Structural Characterization of Drawn and Annealed Poly(trimethylene terephthalate) Fibers

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ABSTRACT: The changes in the structures of the glycol segment of poly(trimethylene terephthalate) (PTT) mono-filaments caused by drawing and annealing were analyzed by ^{13}C solid-state NMR relaxation, wide-angle X-ray diffraction (WAXD), IR spectroscopy, DMA, and DSC measurements. The ^{13}C solid-state NMR relaxation and WAXD studies indicated that the drawn PTT consists of oriented crystalline, amorphous, and intermediate phases. The IR spectra indicated that three methylene bonds of PTT in the crystalline and amorphous regions adopt *gauche–gauche* and *trans–trans* conformations, respectively. The intermediate region consists of aggregates of molecular chains with a *gauche* conformation. On the other hand, as-spun and annealed PTT fibers consist of amorphous and intermediate regions. Although the proportion of intermediate to amorphous regions was unchanged on annealing, the molecular mobility was changed, *i.e.*, the molecular mobility of the intermediate region decreased with increasing annealing time. The DMA and DSC measurements showed that the glass transition temperature (T_g) of PTT fiber increased by 20 °C on annealing for 144 h, whereas drawing induced a more significant increase in the T_g. The T_g of DR = 3 sample was 50 °C higher than that of as-spun fiber, because of the existence of orientational crystallization in the drawn PTT.
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Poly(trimethylene terephthalate) (PTT), as shown in Figure 1, is a member of the family of thermoplastic aromatic polyesters that includes poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT). Historically, PTT was rarely used as an industrial material owing to the high cost of the monomer, 1,3-propanediol (PDO); however, since the 1990s, when Shell Chemicals established a commercial process for producing PDO, PTT has become popular, and many studies of PTT have been carried out.

The molecular chains of the aliphatic components of PET, PTT, and PBT consist of two, three, and four methylene units, respectively. PET and PBT contain even numbers of methylene units, whereas, PTT contains an odd number. This difference between even and odd numbers of methylene groups affects the structures and physical properties of the polymers. For example, although the *trans*-zigzag form is the stable conformation for PET and PBT, the *gauche–gauche* form of the C4–C5–C4 bonds (see Figure 1) is stable for PTT.[1] This conformational difference is also responsible for the modulus of PTT fiber being intermediate between those of PET and PBT, and for the excellent stretchability of PTT. The glass transition temperature (T_g) of PTT has been reported to be

between 35 and 50 °C.[2,3]

The crystal structure of PTT has already studied by many researchers.[2,5–10] The unit cell is triclinic with the following parameters; $a = 4.6$ Å, $b = 6.2$ Å, $c = 18.3$ Å, $\alpha = 98°$, $\beta = 90°$, $\gamma = 112°$, and the space group is $P\bar{1}$. Each cell contains two monomer units of one polymer chain. Both methylene bonds are in the *gauche* conformation.[5,6] The elastic modulus of the crystalline phase of PTT is 2.59 GPa, which is much lower than that of PET (125 GPa).[7] The equilibrium melting temperature of PTT is about 525 K, and the equilibrium enthalpy of fusion is 28.8 kJ/mol.[11] The isothermal crystallization kinetics of PTT has also investigated by Avrami theory and the crystallite morphology from melt and cold-crystallization exhibited typical negative spherulite and sheaf-like crystallite.[12]

Structure development in PTT fibers during drawing has been studied by two groups.[13,14] Simultaneous synchrotron small- and wide-angle X-ray scattering studies by Wu *et al.* indicated the existence of a rigid amorphous phase in the drawn fibers.[13] The orientation and structure of PTT drawn films, studied by infrared dichroism measurements, indicated that the *gauche* content increases with increasing draw ratio.[14]

Physical aging or annealing also induces structural

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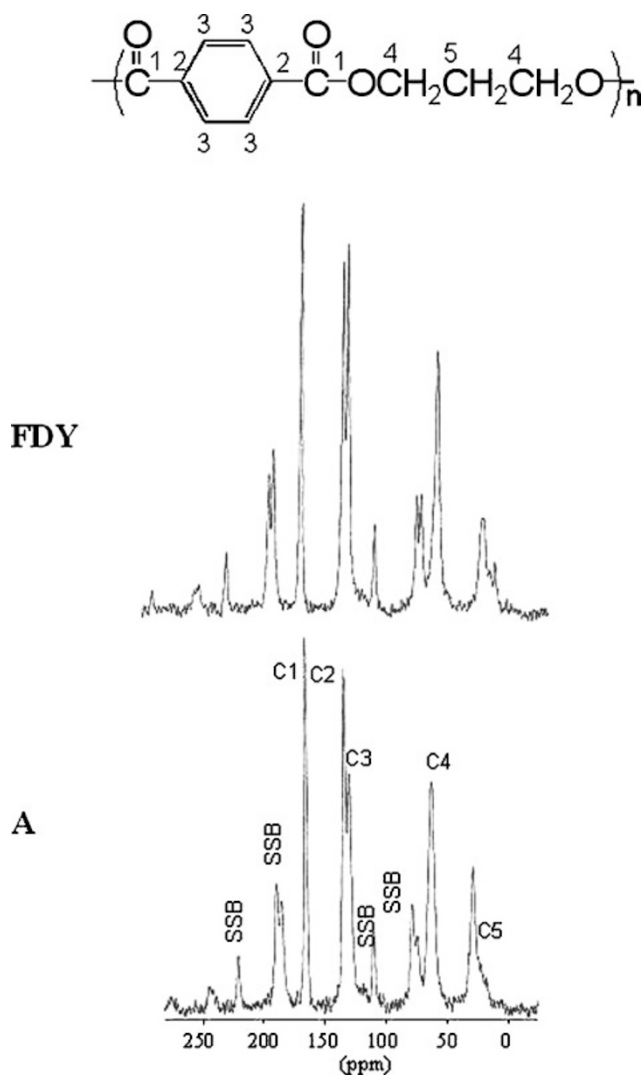
Figure 1. [13]C CP/MAS spectra of the as-spun and the drawn poly(trimethylene terephthalate) fibers together with the assignment. The interpretation on A and FDY is given in the text.

transitions. The changes in the structure of melt-extruded undrawn PTT films caused by physical aging and annealing at ambient temperature for up to 24 h have been investigated in terms of thermal crystallization, glass transition behavior, and mechanical properties.[3] The effect of physical aging and annealing on the mobility of rigid amorphous PTT chains has also been reported. In our previous study, we reported the relationship between the T_g of undrawn PTT fiber and the annealing time at 40 °C. The change in T_g of PTT on annealing is considered to arise from a change in the conformation of the methylene chains of the glycol residue in PTT from a random conformation to a *gauche–gauche* conformation.[15]

Although the intermediate phase in PTT has already been studied as described above, no more details regarding the structure and dynamics of the intermediate phase have been obtained. Therefore, in this study, the structure and dynamics of drawn and annealed PTT

fibers were reinvestigated by means of solid-state nuclear magnetic resonance spectroscopy, wide-angle X-ray diffraction, infrared spectroscopy, thermal analysis, and dynamic viscoelasticity measurements. Moreover, the effects of structural changes induced by drawing and annealing on the fiber properties of PTT were compared.

EXPERIMENTAL

Sample Preparation

PTT material was kindly supplied by Shell Chemical Company and its intrinsic viscosity was 0.92 dL/g, whose Mn was 17,300. The polymer was dried at 100 °C for 2 d under vacuum to reduce moisture. Fiber samples were prepared by melt-spinning. The extrusion temperature of polymer was 265 °C, and the through-put was kept constant value of 5.47 g/min by the gear pump of 0.6 cc/rev. PTT was extruded from the spinneret with one hole whose diameter was 0.3 mm. Then the fiber was cooled by the immersion in water controlled at 45 °C, which was around T_g of PTT in order to prevent from the skin-core formation, and taken-up at 24 m/min. The denier of the obtained monofilament was 2,280 dtex. The sample A was measured within 10 min after taken-up. The samples B and C were annealed at 40 °C for 96, and 144 h, respectively. Also fully drawn yarn (FDY) was produced by the drawing of the sample A, whose drawing was carried out at 70 °C at the draw ratio of 3.0 and then heat-treated at 130 °C under constant length.

Measurements

Solid-state nuclear magnetic resonance (NMR) experiments were carried out on a JEOL EX-400 spectrometer operating at resonance frequencies of 100.4 MHz for [13]C. Samples were spun at the magic angle at a rate of 5.7 kHz. The probe temperature was controlled at 25 °C. The [1]H–[13]C cross polarization contacts time was 1.5 ms, and the repetition time was 1.5 s in all experiments. The chemical shifts of all ^{13}C spectra were determined by taking the methyl carbon of solid hexamethylbenzene as an external reference standard. The spin–lattice relaxation times, T_1, were measured using Torchia pulse sequence.[16] The T_1 values were obtained by fitting the decays of ^{13}C magnetization.

Wide-angle X-ray diffractions (WAXD) patterns were obtained with a Rigaku Denki model RU-200A diffractometer. Nickel-filtered Cu Kα radiation generated at 40 kV and 30 mA was used for recording X-ray pattern using an imaging plate of Rigaku Denki model R-AXIS-DS 3. Fiber samples were carefully wound parallel to one another on a holder.

Fourier transform infrared (FT-IR) spectra were

Table I. ^{13}C spin–lattice relaxation times (T_1 in s) of C=O (C1), C_6H_4 (C2), C_6H_4 (C3) and OCH_2 (C4) peaks of poly(trimethylene terephthalate) determined by Torchia pulse sequence

Sample	A		B		C		FDY	
	T_1 (s)	fraction (%)	T_1 (s)	fraction (%)	T_1 (s)	fraction (%)	T_1 (s)	fraction (%)
C=O	33.1	100	32.6	100	33.5	100	4.6	4
(C1)							112.0	96
C_6H_4	30.6	100	29.2	100	28.7	100	3.7	10
(C2)							92.1	90
C_6H_4	2.2	19	2.2	25	1.8	15	2.8	15
(C3)	18.4	81	19.2	75	21.8	85	20.3	27
							117.7	58
OCH_2	0.38	49	0.80	56	0.85	55	0.71	43
(C4)	4.4	51	4.8	44	10.6	45	9.3	23
							103.3	34

measured with a JASCO model FT-IR550 with an attenuated total reflection (ATR) instrument and an internal reflection element of KRS-5 was used to acquire ATR spectra. Three hundred scans of $4\,cm^{-1}$ revolution were averaged to achieve sufficient single-to-noise ratio. Fiber samples were carefully wound parallel to one another on a holder.

Thermal analyses were made with a calorimeter Seiko DSC210/SSC5000 from 30 to 250 °C at a scanning rate of 20 °C/min, after calibrating the temperature with indium as the standard for temperature readings. The sample weight was about 7 mg.

Measurements of viscoelasticity were carried out by using DMS-200 of Seiko Instruments. The frequency was 10 Hz, the tension applied was 10 g and the heating rate was 1 °C/min from 0 to 200 °C.

RESULTS AND DISCUSSION

Solid-State NMR Measurements

Figure 1 shows the ^{13}C cross-polarization magic-angle spinning (CP/MAS) spectra for sample A and FDY. One carbonyl carbon peak (165.4 ppm; C1), two phenyl carbon peaks (133.9 ppm; C2, and 129.6 ppm; C3), and two aliphatic carbon peaks (62.3 ppm; C4, and 28.3 ppm; C5) can be identified in the spectrum of PTT.[17] No changes were observed for the line shapes and chemical shift values for any of the signals other than that corresponding to C5. The single peak at 28.2 ppm changes to doublet peaks at 26.5 and 28.2 ppm on drawing, as a result of an up-field shift of a part of the lower field peak. This indicates that the chemical shifts of the C1–C4 carbons are insensitive to the molecular structure, whereas that of C5 is sensitive to it. The relation between the chemical shift of C5 and the molecular structure of PTT will be presented in the forth-coming paper.[18]

Next, the changes in the molecular mobility caused by annealing and drawing were analyzed by using spin–lattice relaxation times (T_1) for the C1–C4 peaks of the samples A, B, C, and FDY. The values of T_1 obtained by fitting the decay curves by means of single-, double- or triple-exponential functions are summarized in Table I. For annealed samples, mono-exponential T_1 decays were observed for the C1 and C2 peaks for each sample, whereas, bi-exponential decays were observed for C3 and C4. The bi-exponential fitting indicates that motional heterogeneity exists in these samples. Note that in the case of FDY, an additional component linked to molecular motion is contained in all the peaks, *i.e.*, the T_1 exponential decays for C1 and C2 peaks consist of two components and those of C3 and C4 consist of three components. The longest T_1 components ($T_1 > 92\,s$) for each peak in the drawn sample of FDY were absent in the annealed samples A, B, and C, which suggested that longest T_1 components are attributable to the orientation of the crystalline region induced by drawing. On the other hand, the shortest T_1 components ($T_1 < 2.8\,s$), which exist in all the samples, are attributable to the amorphous region. Moreover, the intermediate T_1 component that exists in the FDY sample is considered to arise from the rigid NMR amorphous region, as pointed out by Gabrielse *et al.*[19] The intermediate T_1 values for FDY are close to those for samples A, B, and C, which indicates that two components for the annealed samples A, B, and C correspond to the amorphous and rigid NMR amorphous regions. In other words, no crystallization occurred during annealing, so there is a distinct difference between drawn and annealed PTT fibers.

Furthermore, in comparing samples A, B, and C, we found that the T_1 values for C3 and C4 carbons changed during annealing. On annealing for 144 h, the T_1 components for the C3 and C4 peaks corresponding to the rigid NMR amorphous phase increas-

ed in intensity, suggesting that localized molecular motions, such as flip-flop reorientation of the phenyl ring and the oscillatory motions that occurred at a frequency of around several hundred MHz, were constrained. This restriction on motion may be caused by a conformational transition from *trans–trans* to *gauche–gauche*, which induces an ordered structure and a more stable state for the rigid NMR amorphous region. Therefore, this structural transition may cause the observed elevation in the T_g. This hypothesis was confirmed by other measurements describe below.

The fractions of T_1 components relating to the rigid NMR amorphous and the oriented crystalline phases for the C3 peak for FDY were 27 and 58%, respectively. The sum of these is 85%, which was close to the fraction of the T_1 component for the rigid NMR amorphous phase in the C3 peak of sample A (81%). A similar relationship between samples A and FDY was also seen in the C4 peak, namely, that the sum of the fractions of the T_1 components for the rigid NMR amorphous and oriented crystalline regions for FDY was close to that observed for sample A. Moreover, a comparison of T_1 values for samples A and FDY showed that the T_1 values of the rigid NMR amorphous components for the C3 and C4 peaks increased on drawing, suggesting that the molecular motion in the rigid NMR amorphous region is restricted by drawing. These results indicated that a part of the rigid NMR amorphous component in undrawn PTT fiber changed to an oriented crystalline region on drawing, whereas components attributed to the amorphous region remained unchanged.

WAXD Measurements

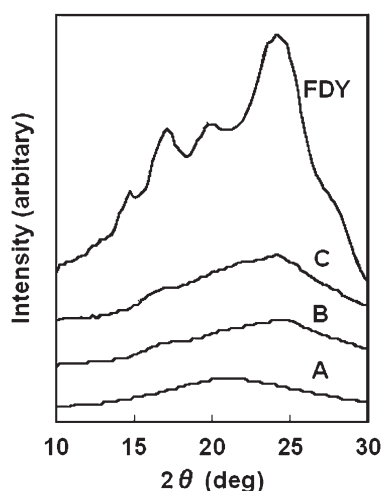Figure 2 shows the WAXD profiles. The intensity shown in Figure 2 was obtained by the integration

Figure 2. X-Ray diffractograms of the annealed and drawn poly(trimethylene terephthalate) fibers. The interpretation on A, B, C and FDY is given in the text.

of WAXD reflction intensities for a specific 2θ over all of the azimuthal angles. The unit cell of PTT is reported as being triclinic with three major diffraction peaks at angular positions of $2\theta = 17°$, $20°$, and $24°$; these can be indexed to $(0\bar{1}2)/(011)$, (012), and $(1\bar{1}3)/(\bar{1}03)$ reflections, respectively. Two minor diffraction peaks centered at $2\theta = 15°$, and $27°$ are assigned to the (010) and $(1\bar{1}4)/(\bar{1}04)$ reflections, respectively.[5] The sample A showed no diffraction peaks, whereas the samples B and C showed two very weak peaks at around $2\theta = 17°$ and $24°$, which are major diffraction peaks of PTT. This indicated that samples B and C had a somewhat more ordered structure than sample A; however, each peak for samples B and C was broad, indicating that the domain for ordered structures were very small. From these results, it is considered that the more-ordered structure in samples B and C is noncrystalline.

In contrast to this, in the case of the drawn PTT sample, FDY, three diffraction peaks at angular positions of $2\theta = 15°$, $20°$, and $24°$ were clearly observed, and two peaks centered at $2\theta = 15°$ and $27°$ were present but were less well defined. These diffraction peaks clearly indicated that the crystallization had definitely occurred during drawing and heat-treatment. The existence of such structural difference between annealed and drawn samples of PTT is in agreement with the solid-state NMR relaxation results described above.

IR Measurements

Ward and Wilding made a detailed comparison of the IR and Raman spectra of PTT, PBT, and PET.[20] The band at $935\,cm^{-1}$ is associated with C–H rocking vibrations of the glycol residue in the amorphous phase. PTT also shows an IR band at $1045\,cm^{-1}$, which has been assigned to an Ag C–C stretching mode of an all *gauche* sequence. Generally speaking, the Ag vibrations are Raman active and IR inactive, however, they discussed in detail.[20,21] Chuah studied the structure of uniaxial and biaxial PTT films by IR dichroism.[10] He focused on the bands at 1358 and $1385\,cm^{-1}$. The band at $1358\,cm^{-1}$ was assigned to Bu CH$_2$ wagging in the crystalline phase with a *gauche–gauche* conformation of PTT's three methylene bonds, and the band at $1385\,cm^{-1}$ was assigned to Ag CH$_2$ wagging in the amorphous phase with a *trans–trans* conformation. Also, a band at $1037\,cm^{-1}$ was assigned to *gauche* C–C stretching of the glycol residue in the crystalline phase. In this study, the conformational change of PTT fibers on annealing and drawing were investigated by means of the IR absorption intensities proposed by Chuah. Figure 3 shows the ATR-FT IR spectra of samples A and FDY, and the three characteristic absorption bands
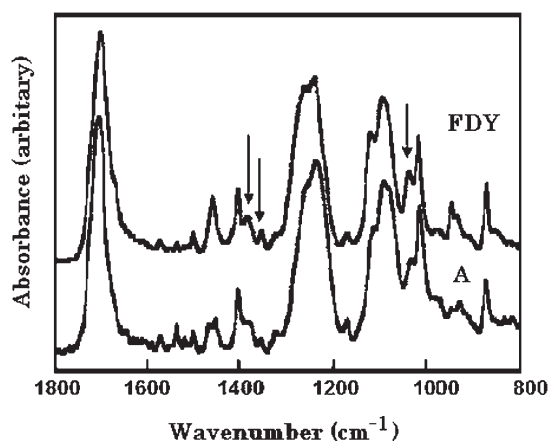
Figure 3. IR spectra of as-spun and drawn poly(trimethylene terephthalate) fibers. The interpretation on A and FDY is given in the text.
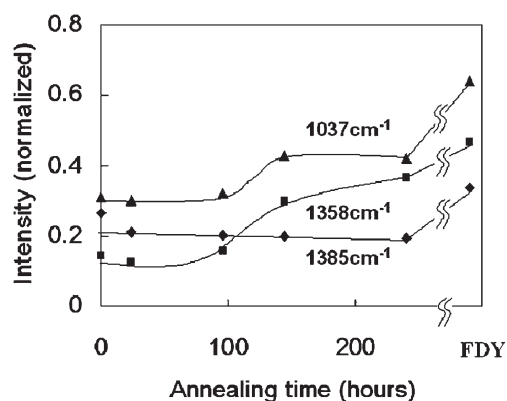

Figure 4. Absorption intensities of $1037 \, \text{cm}^{-1}$ (*gauche* conformation in the crystalline phase), $1358 \, \text{cm}^{-1}$ (*gauche* in the crystalline phase) and $1385 \, \text{cm}^{-1}$ (*trans* in the amorphous phase) in the IR spectra of poly(trimethylene terephthalate) fibers as a function of the annealing time.

are indicated by the arrows in the figure.

Figure 4 shows the relationship between the annealing time and the absorption intensities at 1037, 1358, and $1385 \, \text{cm}^{-1}$. The absorption intensity at 1410 cm^{-1}, which is aromatic ring vibration,[20] was used as an internal reference band. From Figure 4, it can be seen that the absorption intensities at 1037 and $1358 \, \text{cm}^{-1}$ remained constant until 96 h and then increased rapidly between 96 and 144 h, respectively. Both of the absorptions at 1037 and $1358 \, \text{cm}^{-1}$ are associated with the *gauche–gauche* conformation of PTT's three methylene groups. In contrast, the absorption band at $1385 \, \text{cm}^{-1}$ originated from *trans* conformation gradually decreased with increasing annealing time. These results indicated that the conformational change from *trans–trans* to *gauche–gauche* conformation occurred at annealing times of between 96 and 144 h. This structural change from *trans* to *gauche* conformation, as seen in the IR spectra, can be consid-
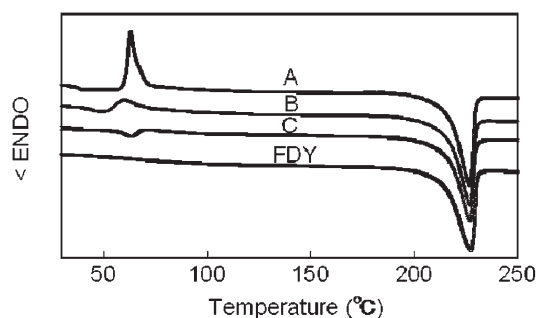

Figure 5. DSC thermograms of the annealed and drawn poly-(trimethylene terephthalate) fibers. The interpretation on A, B, C and FDY is given in the text.

ered to relate with the change in the molecular motion induced by annealing observed from solid-state NMR measurements, as described above.

More noteworthy is that the absorption intensities of the bands of FDY at 1037 and $1358 \, \text{cm}^{-1}$ were more intense than the corresponding bands in the spectra of samples A, B, and C, indicating that the amount of *gauche–gauche* conformer induced by drawing is larger that that produced by annealing. This suggests that orientational crystallization accompanies the significant increase in *gauche–gauche* conformation. Furthermore, the absorption band at $1385 \, \text{cm}^{-1}$ for FDY was also larger than that for the samples A, B, and C, which indicates that the amorphous phase is changed to the *trans* conformer on drawing.

DSC and DMA Measurements

Figure 5 shows the results of DSC measurements for samples A, B, C, and FDY. All the samples showed an endothermic peak with a maximum at 226 °C, corresponding to the melting point of PTT. Although the endothermic peak of T_g was observed at in the vicinity of 30–60 °C, and the exothermic peak corresponding to the crystallization temperature (T_c) was at around 70 °C for samples A, B and C, no such peak was obtained for sample FDY. This suggests that the crystallinity of the FDY sample is higher than that of the annealed samples A, B and C. From the DSC curves, the T_g values for samples A, B and C were determined to be 34, 41, and 56 °C, respectively, which indicates that T_g increases constantly with increasing annealing time. This change in T_g was interpreted as constraints imposed on the amorphous regions by crystals formed newly during cold crystallization.[12] The change in the position of the exothermic peak (T_c) is caused by crystallization during the measurement. Because the T_c value of the constrained amorphous region is higher than that for of the random amorphous region, the fact that the T_c value of the sample C was higher by about 20 °C than that of the
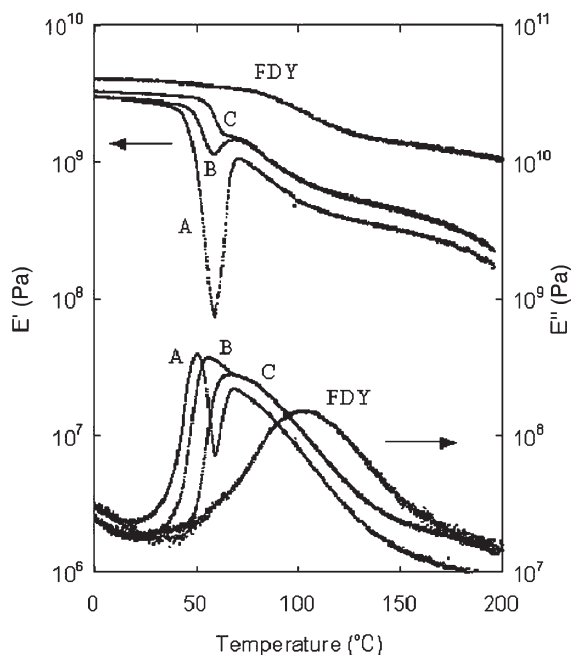
Figure 6. Temperature dependence of the storage (E') and loss (E'') moduli for the annealed and drawn poly(trimethylene terephthalate) fibers. The interpretation on A, B, C and FDY is given in the text.

sample A showed that the fraction of constrained amorphous phase in sample C was higher than that in sample A. The enthalpy of crystallization also decreased with increasing annealing time, which suggests that the proportion of crystal-like (constrained amorphous) structure in sample C was higher than that in samples A and B, which was also confirmed by the NMR relaxation measurements described above.

As can be seen in Figure 5, the FDY sample did not show any features to which the T_g could be related. In practice, mechanical analysis is known to be more sensitive than calorimetric measurements for the detection of glass transitions. Accordingly, we measured the dynamic mechanical relaxation spectra of PTT fibers (Figure 6) in the hope of finding the glass transition of sample FDY. Figure 6 shows the temperature dependence of storage (E') and loss (E'') moduli of PTT fibers as determined by dynamic viscoelasticity measurements. The transition shown by E' and E'' at 75–120 °C may be the glass transition of FDY. On the other hand, the negative and positive transitions that appeared at around 35–70 °C for the annealed samples correspond to the glass transition and crystalline transition (the stiffening of the molecular chains through crystallization during the DMA measurement), respectively. Similarly, two peaks in the E'' vs. temperature curves at around 35–70 °C for samples A, B, and C also correspond to the glass and crys-

talline transitions, respectively. Although two sharp peaks (at 50 and 65 °C) appeared in the temperature region between 40 and 100 °C for sample A, samples B and C had only one broad peak, reflecting that the T_g and T_c for these samples are close to one another. Although the T_g observed from curves of E' and E'' versus temperature for samples A, B, and C increased with increasing annealing time, in agreement with the NMR and DSC results, the T_g values for the annealed samples were lower than that for FDY. The T_g of FDY was higher by 50 °C than that of as-spun fiber, probably because of the existence of orientational crystallization in the drawn sample of PTT. Moreover, the values of E' for FDY were the highest among all the samples at all temperatures. These results suggest that the drawing process is more efficient in effecting a restriction in chain mobility in the rigid amorphous region. The restriction of the rigid amorphous chains in FDY may be induced by strain-induced crystallization. Furthermore, it is clear that E' increased with increasing annealing time. The relation between the T_g and the annealing time and drawing obtained from DMA measurements coincided with that observed by DSC measurements.

CONCLUSIONS

Changes in the structures of monofilament of poly(trimethylene terephthalate) (PTT) following drawing and annealing were identified by ^{13}C solid-state NMR relaxation, wide-angle X-ray diffraction (WAXD), IR spectroscopy, DSC, and DMA measurements. Drawn PTT consists of three components: orientated crystalline, amorphous, and intermediate regions. The crystalline and amorphous regions adopt *gauche–gauche* and *trans–trans* conformations, respectively, whereas the intermediate region consists of a rigid amorphous phase in which several molecular chains that adopt a *gauche–gauche* conformation aggregate with each other. In contrast, as-spun and annealed PTT fibers consist of two components: amorphous and constrained amorphous regions. Although no change in the fractions of the regions was observed on annealing, the molecular mobility was changed, *i.e.*, the molecular mobility of the constrained amorphous region decreased with increasing annealing time. DMA and DSC measurements showed that the T_g of PTT fiber increased by 20 °C within an annealing time of 144 h, whereas drawing induced a more significant rise in the T_g. The T_g of DR = 3 sample was higher by 50 °C than that of as-spun fiber, probably because of the existence of an orientated crystalline region in the drawn PTT.

REFERENCES

1. H. H. Chuah, *Chem. Fibers Int.*, **46**, 424 (1996).
2. M. Pyda, A. Boller, J. Grebowicz, H. Chuah, B. V. Lebedev, and B. Wunderlich, *J. Polym. Sci., Part B: Polym. Phys.*, **36**, 2499 (1998).
3. J. W. Cho and K. S. Woo, *J. Polym. Sci., Part B: Polym. Phys.*, **39**, 1920 (2001).
4. J.-C. Kim, Reprint of Research Group on Fiber Materials, **01-1**, 9 (2001).
5. I. J. Desboroughm, I. H. Hall, and J. Z. Neisser, *Polymer*, **20**, 545 (1979).
6. S. Poulin-Daudurand, S. Perez, J. F. Revol, and F. Brisse, *Polymer*, **20**, 419 (1979).
7. K. Nakamae, T. Nishino, K. Hata, F. Yokoyama, and T. Matsumoto, *J. Soc. Mater. Sci. Jpn.*, **35**, 1066 (1986).
8. J. M. Huang and F. C. Chang, *J. Polym. Sci., Part B: Polym. Phys.*, **38**, 934 (2000).
9. K. J. Kim, J. H. Bae, and Y. H. Kim, *Polymer*, **42**, 1023 (2001).
10. H. H. Chuah, *J. Polym. Sci., Part B: Polym. Phys.*, **40**, 1513 (2002).
11. W. T. Chung, W. J. Yeh, and P. D. Hong, *J. Appl. Polym. Sci.*, **83**, 2426 (2002).
12. P. D. Hong, W. T. Chung, and C. F. Hsu, *Polymer*, **43**, 3335 (2002).
13. J. Wu, J. M. Schultz, J. M. Samon, A. B. Pangelinan, and H. H. Chuah, *Polymer*, **42**, 7141 (2001).
14. H. H. Chuah, *Macromolecules*, **34**, 6985 (2001).
15. M. Ohtaki and S. Murase, *Kobunshi Ronbunshu*, **60**, 616 (2003).
16. D. A. Torchia, *J. Magn. Reson.*, **30**, 613 (1978).
17. J. M. Huang, *J. Appl. Polym. Sci.*, **88**, 2247 (2003).
18. T. Kameda, M. Miyazawa, and S. Murase, *Magn. Reson. Chem.*, **42**, 21 (2005).
19. W. Gabriëlse, H. Angad Gaur, F. C. Feyen, and W. S. Veeman, *Macromolecules*, **27**, 5811 (1994).
20. I. M. Ward and M. A. Wilding, *Polymer*, **18**, 327 (1977).
21. R. Jakeways, T. Smith, I. M. Ward, and M. A. Wilding, *J. Polym. Sci.*, **14**, 41 (1976).