SHORT COMMUNICATIONS

**Structure of Polyamide Fibers in the Non-Crystalline Domain
Studied by ^{15}N Solid State NMR**

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(Received September 3, 1993)

KEY WORDS Non-Crystalline Domain / Aromatic Polyamide / Poly(*m*-phenylene isophthalamide) / Poly(4-methyl-*m*-phenylene terephthalamide) / ^{15}N Solid State NMR / Chemical Shift Tensor /

Aromatic polyamides, poly(*m*-phenylene isophthalamide) (PMIA) and poly(4-methyl-*m*-phenylene terephthalamide) (P4M-MPTA) have excellent thermal stability and high tensile modulus. These excellent physical properties are originated from the unique structures. The structures of these polyamides in the crystalline domain have been reported with using X-ray diffraction methods.^{1,2} However, the fraction of the non-crystalline domain has reported approximately 70% for PMIA¹ and 75% for P4M-MPTA². Thus, the atomic level analysis of these polymer structures in the non-crystalline domain is required.

The recently-developed solid-state ^{13}C or ^{15}N CP NMR methods for the structural analysis of uniaxially aligned proteins or peptides are well studied for the structural analysis of polymers at the atomic level.^{3–6} In solid state NMR studies of oriented samples, orientation-dependent nuclear spin interaction tensors as probes with which the relative orientations of specific bond vectors can be determined. The quantitative analytical approach has been developed to utilize distinct features of the chemical shift and the line shapes

obtained protein fibers placed parallel and perpendicular to the applied magnetic field for restriction of the number of possible orientations of an individual amide plane. This approach has been successfully applied to structural analysis of silk fibers^{7–9}, poly(*p*-phenylene terephthalamide) (PPTA),^{9,10} and poly(*m*-xylene adipamide) (MXD6).¹¹ Especially, in the previous paper,¹⁰ we showed how the ^{15}N chemical shifts of the oriented polymers placed parallel to the angle applied magnetic field are sensitive to the angle between the molecular symmetry axis (MSA) and the orientation axis of the polymers, especially, the angle, θ_{NH} , between the NH bond direction and the fiber axis.¹²

In this communication, ^{15}N CP NMR spectral analysis of PMIA and P4M-MPTA block samples whose fiber axes are parallel to the applied magnetic field will be reported to clarify the non-crystalline domain structure through the determination of the angle, θ_{NH} and the fraction of the assembly of the fiber axes which have different θ_{NH} values. For a comparison, ^{15}N CP/MAS NMR spectra of PMIA and P4M-MPTA powders will be also

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reported.

EXPERIMENTAL

Materials

The oriented PMIA and P4M-MPTA fibers are given from du Pont Japan and Mitsui Toatsu Chemical Inc., respectively. The oriented block samples of PMIA and P4M-MPTA with aligned fiber axes were carefully prepared with ^{15}N free quick-setting bonding reagent.⁷ The bundles of the fiber were cut to prepare 4.5×12 mm sheets which consist of uniaxially aligned fiber. These sheets were stacked together and fixed with bonding reagent to form $4.5 \times 4.5 \times 12$ mm blocks which fit into the radio frequency coil of the NMR probe. The powders were prepared by cutting the fibers.

NMR Measurements

The ^{15}N solid state NMR spectra of oriented block samples were observed at room temperature on JEOL GX-400 spectrometer operating at 40.4 MHz. This temperature is fairly lower than the T_g of these samples. Cross polarization was employed for sensitivity enhancement with high power ^1H decoupling during the signal acquisition period. A $7\ \mu\text{s}$ 90° ^{15}N pulse with a 3 ms mixing time was used. The accumulations with 7 s repetition times were 23000 (PMIA) and 33000 (P4M-MPTA). The ^{15}N CP/MAS NMR spectra of PMIA and P4M-MPTA fibers were observed with JEOL GSX-270 NMR spectrometer operating at 27 MHz; a $4.8\ \mu\text{s}$ 90° ^{15}N pulse with a 5 ms mixing time and 6 kHz spinning rate, and the number of acquisitions with a 5 s repetition time were 6300 (PMIA) and 8200 (P4M-MPTA). All spectra were externally referenced relative to $^{15}\text{NH}_4\text{NO}_3$.

RESULTS AND DISCUSSION

Figure 1 shows the ^{15}N CP/MAS NMR spectra of PMIA (a) and P4M-MPTA (b)

Figure 1. ^{15}N CP/MAS NMR spectra of poly(m-phenylene isophthalamide) (PMIA) (a) and poly(4-methyl-m-phenylene terephthalamide) (P4M-MPTA) (b) powders. The isotropic chemical shift, σ_{iso} are determined as 108 ppm for PMIA and 107 ppm for P4M-MPTA. The number of accumulations were 8200 (PMIA) and 6300 (P4M-MPTA). The chemical shift is in ppm relative to $^{15}\text{NH}_4\text{NO}_3$.

powders. The ^{15}N chemical shift values are 108 ppm (PMIA) and 107 ppm (P4M-MPTA), which coincide with each other within experimental error. These peaks are asymmetric and broad (especially for P4M-MPTA), indicating the presence of the non-crystalline domain except for crystalline domain. Actually, the oriented PPTA powder with more than 80% crystalline domain gives sharp and narrow single peak.¹³ In order to resolve the peaks to the crystalline and non-crystalline parts, it is necessary to observe ^{15}N NMR spectra by

Figure 2. ^{15}N CP NMR spectra of oriented poly(*m*-phenylene isophthalamide) (PMIA) (a) and poly(4-methyl-*m*-phenylene terephthalamide) (P4M-MPTA) (b) block samples, whose fiber axes are parallel to the applied magnetic field. The number of accumulations were 23000 (PMIA) and 33000 (P4M-MPTA). The chemical shift is in ppm relative to $^{15}\text{NH}_4\text{NO}_3$.

considering the difference in the mobility of the chain between both domains or to compare the ^{15}N NMR spectra among the samples with different crystalline fractions.¹⁴

Figure 2 shows the ^{15}N CP NMR spectra of PMIA and P4M-MPTA block samples placed parallel to the applied magnetic field. There is a sharp peak at approximately 70 ppm with broad peak to lower field. This spectral tendency is the same between both spectra although the intensity of the broad peak increases for P4M-MPTA. In our previous paper,¹⁰ it has been shown that the ^{15}N chemical shifts of the oriented polymers placed parallel to the applied magnetic field are sensitive to the angles between various molecular-fixed axes and the axis of polymer

Figure 3. ^{15}N NMR spectral simulation of poly(*m*-phenylene isophthalamide) (PMIA) (a) and poly(4-methyl-*m*-phenylene terephthalamide) (P4M-MPTA) (b). The broken line and solid line are simulated and observed spectra, respectively.

alignment, especially θ_{NH} . In addition, a plot of the ^{15}N chemical shift vs. θ_{NH} has been reported for quantitative structural analysis. Thus, it is noted that the very high resolution of the ^{15}N NMR spectrum which is available in structural analysis with high precision is obtained from the parallel spectra. In order to resolve the spectra, the peak simulations were performed by assuming Gaussian. The presence of, at least, three peaks in each spectrum is suggested from the peak simulation as shown in Figure 3, where the three peaks are noted as A, B, C to higher field. The fraction of each peak determined by the simulation is summarized in Table I, along with the chemical shift and the half-height width. From the plot, chemical shift vs. θ_{NH} reported previously,¹⁰ it is possible to determine the θ_{NH} value for each

Table I. The ^{15}N CP parallel spectral parameters for oriented poly(*m*-phenylene isophthalamide) (PMIA) and poly(4-methyl-*m*-phenylene terephthalamide) (P4M-MPTA) block samples placed parallel to the applied magnetic field

The fraction of each peak and the range of the angle, θ_{NH} between the NH bond and the fiber axis are also listed (see the text).

Parameters peak	Oriented block sample					
	PMIA			P4M-MPTA		
	A	B	C	A	B	C
Fraction/%	37	20	43	61	18	21
Chemical shift/ppm	160	105	68	149	106	72
Half height-width/Hz	1000	880	400	1100	520	520
θ_{NH} range/degree	25—35	46—58	67—90	31—42	44—56	66—90

peak. These values determined are also listed in Table I. Judging from the angles, θ_{NH} , 75° or 80° for PMIA and 86° or 94° for P4M-MPTA in the crystalline domain by the X-ray diffraction analysis,^{1,2} the peak C in both spectra is assigned to the ^{15}N nuclei in the chain in the crystalline domain. This is also reasonable by judging from the fact that the peak C is the narrowest one among three resolved peaks because the peak width reflects the distribution of the θ_{NH} values. However, the fraction of the peak C is slightly different from that of the crystalline domain determined with X-ray diffraction method, 30% for PMIA and 25% for P4M-MPTA. This difference in the fraction between X-ray diffraction and NMR might come from the ambiguity in the determination by X-ray diffraction method, especially the determination of the base line coming from the non-crystalline domain. However, it is also possible to point out that a part of the peak C might be assigned to the ^{15}N nuclei in the chains in the non-crystalline domain; for example, the sequence of the chains with similar θ_{NH} values is too short to form the crystalline domain. Thus, the peaks A and B in both spectra are clearly originated from the chains in the non-crystalline domain, indicating that the chains in the non-crystalline domain have relatively ordered structure rather than randomly distributed one in the view points

of θ_{NH} . This results derived from NMR is supported by the previous report that non-crystalline domain is highly oriented in aromatic polyamides on the basis of the X-ray diffraction studies by Tadokoro *et al.*^{1,15} The relatively broad peaks show wider distribution for each θ_{NH} value compared with the peak C, which is also reasonable. It is interesting that the chemical shifts of the peaks A and B are almost the same between PMIA and P4M-MPTA. This indicates that the non-crystalline structure as well as crystalline structure is similar between these polyamides. It has been reported that the fraction of the non-crystalline domain in P4M-MPTA sample is higher than PMIA. From our NMR results, it is concluded that the increase in the fraction of non-crystalline domain comes predominately from the contribution of peak A, that is, the structure with $\theta_{\text{NH}} = 31^\circ\text{—}42^\circ$.

Acknowledgments. We are grateful to Prof. T. A. Cross, Florida State University and Dr. L. K. Nicholson, National Institute of Health for valuable discussion. This work was, in part, funded through the Grant-in-Aid of the Ministry of Education, Science, and Culture of Japan (No. 05650912), and Yamada Science Foundation, Japan.

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