Sequence Analysis of Polyarylate (U-Polymer) and Its Polyestercarbonate Using ^{1}H and ^{13}C NMR

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ABSTRACT: The dyad and triad-level sequence analyses of polyarylate; U-Polymer, which is an aromatic copolyester of bisphenol-A and 50/50 isophthalic/terephthalic acid, and of polyestercarbonate prepared from U-Polymer and bisphenol-A polycarbonate were reported in a solvent system of *o*-chlorophenol/deuterated chloroform mixture (75/25 v/v) at 80 °C using 600 MHz proton nuclear magnetic resonance (^{1}H NMR). The well-resolved proton peaks were observed, which made the detailed sequence analysis possible. The methyl proton peaks of the bisphenol-A units were split into the dyad sequence in the chain. The aromatic proton peaks of the isophthalic and terephthalic units were split into the triad sequence in the chain. These peaks could be assigned by a comparison with the spectra of homopolymers and the model copolymers. It was confirmed that the sequence distribution in U-Polymer and the polyestercarbonate are random and obey Bernoullian statistics, and the dyad and triad information obtained coincides with each other by a comparison of the number-average sequence lengths from the dyad and triad sequences. ^{13}C NMR peaks of the aliphatic quaternary carbons of bisphenol-A units were also split into the dyad sequence in the chain. It was confirmed that the solvent system of the 75/25 (v/v) mixture of *o*-chlorophenol /deuterated chloroform has the potentiality for the detailed sequence analysis of polyarylate and polyestercarbonate.
KEY WORDS   Polyestercarbonate / U-Polymer / Sequence Distribution / Proton Nuclear Magnetic Resonance (^{1}H NMR) /

Polyestercarnonates (PEC) is a general name for various copolymers containing carbonate and ester units, for example, copolymers of bisphenol-A polycarbonate (PC) and polyarylate (PAr). PECs have been developed in efforts to overcome limitations of PC such as low heat resistance. There are a large number of reports on the microstructure, miscibility, phase behavior, and transesterification in blends of PAr and polyester or PC.[1—16] The blends of these polymers convert first to block copolymers and finally to a random copolymer with increase of the reaction time during tranesterification.

In general, the microstructures are important for the properties of copolymers, so a large number of sequence analyses have been reported by nuclear magnetic resonance (NMR).[17—20] In our previous paper,[21] it was found that the glycol unit peaks of the copolyester derived from two diols and one diacid, poly(ethylene/tetramethylene terephthalate) copolyester, were separated and reflected the triad sequences on the glycol units in the mixture of *o*-chlorophenol/deuterated chloroform solvent at 80 °C. In this paper, we will show the potentiality of the *o*-chlorophenol/deuterated chloroform solvent system for the sequence analyses of PAr and polyestercarbonate

prepared from PAr and PC. U-Polymer, which is an aromatic copolyester of bisphenol-A and 50/50 isophthalic/terephthalic acid, was used as PAr. U-Polymer consists of two diacidic components and one diol component, and the polyeatercarbonate from U-polymer and PC consists of three acidic components (the isophthalic and terephthalic units, and the carbonate unit) and one diol component (bisphenol-A unit). The ^{1}H NMR peaks reflecting the sequences become complicated and overlapped, and therefore the sequences analysis becomes more difficult, with increase of the number of the compornents. We used a 600 MHz ^{1}H NMR apparatus to obtain the sequence information. The dyad and triad level sequence analyses on the bisphenol-A units, the isophthalic units, and terephthalic units were performed.

EXPERIMENTAL

Polymer Preparation

U-Polymer was used as a commercial product, Unitika's Arylef U-100 polyarylate of bisphenol-A and 50/50 isophthalic/terephthalic acid. Bisphenol-A polycarbonate (PC) was used as a commercial product from Teijin Chemicals LTD. Poly(bisphenol-A isophtha-

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late) and poly(bisphenol-A terephthalate) were synthesized by interfacial polycondensation from bisphenol-A and isophthaloyl dichloride or terephthaloyl dichloride. Bisphenol-A (4.6 g) and benzyltriethylammonium chloride (0.12 g) were dissolved in 41 mL of 1 M sodium hydroxide aqueous solution. With stirring vigorously, isophthaloyl dichloride or terephthaloyl dichloride (4.1 g) dissolved in 40 mL of methylene chloride was added at room temperature. The reaction was continued for 30 min, and then 40 mL of methylene chloride was added. The organic phase was separated, and poured into methanol. The precipitate obtained was washed with enough methanol and water, and then dried.

The blend of U-Polymer and PC, of which the polymer ratio was 50/50 mol%, was prepared by dissolving two polymers in chlorofolm and pouring them into a large excess of methanol. The precipitated polymer was filtered and dried under vacuum at 50 °C for 24 h. The blend of 50/50 mol% of poly(bisphenol-A isophthalate)/PC, the blend of 50/50 mol% of poly(bisphenol-A terephthalate)/PC, and the blend of 50/50 mol% of poly(bisphenol-A isophthalate)/poly(bisphenol-A terephthalate) were also prepared.

Heat treatment of the blend of U-Polymer and PC, for the transesterification reaction, was performed on a TA Instruments 2920 differential scanning calorimeter under dry nitrogen atmosphere. The blend was heated from 25 °C to 280 °C with heating rate of 50 K min^{-1}, maintained at that temperature for various time intervals, and quenched into ice-water. Heat treatment of the blend of poly(bisphenol-A isophthalate) and PC or of poly(bisphenol-A terephthalate) and PC was also performed at 310 °C for 5 h. Heat treatment of the blend of poly(bisphenol-A isophthalate) and poly(bisphenol-A terephthalate) was also performed at 350 °C for 15 min.

NMR Measurements

The ^{1}H NMR spectra were recorded by using a JEOL α-600 spectrometer operating at 600 MHz. Deuterated chloroform, deuterated trifluoroacetic acid/deuterated chloroform mixture (50/50 v/v), and *o*-chrolophenol/deuterated chroloform mixture (75/25 v/v) were used as solvent. The observed temperature was room temperature for deuterated chloroform, the deuterated trifluoroacetic acid/deuterated chloroform mixture, but 80 °C for the *o*-chrolophenol/deuterated chroloform mixture. The sample concentration was 1% (w/v). Tetramethylsilane was used as an internal standard chemical shift reference. The spectra were obtained with a digital resolution of 0.31 Hz/point, corresponding to a spectral width of 10 kHz and a

data point of 32 k. The flip angle and the pulse delay were 45° and 4 s, respectively. Double homospin decoupled spectra were obtained by decoupling of the proton of the isophthalic unit. The ^{13}C NMR spectra were also recorded at 150 MHz with the same NMR spectrometer. The spectra were obtained with a digital resolution of 1.22 Hz/point, corresponding to a spectral width of 40 kHz and a data point of 32 k. The flip angle and the pulse delay were 45° and 2 s, respectively. The spectra were obtained with a digital resolution of 0.31 Hz/point after zero-filling.

RESULTS AND DISCUSSION

Selection of Solvent

The selection of solvent is important for detailed sequential analysis of the copolymer. In the case of U-Polymer, deuterated chloroform or the mixture of deuterated trifluoroacetic acid/deuterated chloroform is often used for the NMR measurement.[5,13,15] In our previous paper,[12] it was found that the glycol unit peaks of the copolyester derived from two diols and one diacid, poly(ethylene/tetramethylene terephthalate) copolyester, were separated reflecting the triad sequences on the glycol units in the mixture of *o*-chlorophenol/deuterated chloroform at 80 °C. So the availability of this solvent system was examined getting well-resolved peaks of the U-Polymer by comparing with deuterated chloroform and the mixture of deuterated trifluoroacetic acid/deuterated chloroform. The 600 MHz ^{1}H NMR spectrum of U-Polymer in *o*-chlorophenol/deuterated chloroform mixture is shown in Figure 1. The proton peaks of the isophthalic acid unit ((A), (B), and (C)), the terephthalic acid unit (D), and the bisphenol-A unit (E) in Figure 1 were expanded (Figure 2), comparing with the peaks in deuterated chloroform and 50/50 (v/v) mixture of deuterated trifluoroacetic acid/deuterated chloroform. For the dyad sequence analysis of U-Polymer, the attention was given to the methyl proton peak (E) of the bisphenol-A unit. In the case of deuterated chloroform solvent, as shown in Figure 2a, it is impossible to analyze the sequence at dyad level from the methyl proton peak using ^{1}H NMR because only single peak was observed for the methyl proton of the bisphenol-A unit. In the mixture of deuterated trifluoroacetic acid/deuterated chloroform, although three peaks of the methyl proton of the bisphenol-A unit appeared as shown in Figure 2b, the splitting of the peaks is poor and thus cannot be satisfied for the precise sequence analysis. On the contrary, the well-resolved three peaks of the methyl proton of the bisphenol-A unit were obtained in the 75/25 (v/v) mixture of *o*-chlorophenol/deuterated chlo-
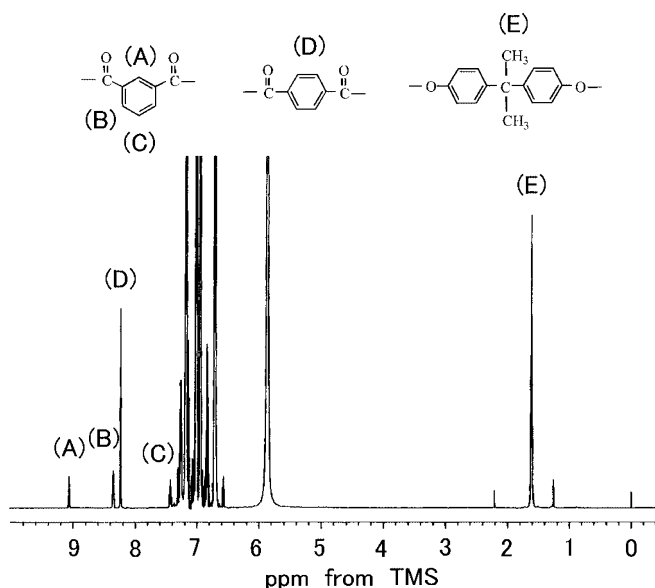
Figure 1. 600 MHz ^{1}H NMR spectrum of U-Polymer. The solvent system is 75/25 (v/v) mixture of o-chlorophenol/deuterated chloroform at 80 °C.

Figure 2. Comparison of the peaks of the 600 MHz ^{1}H NMR spectrum of U-Polymer. The solvent system is (a) deuterated chloroform at room temperature, (b) 50/50 (v/v) mixture of deuterated trifluoroacetic acid/deuterated chloroform at room temperature, and (c) 75/25 (v/v) mixture of o-chlorophenol/deuterated chloroform at 80 °C. (d) The proton peak (A) of the isophthalic unit observed by homospin decoupling of the proton (B) of the isophthalic unit in Figure 1c.

Figure 3. Expanded 600 MHz ^{1}H NMR spectra (the methyl proton region of the bisphenol-A units), (a) U-Polymer, (b) poly(bisphenol-A terephthalate), and (c) poly(bisphenol-A isophthalate).

roform at 80°C. This seems mainly due to the ring current shielding effect from the aromatic ring of o-chlorophenol. Consequently, it was found that the o-chlorophenol/deuterated chloroform solvent system is superior for the analysis of the dyad sequence (I-B-I, I-B-T, and T-B-T, where I, T, and B indicate the isophthalic unit, terephthalic unit, and bisphenol-A unit, respectively) of U-Polymer using ^{1}H NMR.

Dyad and Triad Sequence Analyses of U-Polymer

To assign three methyl proton peaks (E) of the bisphenol-A unit in Figure 2c, ^{1}H NMR spectra of homopolymer, poly(bisphenol-A-terephthalate) and poly(bisphenol-A-isophthalate), were observed. As shown in Figure 3, the observed three methyl proton peaks in Figure 2c were clearly assigned to the protons reflecting the dyad sequences on the isophthalic and terephthalic units (I-B-I, I-B-T, and T-B-T) by a comparison of the peak position.

In Figure 2c, the remarkable peak splittings for the isophthalic and terephthalic units were observed. These fine splitting peaks are considered to be reflecting the long-range sequences; triad sequences on the isophthalic and terephthalic units. To analyze the triad sequences, the spectra for the isophthalic unit were obtained under homospin decoupling of the proton (B) in Figure 1. Consequently, three peaks were observed for the proton (A) of the isophthalic unit in Figure 1, as shown in Figure 2d. The spectra for the terephthalic unit were obtained under non-decoupling condition. The comparison of the peak position and the change of the peak inten-
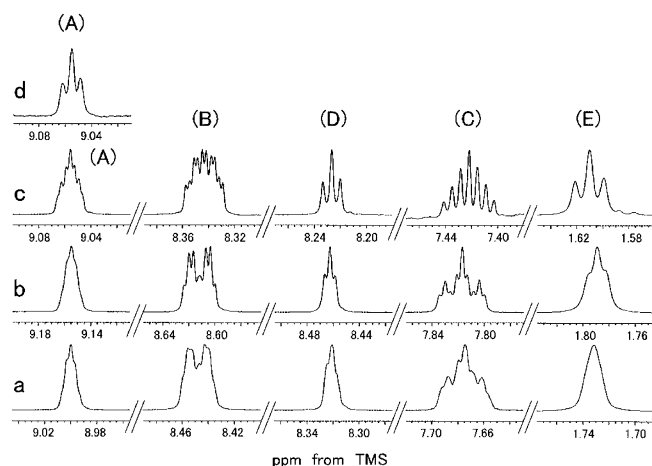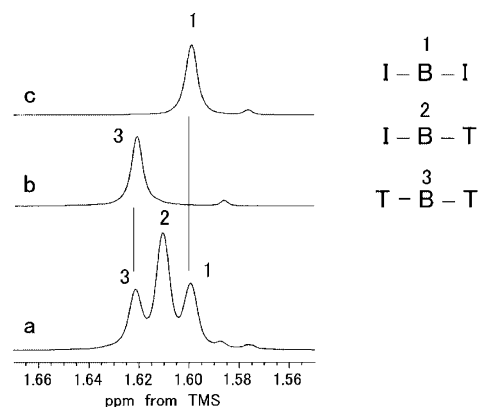
sity by the transesterificarion reaction were investigated using homopolymers, poly(bisphenol-A-terephthalate) and poly(bisphenol-A-isophthalate), and the transesterification product from these homopolymers, as shown in Figure 4. Consequently, the observed fine splittings for the peaks of the isophthalic and terephthalic units were clearly assigned to the protons reflecting the triad sequences on the isophthalic and terephthalic units, I-B-I-B-I, I-B-I-B-T, T-B-I-B-T on the isophthalic unit as shown in Figure 4a, and T-B-T-B-T, T-B-T-B-I, I-B-T-B-I on the terephthalic unit as shown in Figure 4d.

It has been reported that the sequence distribution of U-Polymer is statistically random.[2] To check the sequence distribution from the dyad and triad sequence information obtained above, the dyad and triad molar
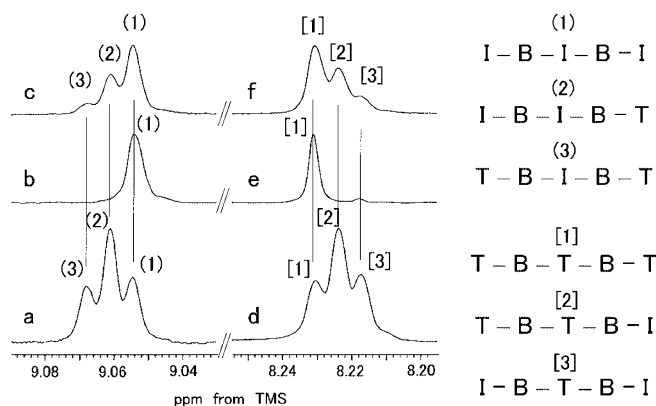
Figure 4. Expanded 600 MHz ^{1}H NMR spectra. (a), (b), and (c) are the proton (A) region of the isophthalic units observed by homospin decoupling of the proton (B) of the isophthalic unit in Figure 1. (d), (e), and (f) are the proton (D) region of the terephthalic units observed by non-decoupling in Figure 1. (a) and (d) are U-Polymer, (b) is poly(bisphenol-A isophthalate), (e) is poly(bisphenol-A terephthalate), (c) and (f) are the transesterification product from the 50/50 mol% blend of poly(bisphenol-A isophthalate)/poly(bisphenol-A terephthalate) by heat treatment at 350 °C for 15 min.

fractions centered on bisphenol-A units, and the isophthalic and terephthalic units were determined on the basis of the observed relative peak area, and the degrees of randomness (R) from the dyad information and the degrees of randomness (R_I and R_T) from the triad information were calculated with the following equations:[22]

$$R = (f_{IT}/2)/F_I + (f_{IT}/2)/F_T \tag{1}$$

$$R_I = (f_{IIT}/2)/F_I + (f_{IIT}/2)/F_T \tag{2}$$

$$R_T = (f_{TTI}/2)/F_I + (f_{TTI}/2)/F_T \tag{3}$$

where R_I and R_T indicate the degrees of randomness centered on the isophthalic and terephthalic units, respectively. f_{IT} indicates the molar fractions of the dyad sequences, I-B-T, (the sum of the molar fractions of I-B-I, I-B-T, and T-B-T equals 1). f_{IIT} and f_{TTI} indicate the molar fractions of the triad sequences, I-B-I-B-T and T-B-T-B-I, respectively, (the sum of the molar fractions of I-B-I-B-I, I-B-I-B-T, and T-B-I-B-T equals 1, and the sum of the molar fractions of T-B-T-B-T, T-B-T-B-I, and I-B-T-B-I equals 1). $F_I = 0.50$ and $F_T = 0.50$ are the molar fractions of the isophthalic and terephthalic units in U-polymer, respectively. $R = 0.97$, $R_I = 0.97$, and $R_T = 0.98$ were obtained. Consequently, it was confirmed that the sequence distribution in U-Polymer is random and obeys Bernoullian statistics as reported,[2] and that the experimental condition of ^{1}H NMR in the present report is efficient for getting the dyad and triad sequence information in U-Polymer.
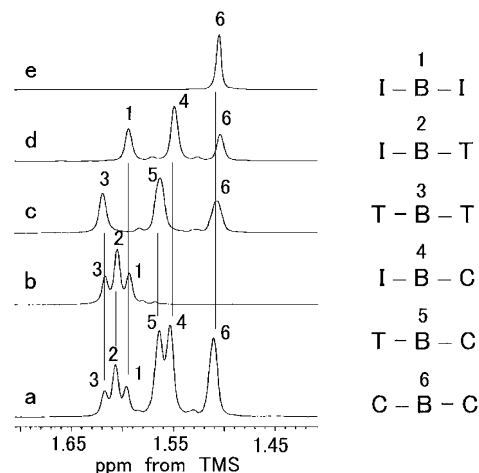

Figure 5. Expanded 600 MHz ^{1}H NMR spectra (the methyl proton region of the bisphenol-A units), (a) the transesterification product from 50/50 mol% blend of U-Polymer/PC at 280 °C for 60 min, (b) U-Polymer, (c) the transesterification product from 50/50 mol% blend of poly(bisphenol-A terephthalate)/PC at 310 °C for 5 h, (d) the transesterification product from 50/50 mol% blend of poly(bisphenol-A isophthalate)/PC at 310 °C for 5 h, and (e) PC.

Dyad and Triad Sequence Analysis of the Transesterification Product between U-Polymer and PC

U-Polymer is a polyarylate which consists of two diacidic components (the isophthalic and terephthalic units) and one diol component (bisphenol-A unit). Because the copolymer of U-Polymer and PC consists of three acidic components (the isophthalic and terephthalic units, and the carbonate unit) and one diol component (bisphenol-A unit), the peaks reflecting the sequences were complicated and overlapped, and thus the sequences analysis becomes more difficult. We investigated the solvent effect of the o-chlorophenol/deuterated chloroform system for the copolymer of U-Polymer and PC. ^{1}H NMR spectrum of the transesterification product between U-Polymer and PC with the polymer ratio of 50/50 mol% was observed. In the copolymer of U-Polymer and PC, there are six possible dyad sequences, and six peaks were clearly observed in the methyl proton region of bisphenol-A unit as shown in Figure 5a. So it was considered that these six peaks reflect the dyad sequences on the isophthalic and terephthalic units and the carbonate unit. To assign these peaks, ^{1}H NMR spectra of the transesterification products between poly(bisphenol-A-terephthalate) and PC, between poly(bisphenol-A-isophthalate) and PC, and PC homopolymer were observed. By a comparison of the peak position, the observed six methyl proton peaks in Figure 5a were clearly assigned to the protons reflecting the dyad sequences on the isophthalic and terephthalic units, and the carbonate unit (I-B-I, I-B-T, T-B-T, I-B-C, T-B-C, and C-B-C, where C indicates the carbonate unit).
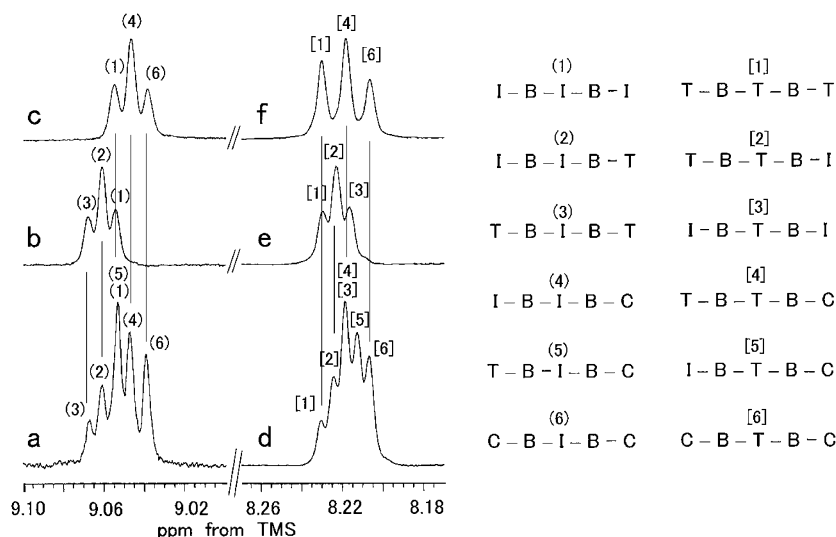
Figure 6. Expanded 600 MHz ^{1}H NMR spectra. (a), (b), and (c) are the proton (A) region of the isophthalic units observed by homospin decoupling of the proton (B) of the isophthalic unit in Figure 1. (d), (e), and (f) are the proton (D) region of the terephthalic units observed by non-decoupling condition in Figure 1. (a) and (d) are the transesterification product from 50/50 mol% blend of U-Polymer/PC at 280 °C for 30 min, (b) and (e) are U-Polymer, (c) is the transesterification product from 50/50 mol% blend of poly(bisphenol-A isophthalate)/PC at 310 °C for 5 h, and (f) is the transesterification product from 50/50 mol% blend of poly(bisphenol-A terephthalate)/PC at 310 °C for 5 h.

As shown in Figure 6a, five peaks were observed for the proton of the isophthalic unit of the transesterification product between U-Polymer and PC by the homospin decoupling of the proton (B) of the isophthalic unit in Figure 1. The spectra for the terephthalic unit were obtained under non-decoupling condition. Five peaks were also observed for the proton of the terephthalic unit as shown in Figure 6d. It was considered that these fine splitting peaks are reflecting the long-range sequences as well as those in U-Polymer. To assign these peaks, the peak position was compared with the spectra of U-Polymer, the transesterification products between poly(bisphenol-A-isophthalate) and PC, between poly(bisphenol-A-terephthalate) and PC, as shown in Figure 6. Consequently, each five peaks of the isophthalic and terephthalic units were clearly assigned to the protons reflecting the triad sequences on the isophthalic and terephthalic units and carbonate unit, I-B-I-B-I, I-B-I-B-T, T-B-I-B-T, I-B-I-B-C, T-B-I-B-C, and C-B-I-B-C on the isophthalic unit as shown in Figure 6a, and T-B-T-B-T, T-B-T-B-I, I-B-T-B-I, T-B-T-B-C, I-B-T-B-C, and C-B-T-B-C on the terephthalic unit as shown in Figure 6d.

To confirm the coincidence of the dyad and triad information obtained here, sequence distributions of several transesterification products between U-Polymer and PC were analyzed using ^{1}H NMR. As shown in Figure 6a, although the peaks (1) and (5) of the isophthalic unit, and also, the peaks [3] and [4] of the terephthalic unit are overlapping, it is possible to analyze the sequence distribution using the result that U-Polymer is random from the dyad and triad sequence analyses. The

Table I. Dyad sequence distributions centered on bisphenol-A unit in U-polymer/PC copolymers determined by ^{1}H NMR[a]

	Reaction time (min)			
	10	12.5	15	30
I-B-I				
I-B-T	0.427[b]	0.345[b]	0.321[b]	0.256[b]
T-B-T				
I-B-C	0.128[c]	0.266[c]	0.329[c]	0.485[c]
T-B-C				
C-B-C	0.445	0.380	0.350	0.256
R[d]	0.26	0.53	0.66	0.97
L_U[e]	7.67	3.66	2.95	2.06

[a]Temperature of transesterification reaction 280 °C; U-polymer/PC = 50/50 mode ratio. [b]Sum of the molar fractions of I-B-I, I-B-T, and T-B-T sequences. [c]Sum of the molar fractions of I-B-C and T-B-C sequences. [d]Degree of randomness calculated from the molar fractions. [e]Number-average sequence length of U-polymer sequence length of U-polymer sequences calculated from the molar fractions.

dyad and triad molar fractions centered on bisphenol-A units, and the isophtalic and terephthalic units, respectively, were determined on the basis of the observed relative peak area. The degrees of randomness (R for the dyad sequences centered on the B units, $R_{(I)}$ and $R_{(T)}$ for the triad sequences centered on the I and T units, respectively) calculated as with eqs 1, 2, and 3 are listed in Table I and II. The number-average sequence length of the U-Polymer unit (L_U for the dyad sequences centered on the B units, $L_{U(I)}$ and $L_{U(T)}$ for the triad sequences centered on the I and T units, respectively) were calculated with the following equations:[22]

$$L_U = (f_{UU} + f_{UC}/2)/(f_{UC}/2) \qquad (4)$$

Table II. Triad sequence distributions centered on isophthalic and terephthalic units in U-polymer/PC copolymers determined by ^{1}H NMR[a]

	Reaction time (min)			
	10	12.5	15	30
I-B-I-B-I				
I-B-I-B-T	0.749[b]	0.516[b]	0.407[b]	0.289[b]
T-B-I-B-T				
I-B-I-B-C	0.222[c]	0.410[c]	0.480[c]	0.505[c]
T-B-I-B-C				
C-B-I-B-C	0.028	0.074	0.113	0.206
$R_{(I)}$[d]	0.44	0.82	0.96	1.01
$L_{U(I)}$[e]	7.75	3.52	2.70	2.15
T-B-T-B-T				
T-B-T-B-I	0.749[b]	0.539[b]	0.406[b]	0.282[b]
I-B-T-B-I				
T-B-T-B-C	0.231[c]	0.395[c]	0.477[c]	0.526[c]
I-B-T-B-C				
C-B-T-B-C	0.020	0.066	0.117	0.192
$R_{(T)}$[d]	0.46	0.79	0.95	1.05
$L_{U(T)}$[e]	7.49	3.73	2.70	2.07

[a]Temperature of transesterification reaction 280 °C; U-polymer/PC = 50/50 mole ratio. [b]Sum of the molar fractions of I-B-I-B-I, I-B-I-B-T, and T-B-I-B-T sequences, or T-B-T-B-T, T-B-T-B-I, and I-B-T-B-I sequences. [c]Sum of the molar fractions of I-B-I-B-C, and T-B-I-B-C sequences, or T-B-T-B-C and I-B-T-B-C sequences. [d]Degree of randomness calculated from the molar fractions. [e]Number-average sequence length of U-polymer sequence length of U-polymer sequences calculated from the molar fractions.

$$L_{U(I)} = (f_{UIU} + f_{UIC}/2)/(f_{UIC}/2) \tag{5}$$

$$L_{U(T)} = (f_{UTU} + f_{UTC}/2)/(f_{UTC}/2) \tag{6}$$

where f_{UU} indicates the sum of the dyad molar fractions of I-B-I, I-B-T, and T-B-T. f_{UC} indicates the sum of the dyad molar fractions of I-B-C, T-B-C. f_{UIU} indicates the sum of the dyad molar fractions of I-B-I-B-I, I-B-I-B-T, and T-B-I-B-T. f_{UIC} indicates the sum of the dyad molar fractions of I-B-I-B-C and T-B-I-B-C. f_{UTU} indicates the sum of the dyad molar fractions of T-B-T-B-T, T-B-T-B-I, and I-B-T-B-C. As shown in Figure 7, the number-average sequence length of the U-Polymer unit calculated from the triad sequences using the isophthalic and terephthalic peaks and the dyad sequences using the bisphenol-A peaks were in good agreement with each other. Consequently, it was confirmed that the dyad and triad information obtained coincide with each other, and the sequence distribution of the copolymer between U-Polymer and PC is random because the randomness (R, $R_{(I)}$, and $R_{(T)}$) increased toward 1 with the increase of transesterification reaction time. It has been reported that the sequence distributions of polyestercarbonates prepared from the monomers are random.[1,6] Therefore, it was confirmed that the transesterification reaction among the monomer
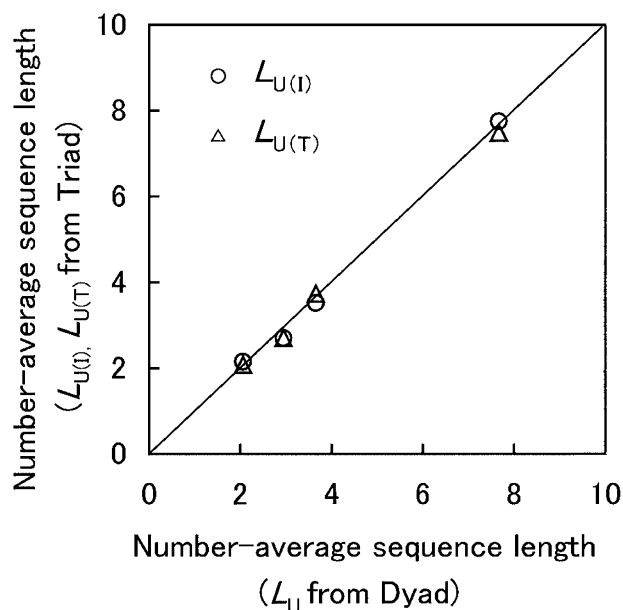

Figure 7. Comparison of the number-average sequence lengths of the U-Polymer units for the several transesterification products from 50/50 mol% blend of U-Polymer/PC at 280 °C. L_U was calculated from the dyad sequences centered on bisphenol-A units, and $L_{U(I)}$ and $L_{U(T)}$ were calculated from the triad sequences centered on the I and T units, respectively.

units of U-Polymer and PC proceeds randomly as the polycondensation reaction among the monomers.

^{13}C NMR Spectrum of the Transesterification Products of U-Polymer and PC

The peaks reflecting the sequence using ^{13}C NMR for the transesterification products between U-Polymer and PC were also studied in the 75/25 (v/v) mixture of *o*-chlorophenol/deuterated chloroform at 80 °C. As shown in Figure 8, the aliphatic quaternary carbons of the bisphenol-A unit gave the peak pattern similar to that of the methyl protons in the ^{1}H NMR. The assignment by a comparison with the spectra of homopolymers and the model copolymers is shown in Figure 8. Consequently, the dyad sequence analysis of the copolymer of U-Polymer and PC is also possible from ^{13}C NMR using this solvent system. As shown in Figure 8b, the dyad sequence analysis of U-Polymer is also possible using ^{13}C NMR. On the other hand, the spectra of the methyl carbon region of the bisphenol-A unit were shown in Figure 9. In this case, only three peaks for the copolymer of U-Polymer and PC (Figure 9a), and only single peak for U-Polymer (Figure 9b) were observed. The assignment by a comparison with the spectra of homopolymers and the model copolymers is shown in Figure 9. Thus the methyl carbons of the bisphenol-A unit cannot give the sequence information on the isophthalic and terephthalic. It is considered that the aliphatic quaternary carbons of the bisphenol-A
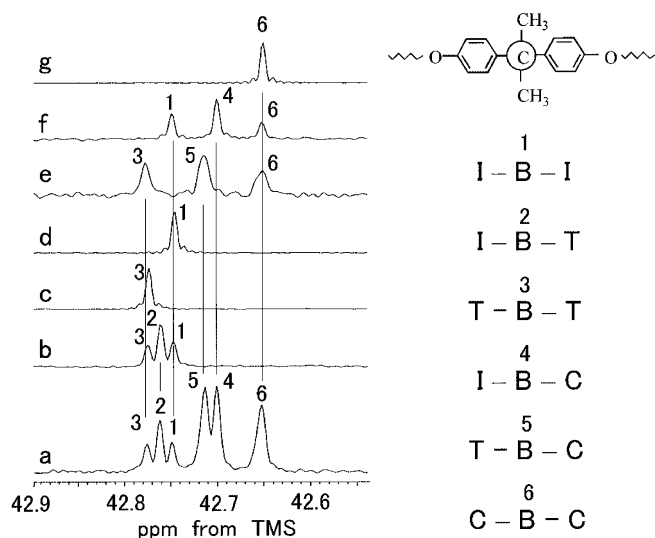
Figure 8. Expanded 150 MHz ^{13}C NMR spectra (the aliphatic quaternary carbon region of the bisphenol-A units), (a) the trans-esterification product from 50/50 mol% blend of U-Polymer/PC at 280 °C for 60 min, (b) U-Polymer, (c) poly(bisphenol-A terephthalate), (d) poly(bisphenol-A isophthalate), (e) the transesterification product from 50/50 mol% blend of poly(bisphenol-A terephthalate)/PC at 310 °C for 5 h, (f) the transesterification product from 50/50 mol% blend of poly(bisphenol-A isophthalate)/PC at 310 °C for 5 h, and (g) PC.
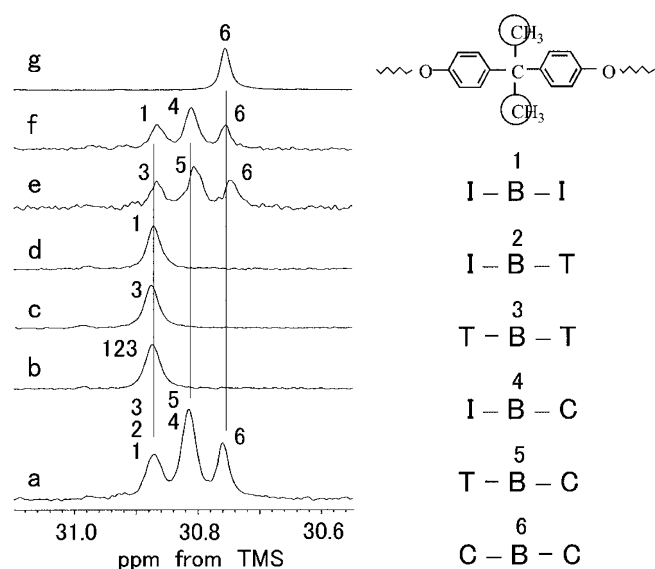

Figure 9. Expanded 150 MHz ^{13}C NMR spectra (the methyl carbon region of the bisphenol-A units), (a) the transesterification product from 50/50 mol% blend of U-Polymer/PC at 280 °C for 60 min, (b) U-Polymer, (c) poly(bisphenol-A terephthalate), (d) poly(bisphenol-A isophthalate), (e) the transesterification product from 50/50 mol% blend of poly(bisphenol-A terephthalate)/PC at 310 °C for 5 h, (f) the transesterification product from 50/50 mol% blend of poly(bisphenol-A isophthalate)/PC at 310 °C for 5 h, and (g) PC.

unit are more sensitive than the methyl carbon for the detailed sequence owing to the shorter bonds from the acidic unit binding to the bisphenol-A unit in addition
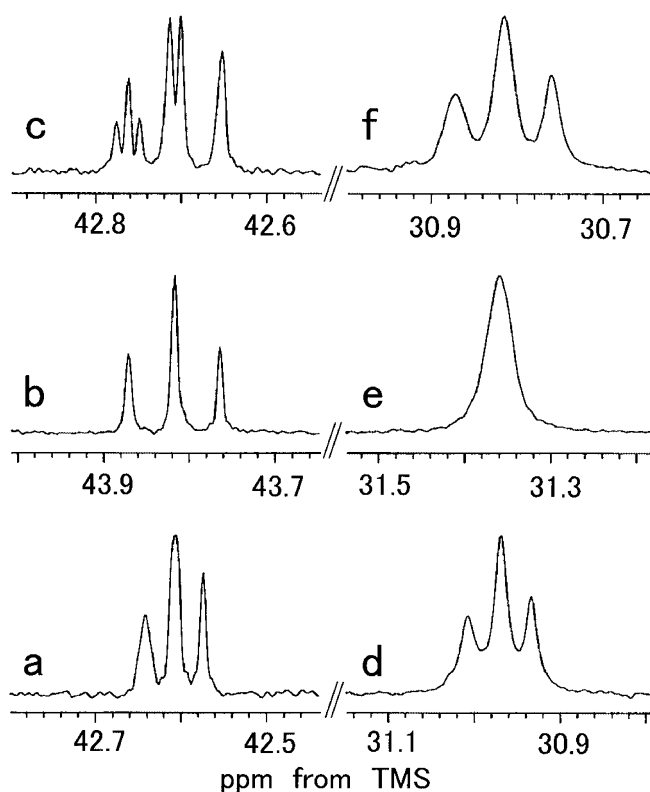

Figure 10. Comparison of the peaks of the 150 MHz ^{13}C NMR spectra. (a), (b), and (c) are the aliphatic quaternary carbon region of the bisphenol-A units, (d), (e), and (f) are the methyl carbon region of the bisphenol-A units. The solvent system is (a) and (d) deuterated chloroform at room temperature, (b) and (e) 50/50 (v/v) mixture of deuterated trifluoroacetic acid/deuterated chloroform at room temperature, and (c) and (f) 75/25 (v/v) mixture of o-chlorophenol/deuterated chloroform at 80 °C.

to being the small structural difference between isophthalic and terephthalic units.

Indeed, Godard et al.[23] also observed the peak splitting of the aliphatic quaternary carbons of the bisphenol-A unit reflecting the sequences for the transesterification products between poly(ethylene terephthalate) and PC. Also in this case, the non-splitting of the methyl carbon peaks was observed. To confirm the solvent effect for the ^{13}C NMR spectrum of the copolymer of U-Polymer and PC, ^{13}C NMR spectra were observed in deuterated chloroform and 50/50 (v/v) mixture of deuterated trifluoroacetic acid/deuterated chloroform at room temperature, respectively. As shown in Figure 10a and 10b, only three peaks were observed, and thus the aliphatic quaternary carbons of the bisphenol-A unit cannot give the sequence information on the isophthalic and terephthalic unit in deuterated chloroform and 50/50 (v/v) mixture of deuterated trifluoroacetic acid/deuterated chloroform. Also, the methyl carbon peaks of the bisphenol-A unit in these solvents cannot give the sequence information on the isophthalic and terephthalic unit as well as the case in the 75/25

(v/v) mixture of *o*-chlorophenol/deuterated chloroform. Consequently, the solvent system of the 75/25 (v/v) mixture of *o*-chlorophenol/deuterated chloroform has the potentiality for the detailed sequence analysis of polyarylate and polyestercarbonate using not only ^{1}H NMR but also ^{13}C NMR.

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