SHORT COMMUNICATION

Detection of Poorly-Oriented Component in Uniaxially Stretched Poly(glycolic acid) Fiber Studied Using ^{13}C Solid-State NMRBy Sokei SEKINE,^{1,2,*} Wataru SAKIYAMA,¹ Kazuo YAMAUCHI,¹ and Tetsuo ASAKURA¹KEY WORDS: Poly(glycolic acid) / ^{13}C CP/MAS NMR / ^{13}C CP NMR / Oriented Structure /

Poly(glycolic acid) (PGA) is the simplest and semi-crystalline aliphatic polyester. The uniaxially stretched PGA fiber has been successfully used as bio-absorbable suture materials for closing surgical wounds because of the high biodegradability and biocompatibility.^{1–3}

However, one of the main disadvantages of PGA fiber is narrow window of processing conditions and therefore this suture has been used as a multi filament made of yarn which bound some of thin fibers. In order to improve such a problem, it seems important to accumulate the structural information on uniaxially stretched PGA fiber in atomic level. X-Ray diffraction study reported planar zig-zag structure for the well-oriented PGA sample⁴ and ^1H NMR relaxation studies showed the presence of the heterogeneous structure.^{5,6}

In this communication, ^{13}C CP NMR spectra of un-stretched and uniaxially stretched PGA fibers were reported, where the spectra were obtained as a function of the angle between the fiber axis and external magnetic field. This gives a detailed information on the heterogeneous structures of the oriented PGA fibers by analyzing angle-dependent spectra on the basis of the theory on the chemical shift tensor transformations.^{7,8} The change in the physical properties of these PGA fibers could be interpreted with change in the heterogeneous structures, especially the fraction of poorly-oriented components.

EXPERIMENTAL

PGA was synthesized by Mitsui Chemicals, Inc. and its molecular weight was determined about 2×10^5 using GPC method. The PGA fiber was prepared at 230°C from the molten state. After cooling at room temperature, the fibers were stretched by 1.5, 2.0, 2.5 and 3.0 times with a stretching rate of 100 mm/min, resulting fibers were heated again at a temperature just above the glass transition temperature of PGA. The blocks of the macroscopically aligned fibers were prepared carefully. The angle-dependent CP NMR spectra were observed using home made probe head prepared by us. A Bruker AVANCE-400 spectrometer was used at 100.6 MHz for ^{13}C nuclei at 30°C.

RESULTS AND DISCUSSION

The ^{13}C CP NMR spectra of the blocks of uniaxially stretched PGA fibers with different stretching ratios were summarized in Figure 1 when the angle of the fiber axis and the external magnetic field was 0°, that is, the fiber axis was parallel to the magnetic field. In order to examine change in the line shape at the lower field region of the spectra among the stretched samples carefully, the size of the line shape at the higher field region in each spectrum was adjusted in Figure 1.

With increasing stretching ratio, the shape of the lower field peak tends to be sharp. The remarkable change was observed between 2.0 and 2.5 times. Namely, a well-oriented component was observed when the stretching ratio is larger than 2.5 times. In order to obtain further

Figure 1. ^{13}C CP NMR spectra (C=O region) of the blocks of uniaxially stretched PGA fibers with different stretching ratio, 1.5(—), 2.0(---), 2.5(—) and 3.0(---). The angle of the fiber axis and the magnetic field was set to be 0°. The line shape of the higher field region was superimposed to emphasize change in the line shape of the lower field region among these samples.

information, a series of ^{13}C CP NMR spectra of PGA fiber blocks were observed as a function of the angle between the fiber axis and magnetic field. As an example, a series of the spectra of the stretched fiber block with stretching ratio, 3.0 were shown in Figure 2. The ^{13}C CP NMR spectra change largely depending on the angle as is expected. Simulation of the spectra on the basis of orientation-dependent spin interaction tensors⁷ indicates the presence of three components in the oriented fibers, that is, two components (well-oriented (1) and poorly-oriented (2)) ones in the oriented region and another component (angle-independent powder pattern). From the simulation, the structural parameters, α_F , β_F and p were also determined for each oriented component. Here, α_F and β_F are defined as follows. To transform the ^{13}C chemical shift anisotropy (CSA) tensor from the principal axis system (PAS: $\sigma_{11}, \sigma_{22}, \sigma_{33}$) representation to the fiber axis system (FAS: x, y, z) representation, the ^{13}C CSA tensor is first rotated about σ_{33} by α_F to bring σ_{22} into the xy plane, followed by a rotation about σ_{22} by β_F to bring σ_{33} coincident with z . The width parameter, p is defined as standard deviation of distribution of the fiber axis. Figure 2 shows that all the angle-dependent spectra of the stretched fibers with stretching ratio, 3.0 were well-reproduced by the simulation. The parameters determined here were summarized in Table I.

With increasing stretching ratio, the fraction of the angle-independent powder pattern component decreases, but no significant change between 2.0 and 2.5 times. However, as shown in Figure 1, a large spectral change

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Figure 2. A series of ^{13}C CP NMR spectra (C=O region) of uniaxially stretched PGA fibers with stretching ratio, 3.0. The angles between the axis of macroscopically aligned fibers and external magnetic field were changed as 0° (a), 30° (b), 55° (c) and 90° (d). The simulations were performed by assuming three components, 1: well-oriented (---), 2: poorly-oriented (....) and powder pattern component (— · —).⁷ (e) is the ^{13}C CP NMR spectrum of un-stretched PGA fiber.

was observed between 2.0 and 2.5 times. Thus, the change is due to structural change in the oriented region in the sample. With increasing stretching ratio, the fraction of well-oriented components increased linearly, but change in the fraction is not linear for the poorly-oriented component, 2. Especially, a remarkable decrease from 0.27 to 0.20 was obtained between 2.0 and 2.5 times for the poorly-oriented component. There are a similar tendency for the parameter, p ; a remarkable decrease from 20 to 11 was also obtained between 2.0 and 2.5 times although only small change was obtained between 1.5 and 2.0 times, and also between 2.5 and 3.0 times. Thus, the remarkable spectral change between 2.0 and 2.5 times in Figure 1 is concluded due to a remarkable change in the fraction of poorly-oriented region.

As mentioned above, the Euler angle, β_F is defined as the angle between the fiber axis and the direction of the chemical shift tensor, σ_{33} .⁷ The latter direction is approximately perpendicular to the C=O bond direction within the plane of the (C=O)-O group. From the X-ray diffraction data reported by Chatani *et al.*,⁴ β_F was calculated to be about 5° for the PGA chains in the crystalline sample. The PGA chains studied by their X-ray analysis correspond to the well-oriented PGA chains with stretching ratio, 3.0 in this study (Table I), where β_F was 0° – 5° with small p value, 6–8. On the other hand, in the poorly-oriented region, β_F was 15° – 20° with relatively wide distribution of the fiber axis, $p = 11$ – 20 .

Table I. The structural parameters after the peak simulation of the angle-dependent ^{13}C CP NMR spectra of the stretched PGA fibers with different stretching ratios, 1.5, 2.0, 2.5 and 3.0, by assuming three components, 1: well-oriented, 2: poorly-oriented and 3: powder pattern components. The definitions of α_F (degrees), β_F (degrees) and width parameter, p are described in the text

Component		Stretching ratio			
		$\times 1.5$	$\times 2.0$	$\times 2.5$	$\times 3.0$
1: well-oriented	α_F	90	90	90	90
	β_F	5	5	0	0
	p	7	8	6	6
	fraction	0.15	0.20	0.28	0.35
2: poorly-oriented	α_F	90	90	90	90
	β_F	18	20	15	17
	p	18	20	11	12
	fraction	0.28	0.27	0.20	0.20
3: powder pattern fraction		0.57	0.53	0.52	0.45

It is interesting to observe thermal properties of these uniaxially stretched PGA fibers with different stretched ratio in relation with the structural analysis in this study. The glass transition temperature was 48.6°C , 49.3°C , 50.7°C and 50.5°C for the stretched PGA fiber with the stretching ratio, 1.5, 2.0, 2.5 and 3.0, respectively. Thus, these temperatures change remarkably between 2.0 and 2.5 times. In general, PGA fiber with more than 2.5 times of the stretching ratio has been used as a suture material because the fiber after hydrolytic acceleration test was not strong at less than 2.5 times. In conclusion, the control of such a poorly-oriented component in the process of suture production seems very important.

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