

Structure and Properties of *N*-Octadecylated Poly(*p*-Phenylene Terephthalamide)

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Synopsis

N-octadecylated PPTA's with various molecular weights were synthesized from PPTA and *n*-octadecyl bromide via the metalation reaction. The polymer exhibited side-chain crystallization at 314 K due to the long alkyl side chains and both crystallinity and the perfection of the crystal increase with increasing in the molecular weight. The results of IR spectra and the wide angle X-ray indicate that the polymer crystallizes in hexagonal form. The mechanical and the dynamic mechanical properties of *N*-octadecylated PPTA's were measured. Two $\tan \delta$ peaks were observed in a temperature range of 310–350 K and at 260 K, respectively, which can be designated α_c and α_a relaxation, respectively. The concentrated solutions of *N*-octadecylated PPTA's in tetrahydrofuran, dichloroethane, tetrachloroethane, and bromoform showed liquid crystalline behavior of lyotropic type.

INTRODUCTION

Since the discovery by Rehberg and Fisher,¹ Kaufman et al.,² and Wiley and Brauer³ that polymers having side chains of long alkyl groups form side-chain crystallization, a lot of articles have been published in the literature describing the structure, the properties, and the applications of these so-called comblike polymers. The matter has been reviewed by Platé and Shibaev.⁴ The typical polymers are the poly(*n*-alkyl acrylates and methacrylates),² the poly(2-*n*-alkyl-1,3-butadiene)s,⁵ the poly(vinyl ester)s,⁶ the poly(*n*-alkylstyrene)s,⁷ the poly(*N*-*n*-alkylacrylamide)s,⁸ the poly(fluoro-*n*-alkyl acrylate)s,⁹ which contain at least four carbon atoms in the side chains and have flexible backbone such as vinyl group.

Recently, Aharoni et al.^{10–14} reported that poly(*n*-alkyl isocyanide)s and poly(*n*-alkyl isocyanate)s, having relatively rigid backbone, which may be planar or helicoidal, to which relatively flexible side groups are attached, are mesogenic in concentrated solutions at ambient temperatures and in bulk at elevated temperatures. However, these polymers are thermally so unstable that they decompose below 470 K, resulting in the limited applications.

A family of polymers fitting polyisocyanides and polyisocyanates having rigid backbone and flexible side groups is the *N*-alkylated poly(*p*-phenylene terephthalamide) (PPTA) family, which was synthesized and characterized in our laboratory.¹⁵ In this paper we present the results of a study of *N*-octadecylated PPTA which is a typical example of *N*-alkylated PPTA and is thermally stable.

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The present results provide some knowledge on thermal properties, side-chain crystallization, mechanical properties, dynamic mechanical properties, and solution properties of *N*-octadecylated PPTA's with various molecular weights.

EXPERIMENTAL

Materials

The PPTA samples were supplied by Asahi Chemical Industry Co., Ltd., in a powder form. Molecular weights of the PPTA samples were determined by measuring intrinsic viscosities in concentrated sulfuric acid (97%) at 298 K. The Mark-Houwink equation was used, the parameters of which were given by Arpin and Strazielle¹⁶:

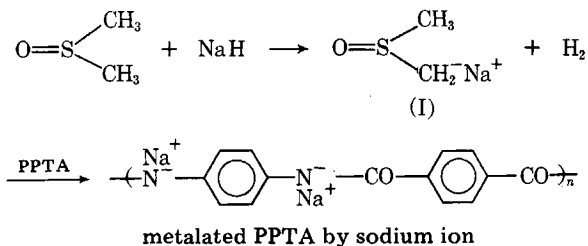
$$[\eta] = 8 \times 10^{-5} M_v^{1.09} \text{ dL/g}$$

Dimethyl sulfoxide was fractionally distilled over calcium hydride in a vacuum and finally dried over 4 Å molecular sieve. Sodium hydride and *n*-octadecyl bromide in a suspension in paraffin were reagent grades and were used as received.

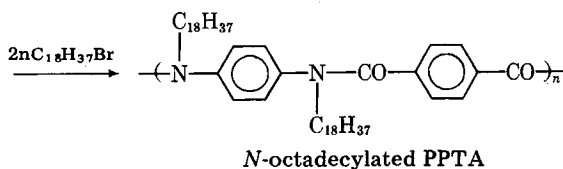
Preparation of *N*-Octadecylated PPTA

N-*n*-octadecylated PPTA's with various molecular weights were synthesized from PPTA and *n*-octadecylated bromide by the polymer reaction in a solution methylsulfinylcarbanion (I) in dimethyl sulfoxide at a low temperature. The polymer reaction via the metalation reaction of PPTA, which was described in detail elsewhere,¹⁵ proceeds in the following schemes:

Metalation reaction:



Substitution reaction:



A 0.025-mol amide unit (3.0 g) of PPTA powder was added to a solution (100 mL) of sodium methylsulfinylcarbanion in dimethyl sulfoxide at 303 K and the metalation reaction was continued for 4 h. Then, 0.025 mol (8.33 g) of *n*-octadecyl bromide was added, and the mixture was stirred at 303 K for 16 h. The product was precipitated in a large excess of water, filtered, and washed several times with water and acetone alternately. After the product was dried at 323 K for 10 h in a vacuum oven, the light yellow powder of product was obtained.

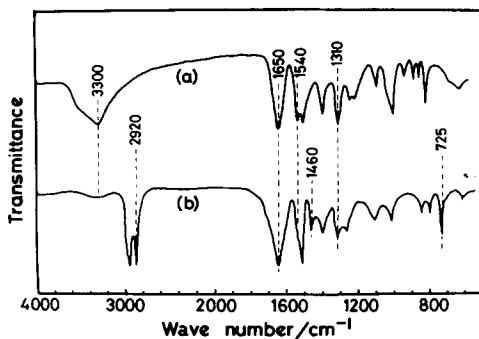


Fig. 1. Infrared spectra of (a) PPTA and (b) *N*-octadecylated PPTA of ST-1.

Characterization

Infrared Spectra. Infrared (IR) spectra were obtained from pulverized samples in KBr pellets by using a grating infrared spectrometer (Perkin-Elmer 567).

X-Ray Diffraction. X-ray diffraction diagrams were taken with an X-ray generator (Rigaku Denki Co.), using Ni-filtered $\text{CuK}\alpha$ radiation.

Thermal Analyses. Thermogravimetric (TGA) and differential thermal analyses (DTA) were performed by using a thermal analyzer (Rigaku Denki Co.) at a heating rate of 10 K/min in nitrogen atmosphere. Differential scanning calorimetry (DSC) diagrams were obtained by using UNIX (Rigaku Denki Co.) at a heating rate of 10 K/min in nitrogen atmosphere.

Tensile Test. For measurements of mechanical properties, the specimens were prepared by compressing at 423 K. The molded specimens were about 0.4 mm thick. Tensile tests were conducted using Tensilon (Toyo Baldwin Co.) at room temperature. An apparent strain rate of 33%/min was used for tests.

Measurement of Dynamic Mechanical Properties. Dynamic mechanical properties were measured at 11 Hz by using Rheovibron (Toyo Baldwin Co.) at a heating rate of about 0.5 K/min in nitrogen atmosphere.

Optical Microscopy. Optical microscopic observations were conducted using a polarization optical microscope with a heating equipment (Nihon Kogaku Co.).

RESULTS AND DISCUSSION

Preparation of *N*-Octadecylated PPTA

IR spectra of PPTA and *N*-octadecylated PPTA's are shown in Figure 1. Spectrum of PPTA displayed a broad absorption peak centered at 3300 cm^{-1} due to hydrogen-bonded NH groups and three peaks attributable to amide I, II, and III bands at 1650 cm^{-1} (C=O stretching), 1540 cm^{-1} (CNH), and 1310 cm^{-1} (CNH), respectively. On the other hand, a broad absorption peak at 3300 cm^{-1} and the amide II were absent in the spectrum of *N*-octadecylated PPTA. Moreover, the spectrum displayed new absorptions due to the methylene groups in the side chains of octadecyl groups at 725, 1460, and 2920 cm^{-1} .

The data of elemental analyses are given in Table I. The degree of substitution was determined by the nitrogen content of polymers. The results indicate that

TABLE I
N-Octadecylated PPTA's

Code	M_v of PPTA	Elemental analysis, found (%)			Degree of substitution (mol %)	Temp of 10% weight loss (K)
		C	H	N		
ST-1	4100	79.07	10.74	3.85	97	665
ST-2	12000	78.83	10.64	4.04	90	683
ST-3	24700	79.56	10.96	3.80	99	688
ST-4	36400	78.95	10.55	4.00	92	691

the PPTA's with various molecular weights reacted almost quantitatively with an equivalent mole of *n*-octadecyl bromide via the metalation reaction.

Side-Chain Crystallization

The TGA and DTA curves of PPTA and *N*-octadecylated PPTA are shown in Figure 2. The TGA curves indicate that a thermal stability of modified PPTA was about 130°C lower than that of PPTA. The effect of molecular weights on the thermal stability of PPTA derivatives is that the thermal stability increases with an increase in molecular weights shown in Table I. The DTA curves of PPTA exhibited only one endothermic peak at about 800 K because of a thermal decomposition mechanism,^{17,18} whereas, the DTA curves of *N*-octadecylated PPTA exhibited two endothermic peaks at 314 K and about 700 K, respectively. A lower endothermic peak should be attributed to the melting of the crystalline structure formed by the long *n*-alkyl side chains which can initiate crystallization at a certain critical chain length. It is well known that long side chain polymers, so-called comblike polymers, have the ability to crystallize, with the three-dimensional order formed entirely due to the side chain packing.⁴ Figure 3 shows the effect of the molecular weights on the melting temperatures. These curves were drawn to equal weights and temperature increments. The overall melting range is similar in all cases, but there is a difference in the shape of endothermic peaks. These curves qualitatively reflect the crystallinity and the perfection of the crystals. Therefore, this indicates that the melting point is independent

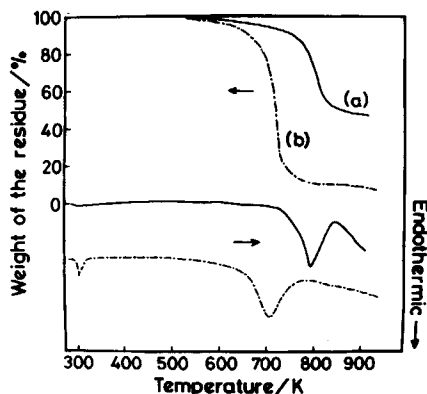


Fig. 2. Thermogravimetric and differential thermal analyses of (a) PPTA and (b) *N*-octadecylated PPTA of ST-1.

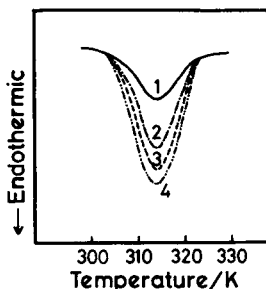


Fig. 3. The effect of molecular weights on DTA curves of *N*-octadecylated PPTA's. M_v : (1) 4100; (2) 12,000; (3) 24,700; (4) 36,400.

of the molecular weight, whereas the crystallinity and the perfection of the crystals are dependent on it. The same tendency was observed in the intensity curves of the wide angle X-ray diffraction in Figure 4, in which *N*-octadecylated PPTA's exhibited a strong and sharp peak at 0.41 nm and increased with an increase in molecular weights. This peak at 0.41 nm is quite different from three sharp peaks due to the crystalline structure of the PPTA and, therefore, should be attributed to side-chain crystalline structure because of the fact that this value is analogous to the diffraction peak on the X-ray patterns of polyethylene and *n*-paraffins.⁴ Taking *n*-alkanes as a basis for comparison, it is known that the molecules of *n*-paraffins are parallelly packed like rotational cylinders whose axes are spaced by a distance of 4.2 Å and which have about six neighbors, that is to say which are packed nearly hexagonally.

Another evidence for the hexagonal packing of the side chains in comb-like polymers such as *N*-octadecylated PPTAs is the IR spectra. As demonstrated by Chapman,¹⁹ different crystalline modifications of low molecular long chain compounds, such as paraffins, esters, alcohols, etc., have corresponding different characteristic absorption bands. Thus, the hexagonal form is characterized by a strong absorption at 725 cm^{-1} , corresponding to the vibration of the C—H groups of the methylene chain. For a more stable rhombic form this absorption

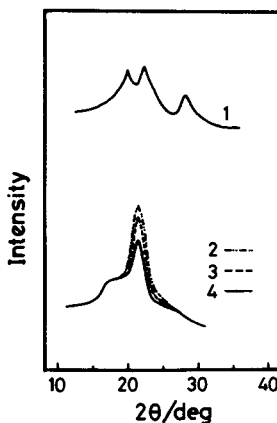


Fig. 4. The intensity curves of the wide angle X-ray diffraction: (1) PPTA; (2) ST-4; (3) ST-3; (4) ST-1.

band splits into two peaks (at 720 and 730 cm^{-1}) of roughly equal intensity, corresponding to the in-phase and out-of-phase vibrations of the C—H methylene groups, respectively. The IR spectra of *N*-octadecylated PPTA's showed a single absorption peak at 725 cm^{-1} shown in Figure 1, indicating that the polymers crystallize in hexagonal form. Thus, greater conformational distortions of the backbone chain such as phenylene groups results in the disordering of packing of the layered structures and in only a one-layer packing of the side chains of a hexagonal packing, depending on the degree of imperfection.

The degree of crystallinity for ST-4, having the highest molecular weight, was 9% on the basis of side chains in *N*-octadecylated PPTA. Moreover, preliminary experiments of other long alkylated PPTA's, such as heptylated and dodecylated PPTA's synthesized in our laboratory,¹⁵ showed that, although common comblike polymers having the same alkyl side chains take part in crystallization, these side chains of PPTA derivatives did not crystallize. These facts indicate that no crystallization of *N*-octadecylated PPTA takes place in the neighborhood of main chains and only long alkyl chains front can take part in crystallization because of long distances of 7–8 Å between side chains which are greater than those of 2.5 Å for common comblike polymers, resulting in a low degree of crystallinity. This hypothesis will be supported by the result of dynamic mechanical measurements in the latter section.

Mechanical and Dynamic Mechanical Properties

For measurements of mechanical and dynamic mechanical properties, the specimens of *N*-octadecylated PPTA's with lower molecular weights such as ST-1, ST-2, and ST-3 could not be prepared by compressing at 423 K because of their fragility, whereas the specimens of *N*-octadecylated PPTA with the highest molecular weight (ST-4) could be prepared by the same procedure.

The ultimate strength of 4.8 MPa and the Young's modulus of 231 MPa for ST-4 were obtained, which are about 1% of those for original PPTA fibers, while the ultimate elongation of 2.3% was obtained. On the other hand, the mechanical properties for comblike homopolymers such as *n*-octadecyl acrylate, *N*-*n*-octadecylacrylamide, and vinyl stearate could not be obtained because of their fragility.²⁰ Higher *n*-alkyl vinyl monomers were copolymerized with methyl methacrylate to improve the tensile strength and the modulus of the copolymers.²⁰ The values of mechanical properties decreased in magnitude with increasing in the content of long *n*-alkyl vinyl comonomers. For example, a copolymer of *N*-*n*-octadecylacrylamide with methyl methacrylate had the tensile strength of 1.6 MPa and the Young's modulus of 200 MPa in the mole fraction of 0.60 of *N*-*n*-octadecylacrylamide. Above this composition the mechanical properties of the copolymers were not measured. This indicates that *N*-octadecylated PPTA of ST-4 with fully long side chains and the highest molecular weight can be fabricated in various complex shapes because of the excellent mechanical properties in spite of a great decrease in those of the original PPTA.

The measurements of dynamic mechanical properties are shown in Figure 5. The $\tan \delta$ peak located in a temperature range of from 310 to 350 K can be designated the α_c (subscript *c* is concerned with the motion of crystalline phase) relaxation, which has been assigned to the molecular motions associated with

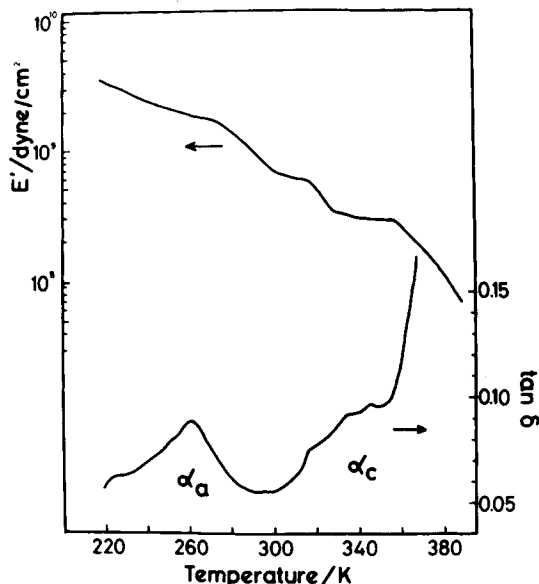


Fig. 5. Plots of E' and $\tan \delta$ vs. temperature for *N*-octadecylated PPTA with the highest molecular weight (ST-4).

the crystalline phase formed by long side chains, on the basis of the results of polyoctadecene-1.²¹⁻²³ The steep increase of the $\tan \delta$ curve at about 310 K is associated with crystal melting. The $\tan \delta$ peak located at 260 K can be designated the α_a relaxation, which has been assigned to the micro-Brownian motion of long side chains associated with amorphous phase (21-23). Manabe and Takayanagi²³ suggested that this dispersion is due to the same mechanism as that of α_a dispersion for branched polyethylene, assigned to the micro-Brownian motion of main chain in the amorphous phase of polyethylene. The separated peaks observed in polyoctadecene-1, designated α'_a and α''_a , which have been assigned to the micro-Brownian motions of main chains including side chains and side chains in the amorphous phase, respectively, could not be observed in *N*-octadecylated PPTA. This peak may be due to the overlapping by the peak of the β relaxation located in a temperature range of 260-270 K for original PPTA fiber, which has been assigned to the motion of the amide groups in the amorphous phase.^{18,24,25} Even if this overlapping is taken into consideration, the $\tan \delta$ peak concerning α_a relaxation was increased in its magnitude due to the micro-Brownian motion of long side chains, compared with that of common comblike polymers such as polyoctadecene-1.²¹ This fact indicates that amorphous phases increased because of long distances of 7-8 Å between side chains, and, therefore, the degree of crystallinity decreased. Furthermore, it supports also the hypothesis on the structure of *N*-octadecylated PPTA described in the previous section.

Solution Properties in Various Solvents

Crystallization and layered ordering in the melts of *n*-alkyl long side chains of *N*-octadecylated PPTA's have been shown in the previous section to be due

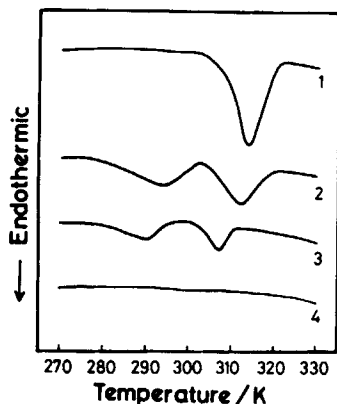


Fig. 6. DSC curves of (1) *N*-octadecylated PPTA of ST-4 and solutions of ST-4 in THF at different polymer concentrations: (2) 50 vol %; (3) 30 vol %; (4) 20 vol %.

to strong intra- and intermolecular interactions of side methylene groups. It has been shown elsewhere¹⁵ that *N*-octadecylated PPTA's are soluble in a number of organic solvents such as benzene (Bz), tetrahydrofuran (THF), 1,2-dichloroethane (DCE), and 1,1,2,2-tetrachloroethane (TCE). Figure 6 shows the DSC curves of ST-4 solution in THF at different polymer concentrations. In a range of the polymer concentration of less than 20 vol %, ST-4-THF system exhibited no endothermic peak because of its complete isotropy, whereas, in a range of the polymer concentration of greater than 30 vol %, the solution exhibited two endothermic peaks which are indicative of an organized structure. A higher endothermic peak located at 307 K (30 vol %) or 312 K (50 vol %) is greatly broader than that of ST-4 only located at 314 K and moves toward a higher temperature as the polymer concentration increases. The intensity curves of the wide angle X-ray diffraction of 20 vol % and 50 vol % solution of ST-4 in THF at 293 K are shown in Figure 7. A 20 vol % solution of ST-4 exhibited no peaks, indicating that its solution is completely isotropic and has thus no ordered structure. However, the 50 vol % solution exhibited a strong and sharp peak at 0.41 nm, which corresponds to the crystalline structure of octadecyl groups for ST-4 described in the previous section. These indicate that a higher endothermic peak is associated with the melting point of crystalline region formed by long alkyl side chains of ST-4 and that the structure of ST-4 in THF is looser than that of ST-4 only.

A lower endothermic peak located at 290 K (30 vol %) or 294 K (50 vol %) is quite different from the melting point (164 K) of THF and is slightly broader than a higher endothermic peak. This indicates that an ordered structure is formed because of a strong interaction between polymer and THF.

This DSC curve having two broad endothermic peaks is very similar to that of concentrated solutions of mesomorphic poly(alkyl isocyanate)s such as polyhexylisocyanate and polynonylisocyanate in TCE, which exhibited liquid-crystalline behavior in solutions above a certain critical concentration.¹¹ Poly(alkyl isocyanate)s form liquid crystals when the alkyl chains are sufficiently long to facilitate high-concentration solutions, yet short enough in order for side chain interactions not to dominate completely the behavior of the polymeric solution or its pure form. Namely, poly(alkyl isocyanate)s between C₆ and C₁₀

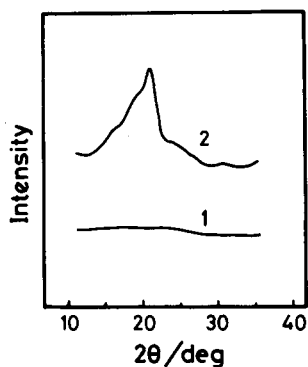


Fig. 7. The intensity curves of the wide angle X-ray diffraction of (1) 20 vol % and (2) 50 vol % solution of ST-4 in THF at 293 K.

of side chains show liquid crystals. On the other hand, preliminary experiments of *N*-alkylated PPTA's having side chains below C_{18} showed no formation of their liquid crystals. However, *N*-octadecylated PPTA liquid crystalline behavior, which seems to be corresponding to poly(nonyl isocyanate) with respect to the degree of crystallinity.

Figure 8 shows the polarization optical micrograph under crossed nicols of the thin layer of 50 vol % solutions of ST-4 in THF at room temperature. The sample was dissolved in THF at room temperature and exhibited a diffuse birefringent pattern under crossed nicols. By raising the temperature of the sample to 333 K, a quite dark image under crossed nicols appeared even after shearing stress, indicating an isotropic state of solution of ST-4 in THF. ST-4 seems to form a liquid crystal of lyotropic type. In other solvents such as DCE, TCE, and bromoform (BF), the same liquid crystalline behavior of solutions of ST-4 were observed in the DSC curves, the intensity curves of wide angle X-ray diffraction, and the polarization optical micrographs. Critical polymer concentrations in DCE, TCE, and BF are about 50 vol %, about 50 vol %, and about 60 vol %, respectively, which are higher than that of ST-4 in THF. On the other hand, a solution of ST-4 in Bz exhibited no liquid crystalline behavior or partially ordered structure even at polymer concentrations as high as 60 vol %. Thus, an insertion

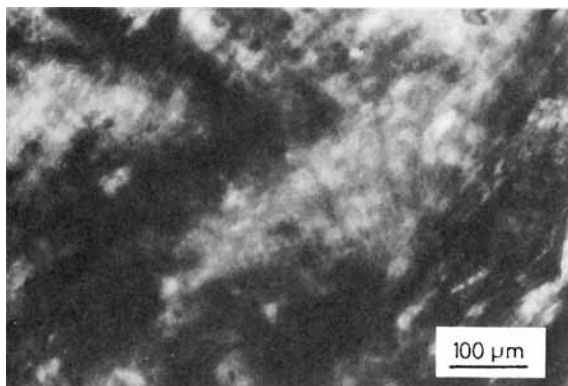


Fig. 8. Polarization optical micrograph under crossed nicols of the thin layers of 50 vol % solution of ST-4 in THF at room temperature.

of a polymer into solvents with polar atoms such as oxygen, bromine, and chlorine gives rise to a new phase, which seems to be formed by a molecular interaction between the amide group of PPTA and such polar atoms. However, benzene with no polar atoms has no ability to form a new phase because it dissolves the polymer at molecular level.

CONCLUSIONS

N-octadecylated PPTA's with various molecular weights were quantitatively synthesized from PPTA and *n*-octadecyl bromide via the metalation reaction.

An endothermic peak at 314 K in DTA curves was attributed to the melting point of crystalline structure and the degree of crystallinity obtained by DSC was 9%. Moreover, a strong and sharp peak at 0.41 nm in the wide angle X-ray was attributed to the crystalline structure because this value is analogous to those of the X-ray patterns of polyethylene and normal paraffins. A single absorption peak at 725 cm^{-1} in the IR spectrum and the result of the wide angle X-ray indicate that *N*-octadecylated PPTA crystallizes in hexagonal form.

N-octadecylated PPTA of ST-4 have the tensile strength of 4.8 MPa and the Young's modulus of 231 MPa and can be fabricated into various complex shapes. The measurements of dynamic mechanical properties showed two $\tan \delta$ peaks. The $\tan \delta$ peak located in a temperature range of from 310 to 350 K can be designated α_c relaxation, which has been assigned to the molecular motions associated with crystalline phase formed by long side chains. The $\tan \delta$ peak located at 260 K can be designated the α_a relaxation, which has been assigned to the micro-Brownian motion of long side chains associated with amorphous phase, and may be due to the overlapping by the peak of the β relaxation located in a temperature range of from 260 to 270 K, which has been assigned to the motion of the amide groups of the original PPTA in the amorphous phase. The fact that the $\tan \delta$ peak concerning the α_a relaxation was increased in its magnitude indicates that the only long alkyl chains front can crystallize and most of long alkyl chains could not crystallize, resulting in a low degree of crystallinity.

The concentrated solutions of ST-4 in THF, DCE, TCE, and BF showed liquid crystalline behavior of lyotropic type observed in the DSC curves, the intensity curves of the wide angle X-ray diffraction, and the polarization optical micrographs. Critical polymer concentrations in THF, DCE, TCE, and BF are about 30%, about 50%, about 50%, and about 60% by volume.

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