

# Dynamic Mechanical Properties of Poly(*p*-phenyleneterephthalamide) Fiber

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## Synopsis

The dynamic mechanical properties of poly(*p*-phenyleneterephthalamide) fiber were investigated. Measurements of the dynamic mechanical properties were carried out on samples of low crystallinity and low orientation over a temperature range from  $-100$  to  $+500^{\circ}\text{C}$  at a frequency of 110 Hz, at a heating rate of  $5^{\circ}\text{C}/\text{min}$ . Five relaxation processes were revealed: at  $-30$ ,  $60$ ,  $170$ ,  $270^{\circ}\text{C}$ , and in the vicinity of  $460^{\circ}\text{C}$ , respectively. The prominent dispersion peaks located at  $-30$ ,  $60$ , and  $460^{\circ}\text{C}$  were termed the  $\gamma$ ,  $\beta$ , and  $\alpha$  relaxations, respectively. The two weak peaks at  $170$  and  $270^{\circ}\text{C}$ , observed in annealed samples, seem to correspond to the  $\beta^*$ -relaxations reported previously by Frosini et al. and Takayanagi et al. The effect of annealing on the behavior of these dispersion peaks was examined, and possible molecular interpretation of these relaxation processes are made.

## INTRODUCTION

It is well known that aromatic polyamide fibers generally have outstanding thermal stability and inherent stiffness. In particular, poly(*p*-phenyleneterephthalamide) fiber, abbreviated here as PPTA fiber, developed by DuPont, is a very useful industrial material of ultrahigh strength and unusually high modulus, together with excellent dimensional stability at elevated temperatures. The excellent thermal and mechanical properties may be attributed to its rigid- and extended-chain structure.

The crystal structure and the extended molecular conformation of the material, therefore, have been studied by many investigators<sup>1-5</sup> and have become fairly clear. Information on the amorphous region or the disordered area on the other hand is poor. In particular, there are few studies<sup>6-8</sup> on molecular movements or relaxation processes of this polymer, because it is technically considerably difficult to detect slight movements of the molecular chains.

In order to overcome the difficulty, we attempted to use a sample having low crystallinity and poor orientation for measurements of dynamic mechanical properties and thereby reveal some relaxation processes. The present paper reports results which provide information concerning the amorphous regions. Furthermore, mechanisms of the detected relaxation processes are discussed on the basis of results of x-ray diffraction, density, and thermogravimetric measurements.

## EXPERIMENTAL

### Preparation of PPTA Fibers

The PPTA fibers used in the present study were prepared by the usual dry-wet spinning method from a 1.5% solution of Kevlar 29 fiber (1.5 denier) in concentrated sulfuric acid, using water as the coagulating solvent. The most important characteristic of this spinning method is that the fiber is obtained from an isotropic solution, as opposed to fiber from an anisotropic solution in the case of the DuPont fiber Kevlar.<sup>9,10</sup> The fibers thus prepared were washed with flowing water for 48 hr and then conditioned for 60 days at 25.0°C at 60% relative humidity. The samples contained about 6% moisture after this conditioning.

### Annealing

The samples were annealed at various temperatures, i.e., 100, 200, 300, 400, 460, and 500°C, for 2 hr under vacuum.

### Dynamic Viscoelasticity

The apparatus used for the measurements was a Vibron DDV-II Type (Toyo-Baldwin Co., Ltd.). The measurements were carried out in two temperature ranges—one from -100°C to room temperature and the other from room temperature to 500°C. In the former range the experiments were performed in a stream of dry air cooled with liquid nitrogen, and in the latter range, in a stream of dry nitrogen gas. Measurements were made at a definite frequency of 110 Hz at a heating rate of 5°C/min. Other driving frequencies, 3.5, 11, and 35 Hz, were also used for the determination of apparent activation energies of some of the relaxation processes. The samples were used in the form of a monofilament 30 mm in length and 200 to 250  $\mu\text{m}$  in diameter.

### Infrared Spectra

Infrared spectra of PPTA were obtained with a Hitachi infrared spectrometer, EPI-G Type, over a range of 400 to 4000  $\text{cm}^{-1}$ . The sample was used in the form of a film about 10  $\mu\text{m}$  thick.

### X-Ray Diffraction

The x-ray diffraction patterns in the equator and meridian directions were measured on a bundle of fibers with an ordinary x-ray diffractometer equipped with a fiber holder. X-Ray Laue photographs of various samples were also taken.

### Density

The density of the samples was measured at 20.0°C by a flotation method using toluene-carbon tetrachloride mixtures.

### Thermogravimetric Analysis

The measurements were carried out on powder samples cut from the fibers at a heating rate of 10°C/min in nitrogen gas or in air up to 900°C.

### RESULTS

In Figure 1 the infrared spectra of PPTA film prepared from a solution with the same concentration used to prepare the fibers are shown. The spectra agree quite well with those of PPTA previously reported by Takayanagi et al.<sup>8</sup> Figure 2 shows x-ray diffraction patterns in the equator and meridian directions for various PPTA fibers. It is apparent from Figure 2 that differences in shape between the patterns in both directions for the as-prepared fiber, A and B, are small and that both patterns are broad. However, the differences between both patterns for the 300°C-annealed fiber, C and D, are larger and these peaks are sharper than those for the as-prepared fiber. This fact indicates that the crystallinity and the orientation anisotropy of the as-prepared fiber are increased somewhat by annealing. On comparing C and D with E and F, however, the crystallinity and the orientation anisotropy of the annealed fiber are found to be still definitely lower than those of Kevlar. This is also obvious from the x-ray Laue photographs in Figure 3. Such significant differences in the x-ray patterns strongly prove that the DuPont sample was spun from an anisotropic dope and ours, from an isotropic dope.

In Figure 4 the values of density at 20.0°C of the fibers are shown as a function of annealing temperature. The density gradually increases with increasing annealing temperature up to 400°C and then rapidly drops. Although the increase in density was considered to indicate an increase in crystallinity, the level of crystallinity could not be calculated from the density values because of the lack of information on the density value for the amorphous regions of this

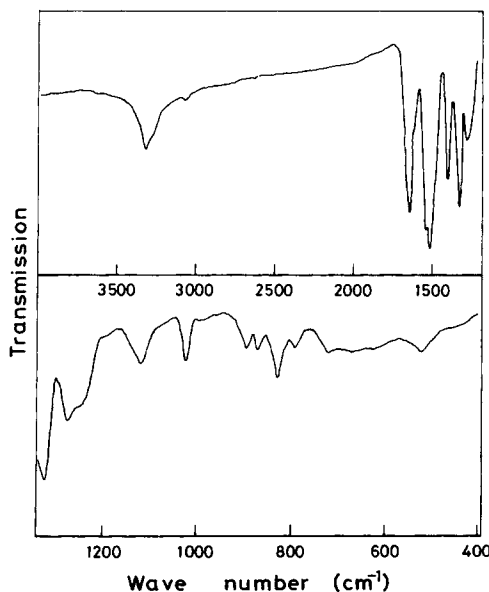


Fig. 1. Infrared spectra for PPTA film prepared in the same way as PPTA fiber.

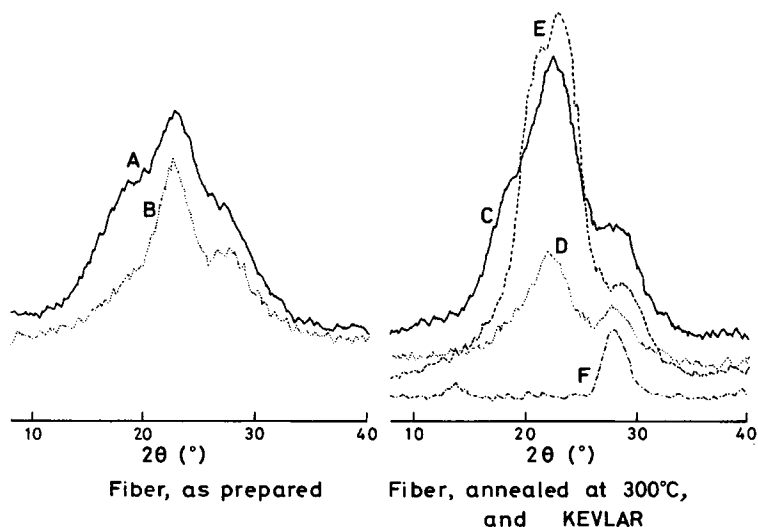


Fig. 2. X-ray diffraction patterns in equator and meridian directions for the as-prepared fiber (A and B), the 300°C-annealed fiber (C and D), and Kevlar (E and F).

polymer. However, even the maximum density value measured here, 1.425 g/cm<sup>3</sup>, is appreciably small in comparison with the determined density of Kevlar, 1.44 g/cm<sup>3</sup>, which precisely agrees with the values measured by Northolt<sup>1</sup> and with the 1.50 g/cm<sup>3</sup> by Tadokoro et al.<sup>2</sup> This strongly suggests again that the samples used in this study have a fairly low degree of crystallinity or of structural regularity.

The temperature dependences of the dynamic storage modulus  $E'$ , the dynamic loss modulus  $E''$ , and  $\tan \delta$  for the PPTA fibers are shown over the temperature range of room temperature to 500°C in Figures 5, 6, and 7, respectively. In each figure the data for the fibers as prepared and annealed at 200 and 300°C are provided, but the data for the fibers annealed at other temperatures, 100, 400, and 500°C, were deleted in order to avoid complexity. The values of  $E'$  increased regularly with increasing annealing temperature, and the maximum value at room temperature reached  $15.3 \times 10^{10}$  dynes/cm<sup>2</sup>, but even this value was very small in comparison with the value published as the modulus of Kevlar,  $65 \times 10^{10}$  dynes/cm<sup>2</sup>. In the  $E'$ -temperature curves, significant reductions of  $E'$  are observed from room temperature and about 400°C. Furthermore, it is apparent from Figure 5 that  $E'$  value increases from almost the same temperature, 460°C, for all the samples examined. In Figure 6, two large dispersion peaks clearly appear at about 60°C and in the vicinity of 400°C. The dispersion peak at about 60°C increases in intensity and shifts to a higher temperature as the annealing temperature is raised, but the annealing temperature dependence of the dispersion peak at about 400°C is unclear. In the range of 100 to 300°C, the temperature dependence of  $E''$  is complex, but in the fibers annealed at 300 and 400°C two weak dispersion peaks can be found at about 170 and 270°C.

The temperature dependence of  $\tan \delta$  is shown in Figure 7; two large peaks are clearly recognized at about 60 and 460°C. In addition, the as-prepared fiber and the 200°C annealed fiber exhibit a broad peak in the vicinity of 200°C, whereas the 300°C-annealed fiber exhibits two weak peaks at about 170 and 270°C. Further, for all the samples a shoulder is observed at 380°C.

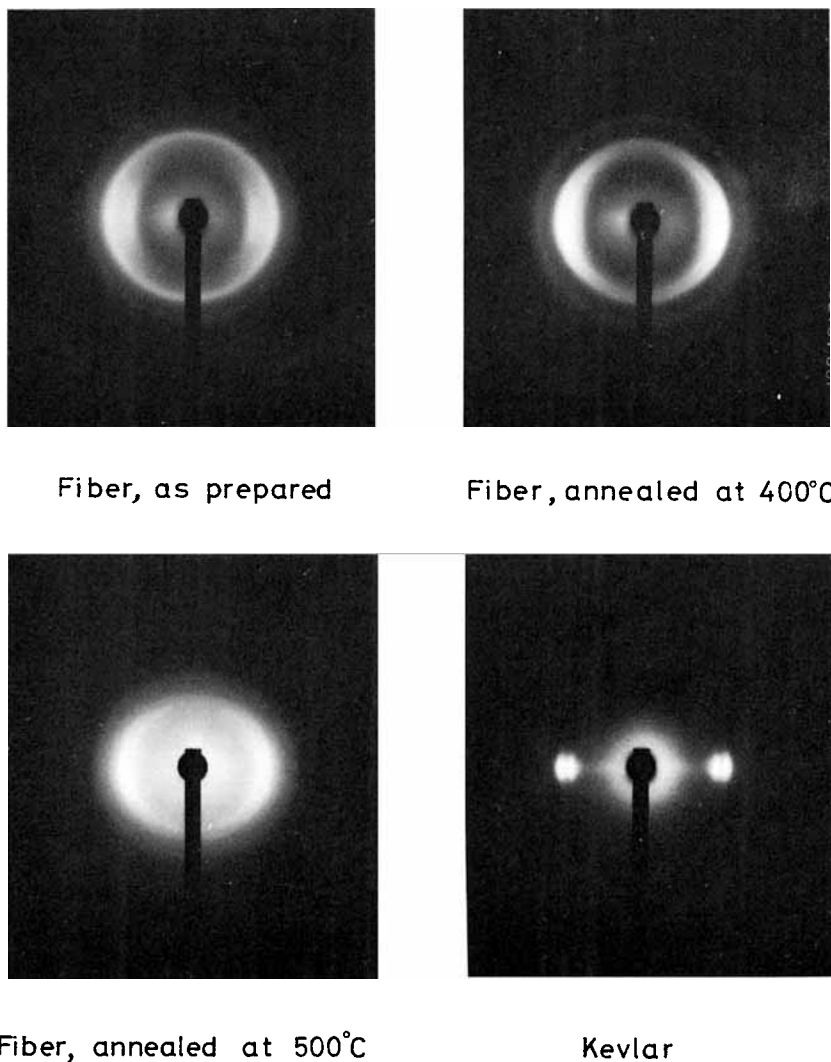


Fig. 3. X-Ray Laue photographs of the as-prepared fiber, the 400°C-annealed fiber, the 500°C-annealed fiber, and the commercially available Kevlar.

Figure 8 shows the temperature dependences of  $E'$ ,  $E''$ , and  $\tan \delta$  over the range of  $-100^{\circ}\text{C}$  to room temperature. In the  $E''$ -temperature curves, a dispersion peak is observed at about  $-30^{\circ}\text{C}$ . This peak becomes sharper and stronger as the annealing temperature is raised. On the other hand, the  $\tan \delta$  peaks, although not as obvious because of broadening, appear at slightly higher temperatures than the  $E''$  peaks, and their intensity decreases slightly with increasing annealing temperature.

Only the dynamic mechanical behavior of the 500°C-annealed fiber differs widely from that of other fibers; namely, its  $E'$  value is unusually small and no dispersion peak was observed in both the  $E''$ -temperature and  $\tan \delta$ -temperature curves. Such a trend had also been recognized in the behavior in the high-

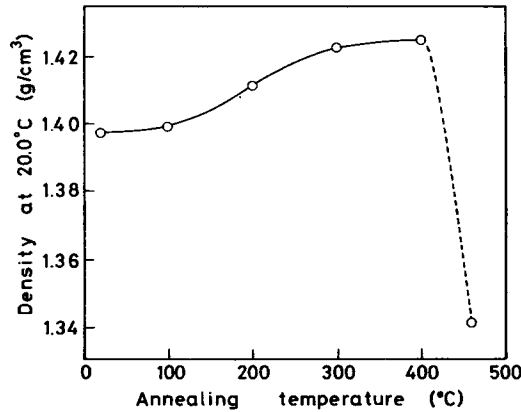


Fig. 4. Relationship between density at 20.0°C of the films and annealing temperature.

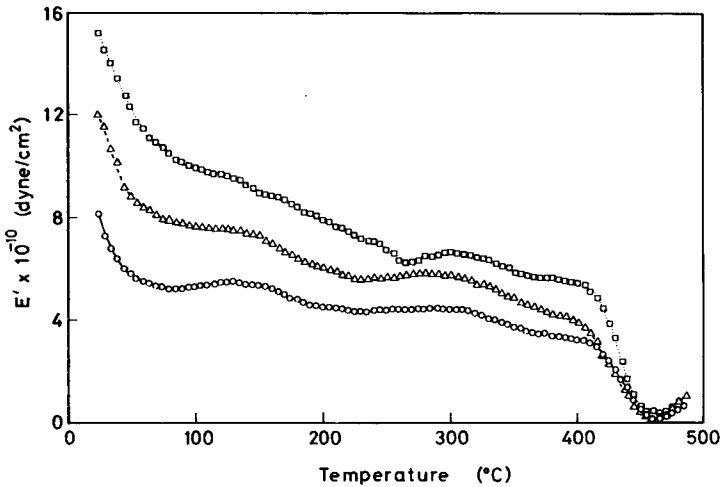


Fig. 5. Temperature dependence of the dynamic storage modulus  $E'$  in the higher temperature range for PPTA fibers: (O) as-prepared fiber; ( $\Delta$ ) 200°C-annealed fiber; ( $\square$ ) 300°C-annealed fiber.

temperature range, although the curves for the 500°C-annealed fiber were deleted from Figures 5, 6, and 7.

## DISCUSSION

The  $\alpha$ -dispersion process in this polymer has not been reported to date. Frosini et al.<sup>6</sup> investigated the dynamic mechanical properties of a number of aliphatic, partially aromatic, and wholly aromatic polyamides. In the case of PPTA, however, they did not observe the  $\alpha$ -dispersion, although they found the  $\beta$ - and  $\beta^*$ -dispersions at 10 and 140°C, respectively. Recently, Takayanagi et al.<sup>8</sup> also discussed the  $\beta$ - and  $\beta^*$ -dispersions of PPTA on the basis of the results

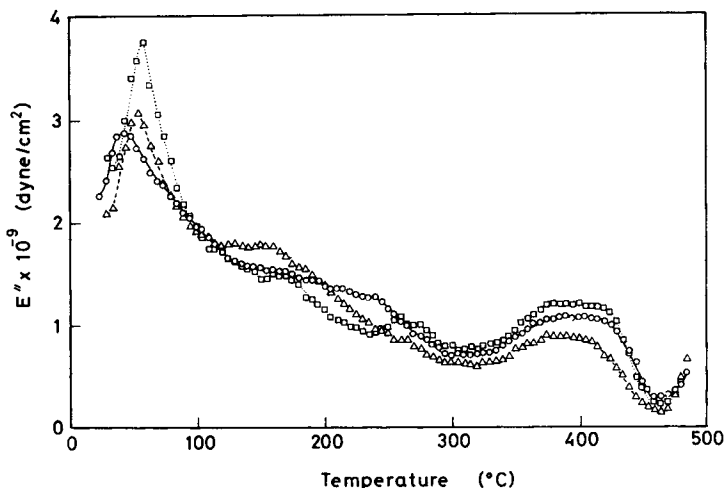


Fig. 6. Temperature dependence of the dynamic loss modulus  $E''$  in the higher temperature range for PPTA fibers: (O) as-prepared fiber; ( $\Delta$ ) 200°C-annealed fiber; ( $\square$ ) 300°C-annealed fiber.

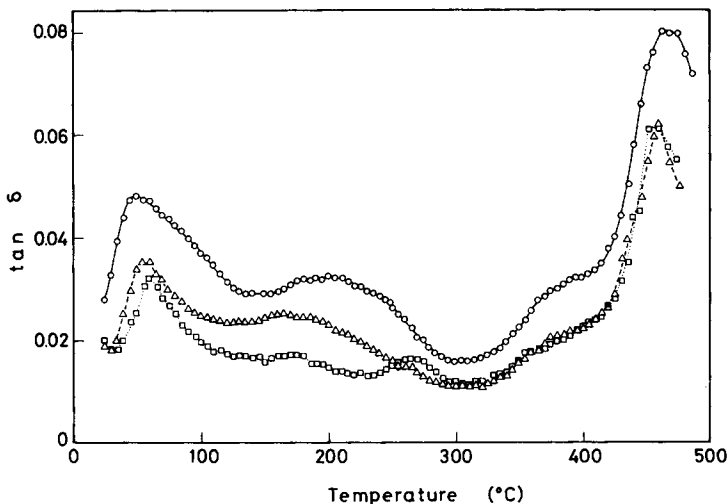


Fig. 7. Temperature dependence of  $\tan\delta$  in the higher temperature range for PPTA fibers: (O) as-prepared fiber; ( $\Delta$ ) 200°C-annealed fiber; ( $\square$ ) 300°C-annealed fiber.

of dynamic mechanical measurements and x-ray measurements but did not describe the  $\alpha$  dispersion in their report. One reason for overlooking the  $\alpha$  dispersion must be that the temperatures at which their experiments were made were too low to observe the dispersion. Frosini et al.<sup>6</sup> used the range of 150 to 300°C, whereas Takayanagi et al.<sup>8</sup> used the range of 150 to 350°C.

Therefore, we extended the range of measurements to 500°C and used samples prepared as amorphous and as unoriented as possible in order to detect small-scale movements of molecular segments. Subsequently, it became clear that a large dispersion peak appeared at about 400°C in the  $E''$ -temperature curve or at about 460°C in the  $\tan\delta$ -temperature curve and that the  $E'$  value decreased considerably in the corresponding temperature range. It can also be seen from Figure 6 that the intensity of the  $\tan\delta$  peak is smaller in the annealed fibers than

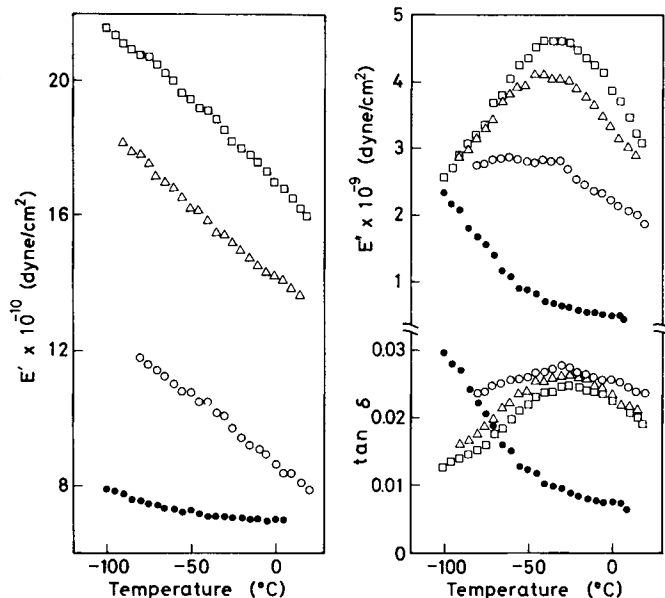


Fig. 8. Temperature dependences of  $E'$ ,  $E''$ , and  $\tan \delta$  in the lower temperature range for PPTA fibers: (O) as-prepared fiber; ( $\Delta$ ) 200°C-annealed fiber; ( $\square$ ) 300°C-annealed fiber; ( $\bullet$ ) 500°C-annealed fiber.

in the as-prepared fiber. Since the annealing treatment results in essentially an increase in crystallinity, this fact indicates that the dispersion is related to the molecular motions in the amorphous regions. On the basis of these facts and the temperature position of the dispersion peak, it seems reasonable to assume that this dispersion is the  $\alpha$  dispersion or the primary dispersion of this polymer, being ascribed to micro-Brownian motions of the main chains in the amorphous regions.

Figure 9 shows the frequency dependence of peak temperature  $T_p$  of the  $\alpha$  dispersion for the as-prepared and the 200°C- and 400°C-annealed fibers. An apparent activation energy of 183 kcal/mole was calculated from the slope of the straight line for the as-prepared fiber. The values obtained for the annealed fibers also agreed quite well with this value, despite the difference in thermal history. The obtained values are extremely high compared to the apparent activation energies for the  $\alpha$  dispersion in other crystalline polymers, for example, 98 kcal/mole in nylon 6<sup>11</sup> or 128 kcal/mole in polyimide (Kapton H),<sup>12</sup> and suggest that the main chains are difficult to move over a wide range because of the rigidity of the molecular chains. In the DSC curve of PPTA, the glass transition corresponding with the  $\alpha$ -dispersion could not be observed at all.

As mentioned above, two weak dispersion peaks were found at about 270 and 170°C and in the  $E''$ -temperature or  $\tan \alpha$ -temperature curves for the 300°C-annealed fiber as well as for the 400°C-annealed one. The peak at 270°C seems to correspond to the  $\beta^*$ -dispersion peak (250°C) proposed by Takayanagi et al.<sup>8</sup> They pointed out that the relaxation process arose from thermal molecular motions in the crystalline regions on the basis of the results of x-ray and density measurements. The fact that in our study the peak at 270°C appears only for the annealed samples with relatively high crystallinity seems to support the as-



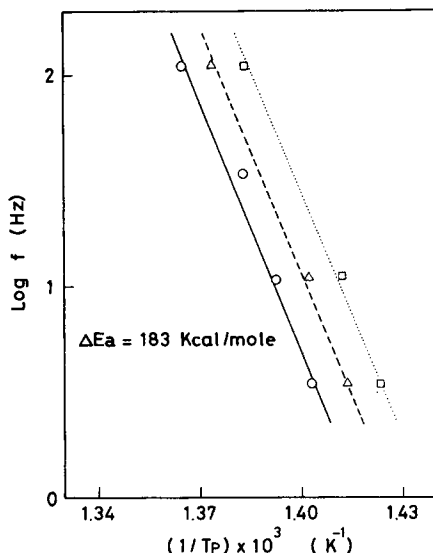


Fig. 9. Plots of the logarithm of frequency vs reciprocal of absolute temperature of the  $\alpha$  dispersion peak at about 450°C. Solid line is as-prepared fiber, broken line is 200°C-annealed fiber, and dotted line is 400°C-annealed fiber.

segment of Takayanagi et al.<sup>8</sup> On the other hand, the dispersion peak at 170°C is considered to correspond with the  $\beta^*$ -relaxation (140°C) labeled by Frosini et al.<sup>6</sup> They explained it as a secondary mechanical relaxation process being connected with motions of the aromatic portions of chains, based on experimental results that an analogous relaxation could be found in most polymers containing aromatic rings in the main chains, such as poly(*p*-phenylene ether), polyimide, and aromatic polyester.

The large dispersion peak occurring at 60°C is considered to be identical to the  $\beta$ -dispersion peak reported by both Frosini et al.<sup>6</sup> and Takayanagi et al.,<sup>8</sup> although the temperature position differs from those in their results, i.e., 10 and 0°C, respectively. Frosini<sup>6</sup> suggested that the relevant relaxation process was due to the motions of free amide groups which did not form inter- or intramolecular hydrogen bonds and that the presence of water molecules or other low molecular weight polar substances played an important role in the relaxation process. Figure 10 shows a comparison of the dispersion of the undried fibers containing about 6% moisture with that of fully dried fibers. When water contained in the fibers is removed, the dispersion peak decreases in intensity and shifts toward a higher temperature for both the as-prepared and the 300°C-annealed fibers. Since the water molecules are generally selectively absorbed by the amorphous regions, it can be said that the dispersion is closely related to the motions of the amide group belonging to the amorphous regions. This hypothesis is also supported by the fact that the dispersion peak gradually decreases in intensity and shifts to higher temperatures as the annealing temperature is raised, as can be seen in Figure 7. Figure 11 shows the frequency dependence of the peak temperature  $T_p$  of the dispersion at 60°C. The plots for both the as-prepared and the annealed fibers gave two good straight lines parallel to each other. An apparent activation energy for this dispersion was estimated at 48.6 kcal/mole from the slope of the lines.

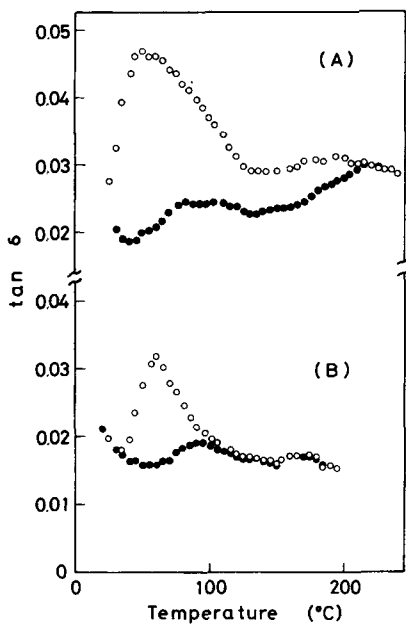


Fig. 10. Effect of water contained in the samples on the behavior of the dispersion peak at about 60°C: (○) undried fiber; (●) fully dried fiber; (A) as-prepared sample; (B) 300°C-annealed sample.

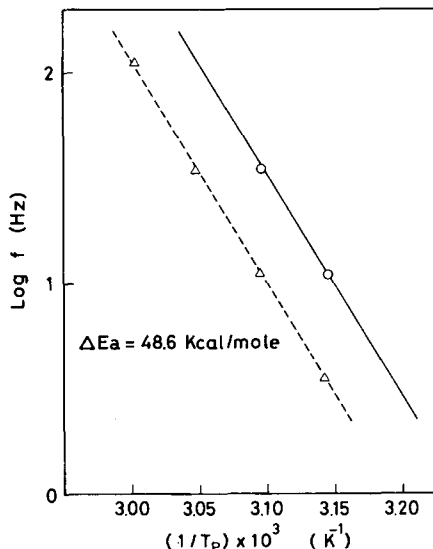


Fig. 11. Plots of the logarithm of frequency vs reciprocal of absolute temperature of the dispersion peak at about 60°C. Solid line is as-prepared fiber and broken line is 200°C-annealed fiber. The data of the 400°C-annealed fiber was in good agreement with those of 200°C-annealed fiber.

The experimental results in the lower temperature range also indicate the existence of a dispersion peak situated in the vicinity of  $-30^\circ\text{C}$ . No relaxation process at this temperature position has been reported in the literature. Although the relaxation mechanism for the dispersion peak is not yet clear, the following behavior was observed. From Figure 8 and from Figure 12, which

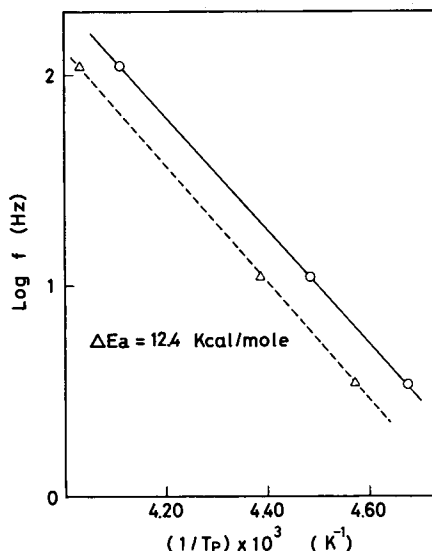


Fig. 12. Plots of the logarithm of frequency vs reciprocal of absolute temperature of the dispersion peak at about  $-30^{\circ}\text{C}$ . Solid line is as-prepared fiber and broken line is  $200^{\circ}\text{C}$ -annealed fiber. The data of  $300^{\circ}\text{C}$ -annealed and  $400^{\circ}\text{C}$ -annealed fibers agree with those of  $200^{\circ}\text{C}$ -annealed fiber.

shows the frequency dependence of  $T_p$ , it is found, respectively, that the intensity of the  $\tan\delta$  peak slightly decreases as the annealing temperature is raised and that  $T_p$  evidently shifts to a higher temperature by annealing, although the extent of shifting is virtually unaffected by the differences in the annealing temperatures ( $200$ ,  $300$ , and  $400^{\circ}\text{C}$ ). From the slope of the straight lines in Figure 12, the apparent activation energy for this dispersion was calculated to be  $12.4$  kcal/mole. On the basis of such behavior for a  $\tan\delta$  peak, the temperature position, and the magnitude of the apparent activation energy, the dispersion was regarded as a  $\gamma$ -relaxation process of this polymer. Furthermore, it seems reasonable to assume that this local mode relaxation is due to slight internal rotation around the single bonds between the carbon of *p*-phenylene and the carbon belonging to the carbonyl group or the nitrogen belonging to the NH group.

Tadokoro et al.<sup>2</sup> reported that the internal rotational angles of the benzene ring measured from the amide plane were about  $30^{\circ}$  in the most stable state with respect to potential energy and that the potential barriers for the internal rotation around the bonds were  $6$ – $12$  kcal/mole.

For poly(*m*-phenyleneisophthalamide) film, a similar dispersion peak was found by us<sup>13</sup> at  $-65^{\circ}\text{C}$  in the  $\tan\delta$ –temperature curve. If the above molecular interpretation is acceptable, the discrepancy in the temperature positions of the dispersion peaks for the two aromatic polyamides can be understood by considering the symmetry of the molecular chains.

The degradation temperature of PPTA has been reported to be  $500^{\circ}\text{C}$  in the literature.<sup>14</sup> As described before, surely the temperature dependence curves of  $E'$ ,  $E''$ , and  $\tan\delta$  for the  $500^{\circ}\text{C}$ -annealed sample differ widely from those for the samples annealed at temperatures below  $400^{\circ}\text{C}$  and are abnormal; namely, the values of  $E'$  are unusually low over the wide temperature range examined, and all the dispersion peaks observed in the samples annealed at temperatures below  $400^{\circ}\text{C}$  could not be detected in the  $500^{\circ}\text{C}$ -annealed sample. In addition,

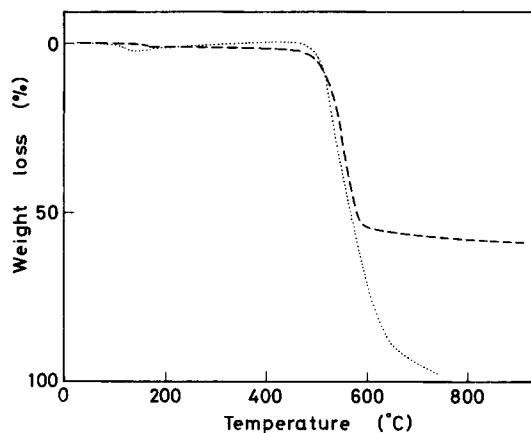


Fig. 13. TG curves for PPTA sample; The broken line is the result measured in nitrogen gas, and the dotted line is that measured in air.

the Laue x-ray photograph of the 500°C-annealed sample displayed an unclear pattern, as seen in Figure 3.

The increase in the modulus with increasing temperature was observed at considerably lower temperature than 500°C, as can be seen in Figure 5. In general, since chemical changes in the structure of a polymer during heat treatment, such as oxidation, crosslinking reaction, and thermal scission of the main chains, are distinctly reflected in static or dynamic mechanical behavior of the polymer, measurements of the mechanical properties of the polymer as a function of temperature can be said to be the most sensitive and effective test for determining thermal stability. As previously reported in the case of polyimide film,<sup>12</sup> the increase in the dynamic tensile modulus at elevated temperature is explained by suggesting the crosslinking and/or chain-stiffening reaction. Onset of the thermal degradation in the vicinity of 450°C is also supported by the experimental facts that the density value of the 460°C-annealed sample is remarkably lower than other values (Fig. 4) and that the onset of the retention in weight of the sample was observed at 460°C (Fig. 13). From these observations it can be concluded that the thermal degradation of this polymer begins at about 450°C. Since this temperature is considerably higher than that of the onset of relatively sharp reduction in  $E'$  (400–410°C), the first half of the  $\alpha$ -relaxation process is not affected by the thermal degradation of the sample. However, it must be kept in mind that the  $\alpha$ -relaxation behavior at temperatures above 450°C is affected more or less directly by the thermal degradation of the samples because the resulting crosslinking apparently reduces the mobility of the molecular segments.

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