at 255 ppm in from Fig. 4(C)–(G), whose position is close to the σ_{11} component of the powder pattern. This

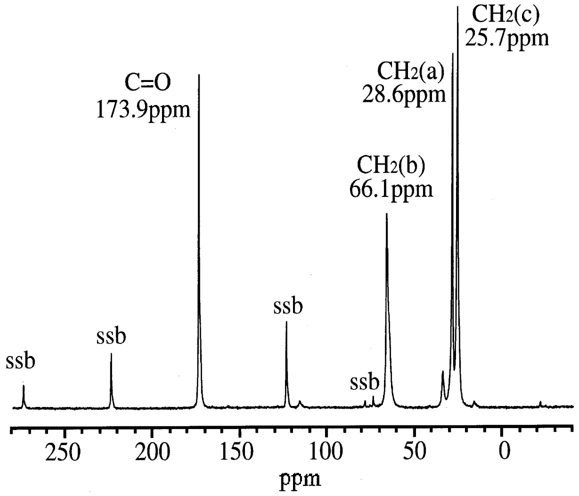

Fig. 3. ^{13}C CP/MAS NMR spectrum of PTMS fiber with α form along with peak assignment. The notation of the methylene carbons is given in Fig. 1.

indicates that the fiber bundle is well aligned and also each single fiber is well oriented since the direction of σ_{11} component is almost parallel to the molecular chain axis.

With increasing the tension to the PTMS fiber from (C) to (G), the positions of the broad singularities in the line shape for the carbonyl carbons were virtually unchanged, which indicates that the tensile stress give no significant change in the orientational distribution of the fiber undergoing active tensile deformation. However, the line shape at the upper field region assigned to the methylene groups, CH_2(a) and CH_2(c), was changed slightly with increasing tension. Namely, with increasing tension to the PTMS fiber, the relative intensity of the peak at 22 ppm decreased slightly and reversely, that at 8 ppm increased. This seems to be upfield shift of the peak at 22 ppm due to the structural transition. To demonstrate this upfield shift for CH_2 carbon under tensile stress (Fig. 4) is indeed due to the transition, Fig. 5 showed three spectra: before tensile deformation (C), undergoing active tensile deformation (B) and after removal of the tension (A).

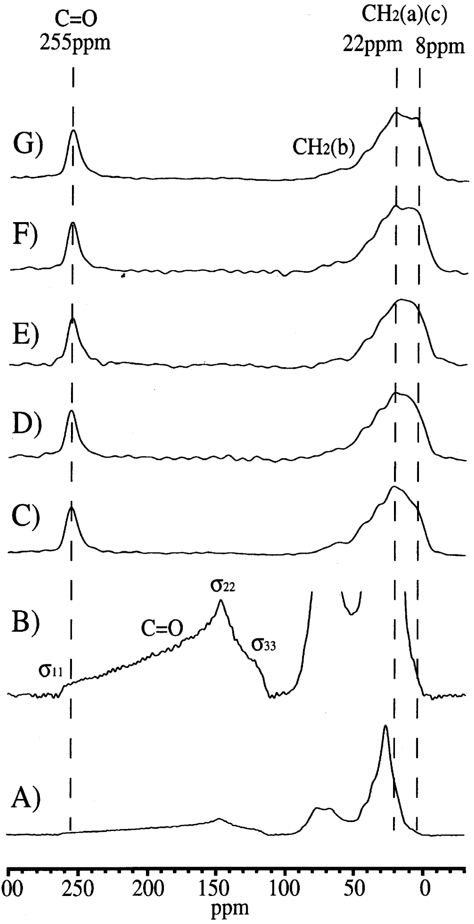

Fig. 4. (A) ^{13}C CP powder pattern spectrum of PTMS with α form. (B) Expanded spectrum of (A). From (C) to (G): ^{13}C CP spectra of oriented PTMS fibers which are set parallel to the external magnetic field as a function of tension. Tensile stress was 6.3 kgf (C) 19.8 kgf (D) 27.1 kgf (E) 33.2 kgf (F) and 45.6 kgf (G).

Thus, α and β forms for PTMS occurred reversibly under the application and removal of strain [10]. The line shapes before and after the application of the tension were identical with the same chemical shift for the methylene carbon in Fig. 4 undergoing active tensile deformation. The complete reversibility in the line shape changes confirms that the upfield shift for CH_2 signal under tensile stress corresponds to the α to β transition. Moreover, Fig. 6 shows the ^{13}C CP spectra of PTMS fiber under a tensile stress of 45.6 kgf oriented parallel to the external magnetic field as a function of time. The line shapes for all of spectra were essentially identical, which indicate no creep of the fiber was occurred during the NMR measurement.

Table 1
The observed and calculated ^{13}C isotropic chemical shifts (in ppm) for poly(tetramethylene succinate) with α form by ^{13}C CP/MAS NMR and ab initio CHF–GIAO method, respectively. The chemical shift of CH_2(a) peak was assumed to be 0 ppm. The observed chemical shifts represented in ppm downfield from TMS were listed in parentheses; (2) The notation of the carbons CH_2(a), CH_2(b) and CH_2(c) was shown in Fig. 1

	CH_2(a)	CH_2(b)	CH_2(c)	C=O
Experimental	0 (25.7)	40.4 (66.1)	−2.9 (28.6)	148.2 (173.9)
Calculation	0	29	−3	139

Two signals of the CH_2 carbons (CH_2(a) and CH_2(c)) were overlapped in the range of 0–50 ppm. In the crystal transition of PTMS from α to β form, it is known that the internal rotation angles for CH_2(a) significantly change from the *gauche* to *trans* conformation, although those for CH_2(c) keep the *trans* conformation. Therefore, it can be considered that the upfield shift form 22 to 8 ppm under tensile stress came from the *gauche*-*trans* transition for CH_2(a), as the semi empirical fashion of 'γ-*gauche* effect' [29–31].

To give a further insight into the chemical-shift behavior of CH_2(a) carbon, the chemical shielding tensors for CH_2(a)

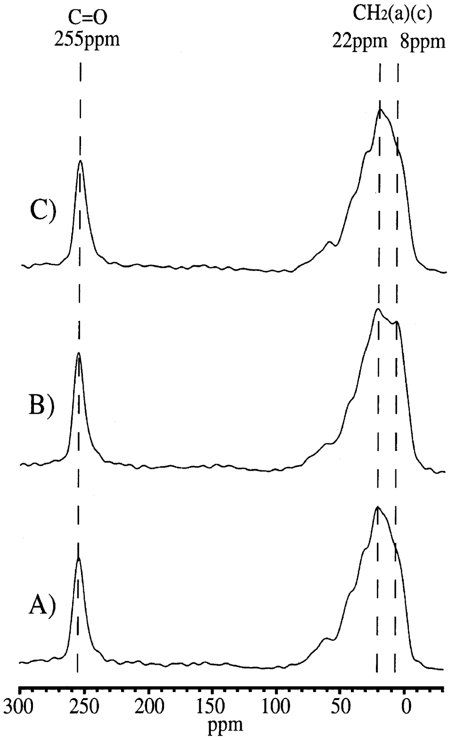

Fig. 5. ^{13}C CP spectra of oriented PTMS fibers which are set parallel to the external magnetic field. The spectra before (C) and after (A) applying tension are compared to the spectrum under a tensile stress of 45.6 kgf (B).

carbon with α and β forms were calculated theoretically with ab initio method and listed in Table 2. In principle, the chemical shifts for the static samples are expressed as a second rank tensor. Thus, the chemical shift tensor components (σ_{11}, σ_{22} and σ_{33}) have potentially more detailed structural information compared with the isotropic chemical shift which is the average of the tensor components. This is due to tensor components being closely associated with the electronic state. Although the difference between the isotropic chemical shielding constants for α and β modifications are less than 3 ppm, the anisotropies for those are more than 10 ppm, i.e. the principal values for CH_2(a) carbon are quite sensitive to the conformation as listed in Table 2. The chain axis (**M**) with respect to the external magnetic field ($\mathbf{B}_0$) was parallel under tensile stress and NMR spectra reflect chemical shift tensor parallel to $\mathbf{B}_0$. Therefore, NMR spectra correspond to the chemical shift tensor component parallel to **M**. The relation between **M** and the principal axis directions for σ_{11}, σ_{22} and σ_{33} of CH_2(a) carbon are also listed in Table 2. The orientation of the chemical shift tensor for the CH_2 (a) carbon, with respect to **M**, is different between α and β forms. For example, the principal axis of the σ_{33} for β form almost aligns parallel to **M**, although that for α form deviates by 37°. From Eq. (1) and Table 2, $\sigma_\mathbf{M}$ for α and β modifications were calculated as 159 and 167, respectively. These results indicated that $\sigma_\mathbf{M}$ moves upfield with changing form α to β modification, which agree with the experimental results in Fig. 4.

Table 2
The isotropic (σ_{iso}) and chemical shift tensor values (σ_{11}, σ_{22} and σ_{33}), and the orientation of the chemical shielding tensors calculated for the CH_2(a) carbon of the model compound of poly(tetramethylene succinate) with α and β forms. The chemical shielding component, $\sigma_\mathbf{M}$, for the molecular chain axis direction calculated is also listed. The larger value means upper field shift

Crystal modification	σ_{iso}	σ_{11}	σ_{22}	σ_{33}	θ_1	θ_2	θ_3	$\sigma_\mathbf{M}$
α	155	147	155	164	58	74	37	159
β	152	140	149	167	82	84	7	167

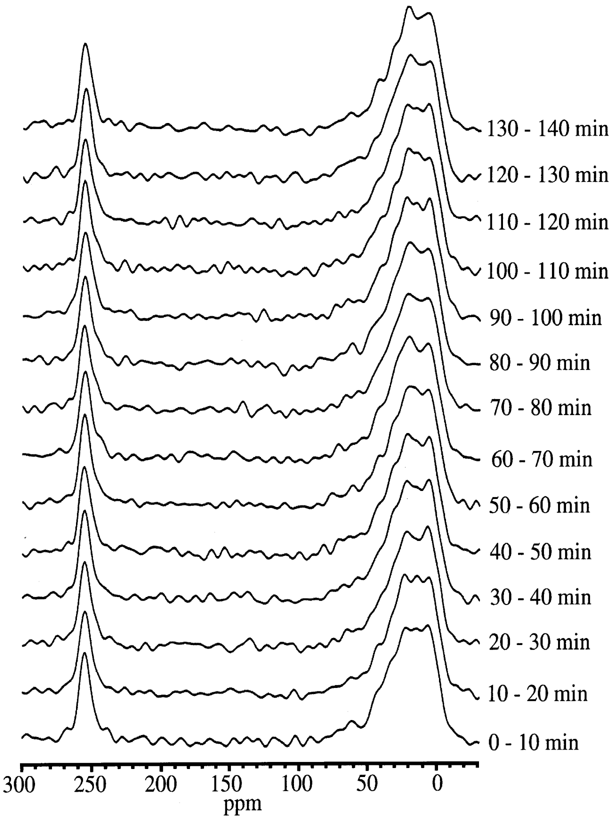

Fig. 6. ^{13}C CP spectra of oriented PTMS fibers which are set parallel to the external magnetic field under a tensile stress of 43.8 kgf as a function of time.

4. Conclusions

We demonstrated ^{13}C CP NMR experiments for PTMS fiber under tensile stress. The crystal transition from α to β modification for PTMS induced by strain was monitored by the chemical shift change for methylene units. The ^{13}C chemical shielding constant for the model compound of tetramethylene succinate was calculated using the GIAO–CHF with ab initio 6-311G** basis set. This calculation acceptably explains the experimental results. The investigation of the shielding calculation procedures provides information as to where a chemical shift change comes from.

Acknowledgements

TA acknowledges support from the Program for Promotion of Basic Research Activities for Innovative Biosciences, Japan.

References

[1] Lin L, Argon AS. J Mater Sci 1994;29:294.
[2] Bartczak Z, Galeski A, Argon AS, Cohen RE. Polymer 1996;37:2113.
[3] Schonherr H, Vancso GJ, Argon AS. Polymer 1995;36:2115.
[4] Sotta P. Macromolecules 1998;31:3872.
[5] Weigand F, Spiess HW. Macromolecules 1995;28:6361.
[6] Schaefer DJ, Schadt RJ, Gardner KH, Gabara V, Allen SR, Einglish AD. Macromolecules 1995;28:1152.
[7] Hansen MT, Boeffel C, Spiess HW. Colloid Polym Sci 1993;271:446.
[8] Loo LS, Cohen RE, Gleason KK. Macromolecules 1999;32:4359.
[9] Ichikawa Y, Kondo H, Igarashi Y, Noguchi K, Okuyama K, Washiyama J. Polymer 2000;41:4719.
[10] Ichikawa Y, Suzuki J, Washiyama J, Moteki Y, Noguchi K, Okuyama K. Polymer 1994;35:3338.
[11] Cross TA. In: Webb GA, editor. Annual reports on NMR spectroscopy, vol. 29. London: Academic Press, 1994. p. 123.
[12] Asakura T, Demura M, Nishikawa N. In: Webb GA, editor. Annual reports on NMR spectroscopy, vol. 34. London: Academic Press, 1997. p. 302.
[13] Asakura T, Demura M. In: Ando I, Asakura T, editors. Solid state NMR of polymers. Amsterdam: Elsevier, 1998. p. 307.
[14] Nicholson LK, Asakura T, Demura M, Cross TA. Biopolymers 1993;33:847.
[15] Asakura T, Minami M, Shimada R, Demura M, Osanai M, Fujito T, Imanari M, Ulrich AS. Macromolecules 1997;30:2429.
[16] Demura M, Yasunobu Yamazaki, Asakura T, Ogawa K. J Mol Struct 1998;441:155.
[17] Demura M, Minami M, Asakura T, Cross TA. J Am Chem Soc 1998;120:1300.
[18] Asakura T, Ito T, Okudaira M, Kameda T. Macromolecules 1999;32:4940.
[19] Kameda T, Ohkawa Y, Yoshizawa K, Naito J, Ulrich AS, Asakura T. Macromolecules 1999;32:7166.
[20] Asakura T, Yeo J-H, Demura M, Itoh T, Fujito T, Imanari M, Nicholson LK, Cross TA. Macromolecules 1993;26:6660.
[21] Yeo J-H, Demura M, Asakura T, Fujito T, Imanari M, Nicholson LK, Cross TA. Solid State NMR 1994;3:209.
[22] Asakura T, Yeo J-H, Ando I. Polym J 1994;26:229.
[23] Yeo J-H, Asakura T, Shimazaki H. Makromol Chem Phys 1994; 195:1423.
[24] Asakura T, Konakazawa T, Demura M, Ito T, Maruhashi Y. Polymer 1996;37:1965.
[25] Ito T, Maruhashi Y, Demura M, Asakura T. Polymer 2000;41:859.
[26] Ito T, Yamaguchi Y, Watanabe H, Asakura T. J Appl Polym Sci 2001;80:2376.
[27] Bennett AE, Rienstra CM, Auger M, Lakshmi KV, Griffin RG. J Chem Phys 1995;103:6951.
[28] Stejskal EO, Memory JD. High resolution NMR in the solid state. New York, Oxford, 1994.
[29] Grant DM, Cheney BU. J Am Chem Soc 1967;89:5315.
[30] Tonelli AE. NMR spectroscopy and polymer microstructure. New York: VCH Publishers, 1989.
[31] Asakura T, Demura M, Hayashi T. In: Webb GA, editor. Annual reports on NMR spectroscopy, vol. 29. London: Academic Press, 1994. p. 325.