Sequence Analysis of Technora (Copolyamide of Terephthaloyl Chloride, *p*-Phenylenediamine, and 3,4′-Diaminodiphenyl Ether) Using ^{13}C NMR

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ABSTRACT: The dyad sequence analysis of Technora (copolyamide prepared from terephthaloyl chloride, *p*-phenylenediamine, and 3,4′-diaminodiphenyl ether) was reported using ^{13}C NMR in trifluoromethanesulfonic acid at 100 °C. For the detailed peak assignment, some model copolymers were synthesized and the ^{13}C NMR spectra were observed. Well-resolved carbonyl carbon peaks of the terephthalic units of Technora were observed, which made it possible to analyze the *p*-phenylenediamine units and the 3,4′-diaminodiphenyl ether units at dyad level. The information on the head-to-head, tail-to-tail, and head-to-tail sequences of the 3,4′-diaminodiphenyl ether units was also obtained. It was concluded that the sequence of Technora was completely random.

Introduction

A few fully aromatic polyamide (aramid) fibers, for example, under the trade names Kevlar (du Pont) and Technora (Teijin Technoproducts) have been processed and provided as high-strength and high-modulus fibers. Kevlar is a homopolyamide, that is, poly(*p*-phenylene terephthalamide) (PPTA), whereas Technora[1−3] is a copolyamide prepared from terephthaloyl dichloride (TPC), *p*-phenylenediamine (PPDA), and 3,4′-diaminodiphenyl ether (3,4′-DAPE), with a TPC/PPDA/3,4′-DAPE monomer mole ratio of 100/50/50, as shown in Figure 1. Copolymerization has been performed in order to improve solubility of aromatic polyamide, and thus, Technora is processed by dry-jet wet spinning from the solution of *N*-methyl-2-pyrrolidone. Ozawa[3] has reported that the physical properties of Technora fiber such as tenacity, elongation, and modulus change depending on the molar ratio of two diamine components, and there is a optimum composition for obtaining excellent physical properties. However, there are no detailed report about the sequence of the polymer.

Thus far, a large number of sequence analyses have been reported using nuclear magnetic resonance (NMR).[4−13] In general, the melt condensation copolymers are formed in thermodynamically equilibrium state, and therefore most of the sequences should be random in statistically. However, because Technora is the condensation copolyamide prepared irreversibly in nonequilibrium state in *N*-methyl-2-pyrrolidone solution, the sequence is not necessarily random. It is important whether the sequence of the Technora polymer is random or blocky in connection with the physical properties such as solubility or hydrolytic stability. One of the reasons why there are no reports on the sequence analysis is insoluble character of the polymer in common NMR solvents. Tashiro et al.[14] have suggested that the sequence of Technora is blocky using X-ray diffraction. They have also tried the sequence analysis of the polymer in sulfuric acid using^{13}C NMR, but they could not obtain the information on the sequence because of the low-resolution spectrum. Contrary to this, Blackwell et al.[15,16] have reported that the sequence of Technora is random using X-ray diffraction. Aoki[17] has also reported that the sequence of the polymer should be random using computer simulation of the polymerization. Thus, to obtain the conclusive information on the sequence, it is better to find out the suitable condition including solvent for obtaining a well-resolved NMR spectrum. Thus far, solvents such as *N*,*N*-dimethylformamide or *N*,*N*-dimethylacetamide have been used for ^{1}H NMR studies of fully aromatic copolyamide consisting of isophthalic acid and two aromatic diamines, i.e., 4,4′-oxybisaniline and bis(4-aminophenyl)sulfone.[18−20] However, the solubility is quite different between isophthalic and terephthalic unit. Actually, ^{13}C NMR spectra of PPTA homopolymer in sulfuric acid have been reported by English[21] because PPTA is insoluble in *N*,*N*-dimethylformamide or *N*,*N*-dimethylacetamide. The solvents such as formic acid, trifluoroacetic acid, and sulfuric acid have been used for fully aliphatic and mixed aliphatic/aromatic polyamides.[22−30] However, fully aromatic polyamides are insoluble in formic acid. As will be mentioned in the text, Technora is decomposed in sulfuric acid (97%).

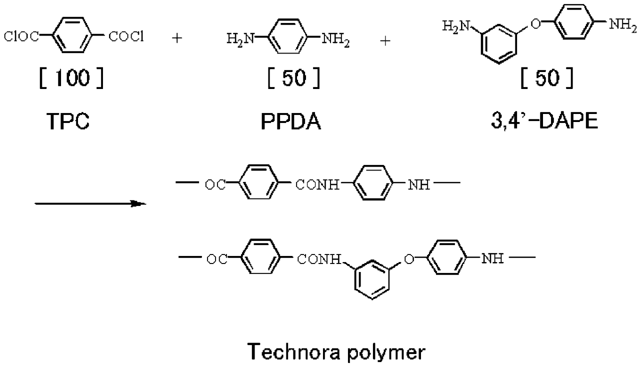

Figure 1. Production scheme of the Technora polymer.

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In this paper, we tried to find out suitable condition for getting a well-resolved ^{13}C NMR spectrum of the polymer (solvent; trifluoromethanesulfonic acid and observed temperature; 100 °C). In addition, for the peak assignment at dyad level, some rational model copolymers were synthesized. On the basis of the conclusive peak assignments of the well-resolved ^{13}C NMR spectra, the detailed sequential analysis was performed.

Experimental Section

Polymer Preparation. Technora, a copolyamide prepared from terephthaloyl chloride, *p*-phenylenediamine, and 3,4′-diaminodiphenyl ether, was obtained from Teijin Technoproducts as the precipitate from the *N*-methyl-2-pyrrolidone (NMP) solution after the polymerization. Kevlar-29 fibers (du Pont) were obtained in a parallel bundle. Three model copolyamides were synthesized for the assignment of the ^{13}C NMR spectrum of Technora. Two of the model copolyamides were synthesized from the aromatic diamine monomers that have unsymmetrical and symmetrical structures containing amide linkages. The aromatic unsymmetrical diamine monomer containing amide linkages was prepared from 3-amino-4′-nitrodiphenyl ether, *p*-nitroaniline, and terephthaloyl dichloride; the mole ratio was 100/100/100, respectively, with subsequent reduction of the dinitro intermediate. A solution of 116 g of 3-amino-4′-nitrodiphenyl ether in 300 mL of NMP was added dropwise to a solution of 101 g of terephthaloyl dichloride in 1000 mL of NMP at −20 °C, taking 30 min. After stirring for more 20 min, a solution of 69 g of *p*-nitroaniline in 200 mL of NMP was added at −20 °C. After the neutralization by a solution of 40 g of sodium hydroxide in 5000 mL of water, the dinitro intermediate obtained was repeatedly purified by recrystallization from a dimethylformamide/water solvent mixture. The dinitro intermediate obtained was subjected to catalytic hydrogenation to the corresponding diamine. The catalytic hydrogenation was performed with Pd/C as catalyst and NMP as solvent with vigorous agitation under 75 kg/cm^2 hydrogen pressure at 660 °C in an autoclave. The diamine obtained was repeatedly purified by recrystallization from a dimethylformamide/water solvent mixture. The aromatic symmetrical diamine monomer containing amide linkages was prepared from 3-amino-4′-nitrodiphenyl ether and terephthaloyl dichloride; the mole ratio was 200/100, respectively, with subsequent reduction of the dinitro intermediate. The model copolyamides were prepared by solution polymerization. Terephthaloyl dichloride was added to an NMP solution of an equimolar amount of the unsymmetrical or symmetrical diamine monomer at room temperature. The reaction mixture was allowed to stand with stirring at room temperature for 2 h and then neutralized by addition of an aqueous solution of sodium hydroxide. The precipitate was washed with a large amount of water and then dried. Another model copolyamide was prepared similarly from an equimolar amount of terephthaloyl dichloride and 3,4′-diaminodiphenyl ether.

NMR Measurements. 100 mg of the polymer in a 10 mm diameter NMR tube was dissolved in 3.5 mL of sulfuric acid (97%), methanesulfonic acid, and trifluoromethanesulfonic acid by standing overnight at room temperature. Deuterated dimethyl sulfoxide was inserted as the NMR lock solvent. The ^{13}C NMR spectra were recorded by using a JEOL α-400 spectrometer operating at 100 MHz. The observed temperature was room temperature or 100 °C. Tetramethylsilane in deuterated dimethyl sulfoxide was used as a standard chemical shift reference. The spectra were obtained with a digital resolution of 0.83 Hz/point, corresponding to a spectral width of ca. 27 kHz and a data point of 32K. The flip angle and the pulse delay were 45° and 2.5 s, respectively. The spectra were obtained with a digital resolution of 0.21 Hz/point after zero-filling. Two-dimensional NOESY spectra of the model monomers synthesized were obtained with a mixing time $\tau = 800$ ms in deuterated dimethyl sulfoxide at room temperature.

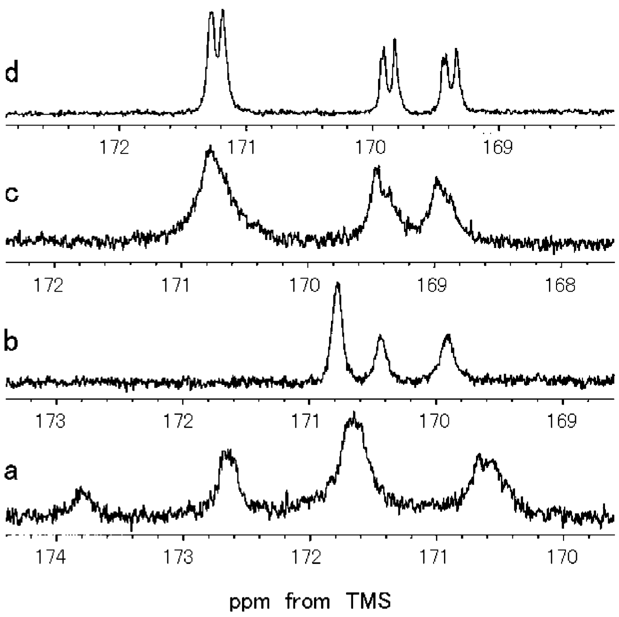


Figure 2. Expanded 100 MHz ^{13}C NMR spectra (the carbonyl carbon region) of the Technora polymer. The solvents are (a) sulfuric acid at room temperature, (b) methanesulfonic acid at 100 °C, (c) trifluoromethanesulfonic acid at room temperature, and (d) trifluoromethanesulfonic acid at 100 °C.

Results and Discussion

Selection of Solvent. It is important to find out the suitable solvent for obtaining a well-resolved NMR spectrum without decomposition during NMR measurement. For the copolyamide containing the isophthalic unit as the acidic component, Curnuck et al.[19] used *N*,*N*-dimethylacetamide (DMAc) for the NMR solvent. Kang et al.[31] used *N*,*N*-dimethylformamide (DMF)/CCl_4 solvent system for the analysis of the NH proton peaks of the ^{1}H NMR spectrum of similar copolyamides. However, Technora having the terephthalic unit as the acidic component is insoluble in such solvents. We tried to use sulfuric acid, methanesulfonic acid, and trifluoromethanesulfonic acid as the solvent. Although these solvents have been used for the sequence analyses of the fully aliphatic and mixed aliphatic/aromatic copolyamides,[22−30] the applications for the fully aromatic copolyamides have not been reported. Technora could be dissolved in these solvents after standing the mixtures overnight. The carbonyl carbon regions of the ^{13}C NMR spectra in sulfuric acid, methanesulfonic acid, and trifluoromethanesulfonic acid are shown in Figure 2. In the case of sulfuric acid (97%), four peaks were observed (Figure 2a), but the peak observed at 173.8 ppm seems to be assigned to the decomposition product of polymer or reaction product with sulfuric acid. Thus, sulfuric acid (97%) is not suitable for the sequence analysis of the polymer. As shown in Figure 2b, three peaks were observed in the case of methanesulfonic acid at 100 °C. However, there are no further well-resolved peaks, and therefore methanesulfonic acid is also not suitable for the sequence analysis of the polymer. The roughly three peaks were also observed in the case of trifluoromethanesulfonic acid even at room temperature as shown in Figure 2c. However, at 100 °C (Figure 2d), the spectrum was dramatically changed and the well-resolved peaks could be observed. Thus, we used the experimental condition, trifluoromethanesulfonic acid at 100 °C, for NMR measurement of Technora in this paper.

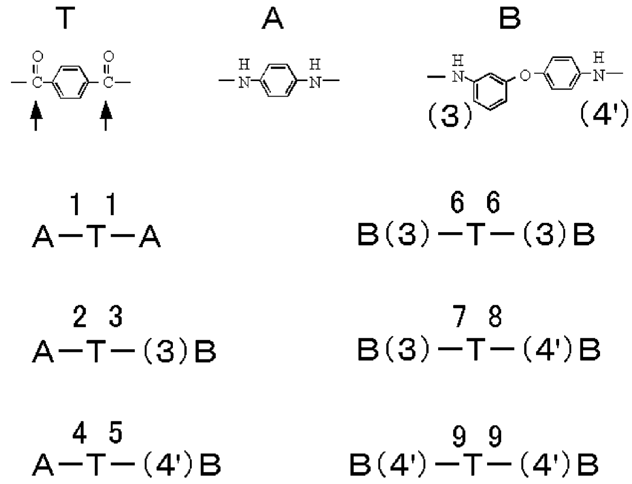


Figure 3. Possible dyad sequences on the diamine units of the Technora polymer along with the notations of carbonyl carbons. T, A, and B indicate terephthalic unit, *p*-phenylenediamine unit, and 3,4′-diaminodiphenyl ether unit, respectively. (3) and (4′) indicate the binding site of the B unit for the T unit, 3-position and 4′-position, respectively.

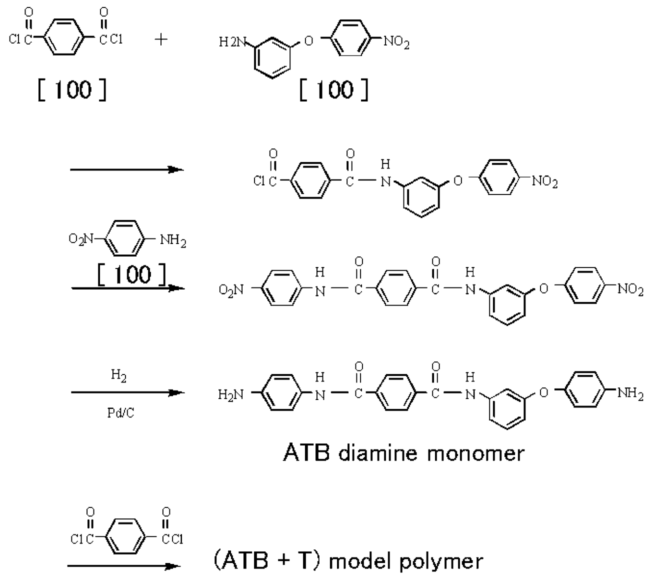


Figure 4. Synthetic scheme of the (ATB + T) model polymer for the assignment of the NMR spectrum of the Technora polymer.

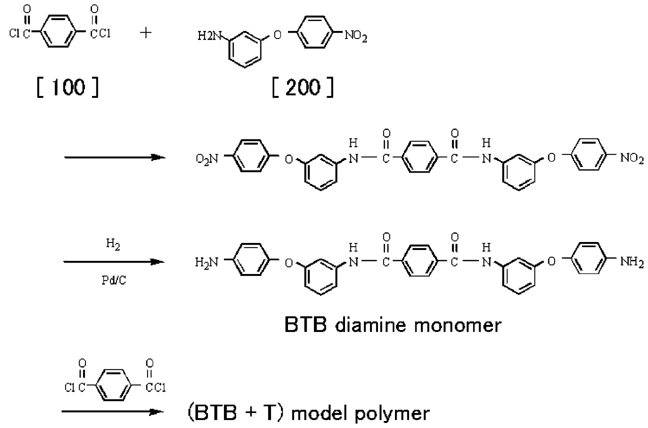


Figure 5. Synthetic scheme of the (BTB + T) model polymer for the assignment of the NMR spectrum of the Technora polymer.

If there are small amounts of water in sulfuric acid, the decomposition of PPTA occurs at modest temperature as pointed out by English previously.[21] Thus, sulfuric acid (97%) used here is expected to decompose Technora. However, in the case of trifluoromethanesulfonic acid, the crystalline of the monohydrate with melting point: 34 °C will be formed in the solid state if there is trace of water in this acid. Therefore, if the liquid part was used for the solvent, it is possible to used the acid without trace of water which is one reason why trifluoromethanesulfonic acid is favorable than sulfuric acid as the solvent for Technora.

Model Polymers for the Assignment. As shown in Figure 3, there are six possible dyad sequences on the diamine units in Technora because of unsymmetrical structure of diamine unit B. Therefore, nine different carbonyl carbons should be considered.

For the assignment of the peaks in Figure 2d to the dyad sequences (Figure 3), the ^{13}C NMR spectra of the model polymers, (ATB + T) and (BTB + T), prepared according to the schemes of Figures 4 and 5,[32] respectively, were used. Here, ATB and BTB indicate the unsymmetrical and symmetrical diamine monomers, respectively, that have a selective binding site of the B unit to the T unit. The structures of ATB and BTB monomers were checked by two-dimensional NOESY spectra as shown in Figures 6 and 7, respectively. It was confirmed that synthesized ATB monomer has the unsymmetrical diamide structure centered on terephthalic unit because two amide proton peaks, (7) and (10), were observed, as shown in Figure 6. For the amide proton peak (7), the NOE's were observed between the proton peaks (3) and (6). Peaks (3) and (6) could be assigned to the protons of meta-disubstituted benzene of the 3,4′-diaminodiphenyl ether unit, as shown in Figure 6. There is NOE between the proton peak (11) and the other amide proton peak (10). Peak (11) could be assigned to the proton of the *p*-phenylenediamine unit. Therefore, it made clear that the ATB monomer has the unsymmetrical diamide structure centered on terephthalic unit, as shown in Figure 6. Arrows in the structural formula in Figure 6 indicate that the NOE was observed between the corresponding protons. Similarly, it was checked that synthesized BTB monomer has the symmetrical diamide structure centered on terephthalic unit because one amide proton peak (7) was observed. There are NOE's between proton peaks (3) and (7) and the peaks (6) and (7). Peaks (3) and (6) could be assigned to the protons of the meta-disubstituted benzene of the 3,4′-diaminodiphenyl ether unit. The NOE between peak (1) and peaks (3) or (6) of the para-disubstituted benzene of the 3,4′-diaminodiphenyl ether unit was not observed. Therefore, it is clear that the BTB monomer has the symmetrical diamide structure centered on terephthalic unit, as shown in Figure 7. Arrows in the structural formula in Figure 7 indicate that the NOE was observed between the corresponding protons. The structure of these ATB and BTB monomers was also confirmed by 1D NOE difference spectra (data not shown). DQF-COSY spectra were also used for the assignment of the aromatic proton peaks of diamine units. The (B + T) model polymer that has no selective binding site of the B unit to the T unit was also synthesized. The relationship between these model polymers and dyad sequences is shown in Figure 8. By using this relationship, the assignment of the carbonyl

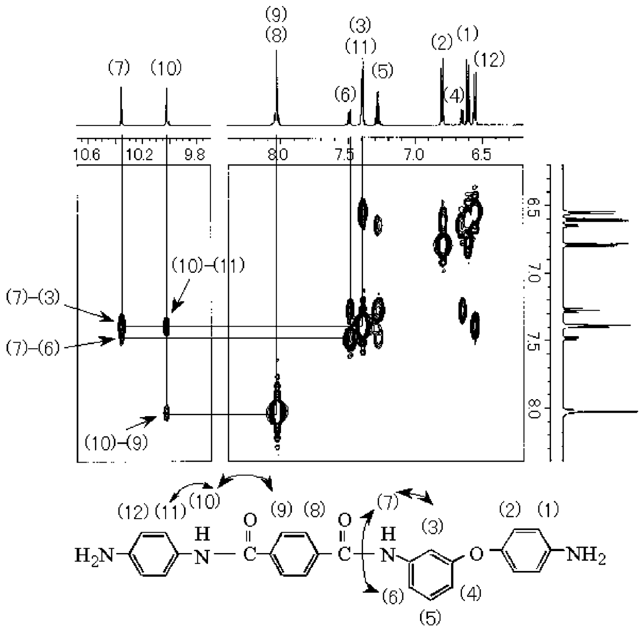


Figure 6. NOESY spectrum of the synthesized ATB diamine monomer. A mixing time $\tau = 800$ ms. The solvent is deuterated dimethyl sulfoxide at room temperature. Arrows in the structural formula indicate that the NOE was observed between corresponding protons.

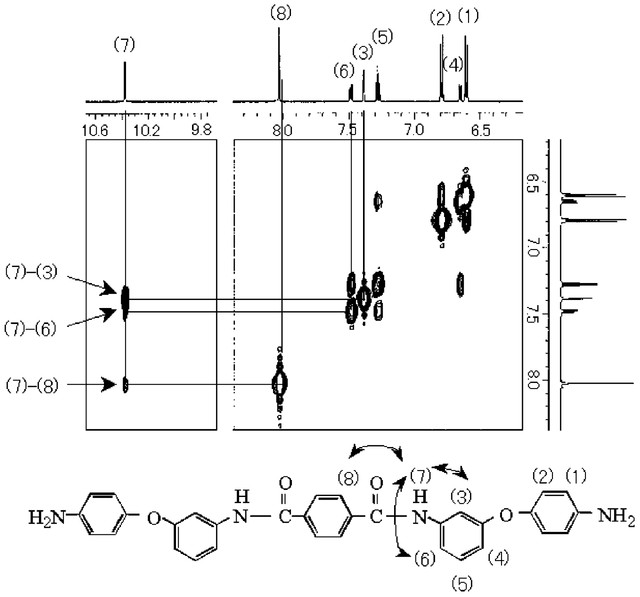
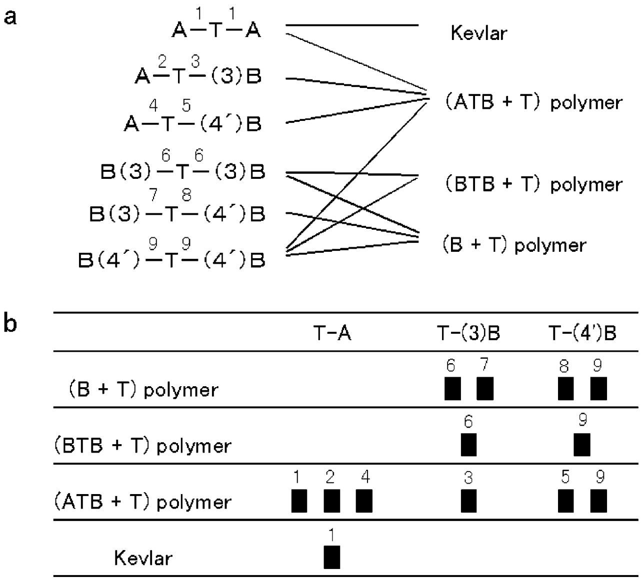


Figure 7. NOESY spectrum of the synthesized BTB diamine monomer. A mixing time $\tau = 800$ ms. The solvent is deuterated dimethyl sulfoxide at room temperature. Arrows in the structural formula indicate that the NOE was observed between corresponding protons.



	T-A	T-(3)B	T-(4′)B
(B + T) polymer		6 7 ■ ■	8 9 ■ ■
(BTB + T) polymer		6 ■	9 ■
(ATB + T) polymer	1 2 4 ■ ■ ■	3 ■	5 9 ■ ■
Kevlar	1 ■		

Figure 8. (a) Relationship between the model polymers and the dyad sequences. The solid lines show the dyad sequences to be present in the model polymers. (b) The observable peak patterns of the carbonyl carbons of each model polymer. The numbers indicate the notations of carbonyl carbons in Figure 3. The order of the numbers in a block is indefinite.

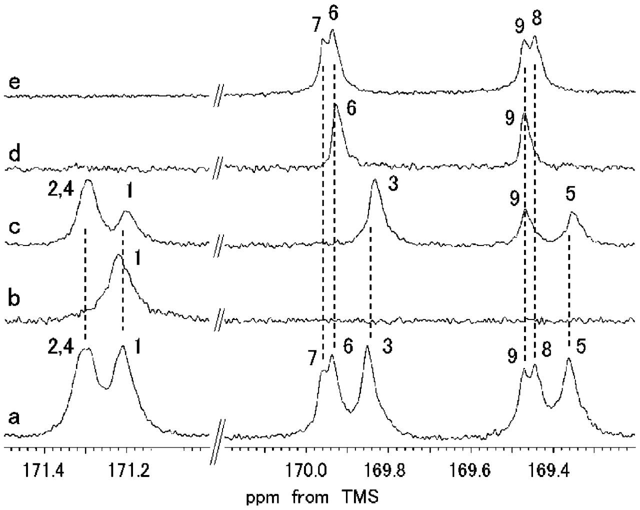


Figure 9. Expanded 100 MHz ^{13}C NMR spectra (the carbonyl carbon region) of the Technora polymer and the model polymers in trifluoromethanesulfonic acid at 100 °C: (a) Technora, (b) the Kevlar-29, (c) the (ATB + T) model polymer, (d) the (BTB + T) model polymer, and (e) the (B + T) model polymer. The assignments of the carbonyl carbons in Figure 3 are shown.

carbon peaks of all dyad sequences of Technora is possible. For example, the (BTB + T) polymer have two dyad sequences of B(3)-T-(3)B and B(4′)-T-(4′)B, as shown in Figure 8. On the other hand, the (ATB + T) polymer has also B(4′)-T-(4′)B sequences. Therefore, the peaks of (3)-T-(3)B and B(4′)-T-(4′)B sequences will be assigned respectively by a comparison of the spectra of the (BTB + T) and (ATB + T) polymers. The observable peak patterns of the carbonyl carbons of each model polymer were also summarized in Figure 8. The numbers indicate the notations of the carbonyl carbons in Figures 3. The order of the numbers in a block is indefinite. For example, in the case of the (ATB + T) polymer, maximally six carbonyl carbon peaks, 1, 2, and 4 of the T-A bond, 3 of the T-(3)B bond, and 5 and 9 of the T-(4′)B bond, are expected to observe.

Assignment of the Peaks Using Model Polymers. For the assignment of the peaks in Figure 2d to the dyad sequences in Figure 3, the Kevlar-29 corresponding to the (A + T) polymer and three model polymers were dissolved in trifluoromethanesulfonic acid, and the ^{13}C NMR spectra were measured at 100 °C. Expanded 100 MHz ^{13}C NMR spectra (the carbonyl carbon region) are shown in Figure 9. To assign the peaks observed in the region from 171.0 to 171.5 ppm that is the region of the carbonyl carbon of the T-A bond, the peak position was

Table 1. Results of the Sequence Distribution Analysis of the Technora Polymer by ^{13}C NMR[a]

dyad sequences	fractions[b]		randomness		average sequence lengths	
A-T-A	f_{AA}	0.248 (0.250)	R_{AB}	1.03 (1.00)	L_A	1.96 (2.00)
A-T-B	f_{AB}	0.514 (0.500)			L_B	1.93 (2.00)
B-T-B	f_{BB}	0.238 (0.250)				
A-T-(3)B	f_{A3B}	0.499 (0.500)				
A-T-(4′)B	$f_{A4'B}$	0.501 (0.500)				
B(3)-T-(3)B	f_{3B3B}	0.251 (0.250)	R_{BB}	0.99 (1.00)		
B(3)-T-(4′)B	$f_{3B4'B}$	0.496 (0.500)				
B(4′)-T-(4′)B	$f_{4'B4'B}$	0.253 (0.250)				

[a] The values in parentheses were theoretical values on the basis of a Bernoullian dyad distribution. [b] The molar fractions were calculated as $f_{AA} + f_{AB} + f_{BB} = 1$, $f_{A3B} + f_{A4'B} = 1$, and $f_{3B3B} + f_{3B4'B} + f_{4'B4'B} = 1$.

compared among Technora, Kevlar-29, and the (ATB + T) polymers. As summarized in Figure 8, three carbonyl carbon peaks, 1, 2, and 4, are expected to observe in the region of the carbonyl carbon of the T-A bond of (ATB + T) polymer. From the relative peak area in Figure 9c and the corresponding peak position of Kevlar-29 (Figure 9b), peaks 2 and 4 are considered to be overlapping. Consequently, peaks 1, 2, and 4 of the Technora polymer as shown in Figure 9a were assigned to the carbonyl carbons 1, 2, and 4 in Figure 3, respectively. Then, the peaks observed in the region from 169.2 to 170.2 ppm in Figure 9 can be assigned to the carbonyl carbon peaks of the T-(3)B and T-(4′)B bond. In the spectrum of the (ATB + T) polymer as shown in Figure 9c, one peak was observed in the region from 169.7 to 170.1 ppm was assigned to the carbonyl carbon of the T-(3)B bond, and two peaks in the region from 169.2 to 169.6 ppm were assigned to the carbonyl carbon of the T-(4′)B bond because one peak, 3, and two peaks, 5 and 9, are expected to observe in the each region of the (ATB + T) polymer, as shown in Figure 8. On the other hand, because only two peaks, 6 and 9, are expected to be observed in the (BTB + T) polymer (Figure 8), peaks 6 and 9 of the (BTB + T) polymer could be easily assigned as shown in Figure 9d. Therefore, two peaks, 5 and 9, of the (ATB + T) polymer observed in the region from 169.2 to 169.6 ppm could be assigned by comparison of the peak position between parts c and d of Figure 9. Similarly, by comparison of the peak position between (BTB + T) and (B + T) polymers, peaks 6, 7, 8, and 9 of the (B + T) polymer could be assigned (Figure 9e). By comparison of the peak position among Technora, the (ATB + T) polymer, the (BTB + T) polymer, and the (B + T) polymer, peaks 3, 5, 6, 7, 8, and 9 of the Technora in Figure 9a were clearly assigned to the carbonyl carbons 3, 5, 6, 7, 8, and 9 in Figure 3, respectively. Consequently, all of the carbonyl carbon peaks of dyad sequences of Technora were assigned. Thus, the ^{13}C NMR spectrum of Technora observed in trifluoromethanesulfonic acid at 100 °C gives not only the dyad sequence information on the A and B units but also the head-to-head, tail-to-tail, and head-to-tail sequence information on the B units.

Sequence Distribution Analysis of the Technora Polymer. To estimate the degree of randomness of Technora, the dyad molar fractions centered on terephthalic unit were determined on the basis of the observed relative peak area. The degree of randomness and the number-average sequence length are summarized in Table 1. These parameters on the sequence of X-T-X (X = A or B) were calculated with the following equation:[33]

$$R_{AB} = (f_{AB}/2)/F_A + (f_{AB}/2)/F_B \qquad (1)$$

$$L_A = (f_{AA} + f_{AB}/2)/(f_{AB}/2) \qquad (2)$$

$$L_B = (f_{BB} + f_{AB}/2)/(f_{AB}/2) \qquad (3)$$

where subscripts A and B indicate the A (*p*-phenylenediamine unit) and B (3,4′-diaminodiphenyl ether unit) units, respectively. f_{AA}, f_{AB}, and f_{BB} indicate the molar fractions of the dyad sequences, A-T-A, A-T-B, and B-T-B, respectively ($f_{AA} + f_{AB} + f_{BB} = 1$). Here, the binding site of the B unit, 3-position or 4′-position, is ignored. $F_A = 0.50$ and $F_B = 0.50$ are the molar fractions of the A and B units in the polymer, respectively. R_{AB} indicates the degrees of randomness, and L_A and L_B indicate the number-average sequence lengths of the T-A and T-B units, respectively. As is listed in Table 1, $R_{AB} = 1.0$ and $L_A = L_B =$ ca. 2.0 were obtained. Therefore, it is clear that the sequential unit distribution on the A and B units in the polymer is random.

The molar fractions of A-T-(3)B and A-T-(4′)B in A-T-B units, f_{A3B} and $f_{A4'B}$ ($f_{A3B} + f_{A4'B} = 1$), respectively, are also shown in Table 1. Because of $f_{A3B} = f_{A4'B} = 0.5$, it is also clear that the sequential unit distribution on the binding site (3-position or 4′-position) of the B unit for the A-T unit is random in the polymer. Furthermore, the molar fractions of B(3)-T-(3)B, B(3)-T-(4′)B, and B(4′)-T-(4′)B in the B-T-B unit, f_{3B3B}, $f_{3B4'B}$, and $f_{4'B4'B}$ ($f_{3B3B} + f_{3B4'B} + f_{4'B4'B} = 1$), respectively, and its degrees of randomness (R_{BB}) are also shown in Table 1. Here, (3) and (4′) indicate the binding site of the B unit for the T unit, 3-position and 4′-position, respectively. $R_{BB} = 1.0$ was calculated with eq 1; therefore, it is also clear that the sequential unit distribution on the binding site (3-position or 4′-position) of the B unit for T-B unit is random in the polymer. Thus, it can be concluded that all of the possible dyad sequences in Technora are random.

On the sequence of Technora, different views have been reported by different analytical methods. Tashiro et al.[14] have used the Technora fiber annealed at 400 °C, and the structure was analyzed with X-ray diffraction and infrared spectra. They have suggested the possibility that the sequence of the polymer is blocky because some crystalline domains consisting only poly(*p*-phenylene terephthalamide) (T-A segment in the present paper) remained after annealing. Although they have tried the analysis of the polymer in sulfuric acid using ^{13}C NMR, it could not obtain the information on the sequence because of the low-resolution NMR spectrum. On the other hand, Blackwell et al.[15,16] have also applied the X-ray diffraction method for the Technora fiber. They have reported that the sequence of the Technora polymer is random because the best agreement between the positions of the observed aperiodic meridional maxima and those calculated for a completely random sequence was obtained. Aoki[17] predicted that the sequence of Technora is random by means of computer simulation of the polymerization. From our NMR analysis reported here, it was concluded that the sequence of Technora is completely random as reported by Blackwell et al.[15,16] and Aoki.[17] Because Tashiro et al.[14] have analyzed the residue after heat treatment, the parts of the short sequence lengths of *p*-phenylene terephthalamide units or the parts of the 3,4′-diaminodiphenyl ether units were expected to be degraded.

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