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Sequence analysis of poly(ethylene/1,4-cyclohexanedimethylene terephthalate) copolymer using ^{1}H and ^{13}C NMR

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Abstract

The triad-level sequence analysis of poly(ethylene/1,4-cyclohexanedimethylene terephthalate) copolymer was reported in a solvent system of *o*-chlorophenol/deuterated chloroform mixture (50/50 v/v) at 80 °C using 600 MHz ^{1}H NMR. The well-resolved alcoholic CH$_2$ proton peak of the glycol units was observed, which made the detailed sequence analysis possible. The peaks of the *cis*- and *trans*-forms of the 1,4-cyclohexanedimethylene glycol units were split into the triad sequence in the chain and could be assigned by a comparison of the spectra with those of homopolymers and by an additional two-dimensional heteronuclear multiple bond correlation observation. The triad sequence distributions centered on 1,4-cyclohexanedimethylene glycol units were determined, which was independent of the *cis*- and *trans*-forms of the units and controlled according to Bernoullian statistics.

Keywords: Poly(ethylene/1,4-cyclohexanedimethylene terephthalate); ^{1}H and ^{13}C NMR; Triad sequence analysis

1. Introduction

Poly(ethylene terephthalate) (PET) is a semi-crystalline polymer used in large quantities in the textile industry and also in the manufacture of electronic tapes, food packaging, and beverage containers. However, the disadvantage of PET is to crystallize very rapidly and to have relatively low glass transition temperature. In order to improve such undesirable properties, the copolymerization of PET has been performed, for example, with other dicarboxylic or glycolic monomers, or the transesterification with other polyesters.

Poly(ethylene/1,4-cyclohexanedimethylene terephthalate) copolymer, P(ET/CT), is known to exhibit lower melting temperatures and slower crystallization rate and therefore, the molding is more easily than PET [1]. The 1,4-cyclohexanedimethylene glycol unit has two isomers, *cis* (equatorial–axial) and *trans* (axial–axial or equatorial–equatorial); the *trans*-form is more stable than the *cis*-form. Therefore, this copolymer can be regarded as the copolymer consists of the three components on the glycol units [2–4].

Nuclear magnetic resonance (NMR) is a powerful tool for the investigation of the microstructure of copolymers [5–13]. It has been reported that the sequence distributions of the ethylene glycol units and the 1,4-cyclohexanedimethylene glycol units in this copolymer are statistically random by the analysis using ^{13}C NMR [3,4]. However, it was limited to the dyad analysis on the ethylene glycol units and the 1,4-cyclohexanedimethylene glycol units centered on the terephthalic units, and has not been reported on the sequences of the *cis*- and *trans*-forms of the 1,4-cyclohexanedimethylene glycol units because of difficulty of the peak splitting reflecting the sequences of the isomers. In our previous paper [14], the triad-level sequence analysis on the glycol units of poly(ethylene/tetramethylene terephthalete) copolymer was reported. The careful selection of the suitable solvent for NMR observation and use of 600 MHz ^{1}H NMR made possible the triad-level analysis. Actually, the sensitivity and resolution were much improved compared with the previous spectra of this copolymer.

In this paper, we also used a 600 MHz ^{1}H NMR apparatus to obtain the sequence information on the *cis*- and *trans*-forms of the 1,4-cyclohexanedimethylene glycol units. The NMR solvent was selected carefully to obtain a well-resolved spectrum. Then the two-dimensional heteronuclear multiple bond correlation (HMBC) spectrum was

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observed to assign the spectrum at triad level. The triad level sequence analysis on the ethylene glycol units, *cis*- and *trans*-forms of the 1,4-cyclohexanedimethylene glycol units was performed.

2. Experimental

2.1. Polymer preparation

P(ET/CT) copolymer, the molar ratio of ET/CT is 67/33, a *cis* to *trans* molar ratio of cyclohexanedimethylene glycol unit is 30/70, is a commercial product available from Eastman Chemical Co. PET and poly(1,4-cyclohexane dimethylene terephthalate) (PCT), a *cis* to *trans* molar ratio of cyclohexanedimethylene glycol unit is 27/73, were synthesized by melt polycondensation. The weight-average molecular weights of these polymers which were determined by GPC, were 5.00×10^4, 5.26×10^4, and 4.83×10^4 g mol^{-1}, respectively.

2.2. Blend preparation

The blend of PET and PCT, of which the polymer ratio was 45/55 mol%, was prepared by dissolving two polymers in hexafluoroisopropanol and pouring them into a large excess of acetone. The precipitated polymer was filtered and dried under vacuum at 50 °C for 24 h.

2.3. Transesterification between PET and PCT

Heat treatment of the blend of PET and PCT, for the transesterification reaction, was performed on a TA Instruments 2920 differential scanning calorimeter under dry nitrogen atmosphere. Samples were heated from room temperature to 300 °C with heating rate of 50 K min^{-1}, maintained at that temperature for various time intervals, and quenched into ice-water.

2.4. Shift reagent

Tris[3-(trifluoromethylhydroxymethylene)-d-camphorato]europium, Eu(tfc)$_3$, obtained from Aldrich, was partially used for NMR measurement of PCT as the shift reagent. The concentration in the solution was 0.03 M.

2.5. NMR measurements

The ^{1}H NMR spectra were recorded by using a JEOL α-600 spectrometer operating at 600 MHz. Deuterated trifluoroacetic acid/deuterated chloroform mixture (50/50 v/v) and *o*-chrolophenol/deuterated chroloform mixture (50/50 v/v) were used as solvent. The observed temperature was room temperature for the former case, but 80 °C for the latter case. 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 32k. The flip angle and the pulse delay were 45° and 4 s, respectively. Double homospin-decoupled spectra were obtained by decoupling of the non-alcoholic CH protons of the 1,4-cyclohexanedimethylene glycol units. 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 1.07 Hz/point, corresponding to a spectral width of 35 kHz and a data point of 32k. The flip angle and the pulse delay were 45° and 2 s, respectively. Two-dimensional HMBC spectrum was obtained with a delay time $\tau = 160$ ms calculated for $^3J_{H-C} = 3$ Hz. The time domain signals consisted of 256 t_1 slices, each with 2048 data points. In t_2 and t_1 dimensions the sweep width was 2.56 and 1.28 kHz, respectively. The digital resolution of the spectrum was 1.25 Hz/point in the F_2 dimension and 1.25 Hz/point in the F_1 dimension after zero-filling. The window function was sine-bell in both dimensions.

3. Results and discussion

3.1. ^{1}H NMR spectrum of poly(ethylene/1,4-cyclohexanedimethylene terephthalate) copolymer

The selection of solvent is important for detailed sequential analysis of the copolymer. In our previous paper [14], 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. Therefore, we used this solvent system. The 600 MHz ^{1}H NMR spectrum of P(ET/CT) copolymer in *o*-chlorophenol/deuterated chloroform mixture is shown in

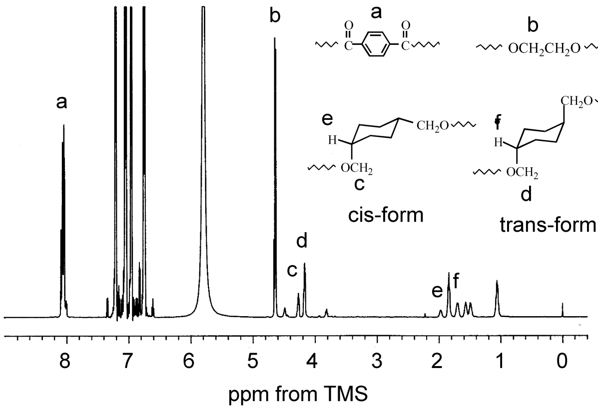

Fig. 1. Six hundred MHz ^{1}H NMR spectrum of P(ET/CT) copolymer at 80 °C. The solvent is 50/50 (v/v) mixture of *o*-chlorophenol/deuterated chloroform. The spectrum for sequence analysis was observed by double homospin decoupling of the non-alcoholic CH protons, e and f, of 1,4-cyclohexanedimethylene glycol units.

Fig. 1 together with the assignment. The resonance region, 4.10 to 4.70 ppm was expanded in Fig. 2(a). The well-resolved alcoholic CH_2 peaks of the 1,4-cyclohexanedimethylene glycol units were obtained. This seems mainly due to the ring current shielding effect from the aromatic ring of *o*-chlorophenol. Actually, only two broad peaks of the alcoholic CH_2 protons of the 1,4-cyclohexanedimethylene glycol units were observed in 50/50 (v/v) mixture of deuterated trifluoroacetic acid/deuterated chloroform as shown in Fig. 2(c). Although, these two peaks at 4.435 and 4.325 ppm have been assigned to the *cis* and *trans* isomers, respectively [4,15–17], it is difficult to assign these peaks to the triad-level sequences because of no further splitting. Thus, it seems quite useful to use the solvent system; 50/50 (v/v) mixture of *o*-chlorophenol/deuterated chloroform. In order to analyze the alcoholic CH_2 protons of the 1,4-cyclohexanedimethylene glycol units in detail, decoupling of the non-alcoholic CH protons, e and f, was also performed (Fig. 2(b)). The separated peaks in Fig. 2(b) seem to reflect the triad sequences of the glycol units centered on the *cis* and *trans* isomers of the 1,4-cyclohexanedimethylene glycol units; that is, C−T−Cc−T−C, C−T−Cc−T−E and E−T−Cc−T−E for *cis* isomer, and C−T−Ct−T−C, C−T−Ct−T−E and E−T−Ct−T−E for *trans* isomer, where Cc and Ct are *cis*- and *trans*-forms of 1,4-cyclohexanedimethylene glycol unit, respectively, C is 1,4-cyclohexanedimethylene glycol unit, E is ethylene glycol unit, and T is terephthalic unit.

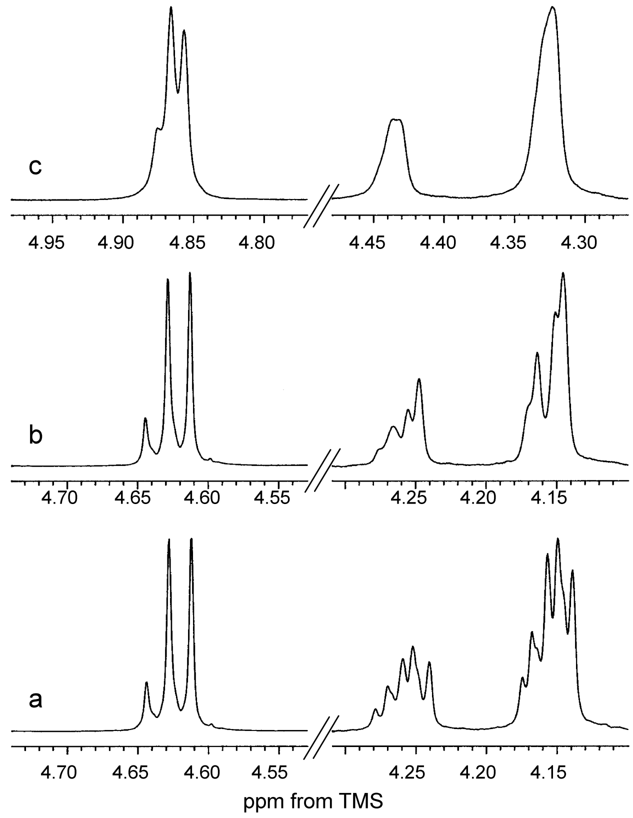

Fig. 2. Expanded 600 MHz ^1H NMR spectra (the alcoholic CH_2 proton region) of P(ET/CT) copolymer; (a) is non-decoupling spectrum, (b) and (c) are double homospin decoupling spectra of the non-alcoholic CH protons, e and f, in this figure. The solvent systems are (a) and (b) 50/50 (v/v) mixture of *o*-chlorophenol/deuterated chloroform at 80 °C, (c) 50/50 (v/v) mixture of deuterated trifluoroacetic acid/deuterated chloroform at room temperature.

3.2. Peak assignment of the alcoholic CH_2 protons at triad-level

The possible triad sequences of the glycol units of this copolymer are shown in Fig. 3. For the assignment of the peaks in Fig. 2(b) to triad sequence, the ^1H NMR spectrum of homopolymer, PCT was observed as shown in Fig. 4(b). The peaks (1) and [1] in Fig. 4(a) are clearly assigned to the CH_2 protons (1) and [1] in Fig. 3, respectively. For further assignment, the HMBC observation is planned. For the purpose, the peak position among the copolymer and homopolymers, PET and PCT was compared in the ^{13}C NMR spectra (Fig. 5). Four peaks assigned to the carbonyl carbons of the copolymer are observed which is reflecting the dyad sequences of the glycol units centered on the terephthalic units. The peaks A and D in Fig. 5(a) were clearly assigned to the carbonyl carbons (A) and (D) in Fig. 3, respectively. To assign the other peaks, the HMBC spectrum was observed as shown in Fig. 6. The cross-peaks were observed between the alcoholic CH_2 protons of glycol units and the carbonyl carbons of terephthalic units through $^3J_{H-C}$ coupling. The carbonyl carbon peak (D), which was already assigned to dyad sequence, C−T−C, was correlated with peaks (1) and [1] of the 1,4-cyclohexanedimethylene glycol units. As mentioned above, these peaks were already assigned to the triad sequences, C−T−Cc−T−C and C−T−Ct−T−C, respectively. The peak (D) was also correlated with peaks (2) and [2]. Therefore, the peaks (2) and [2] were assigned to the protons (2) and [2] in Fig. 3, respectively. The carbonyl carbon peak (C) was correlated with the peaks (3) and [3]. Therefore, the peaks (3) and [3] were assigned to the protons (3) and [3] in Fig. 3, respectively. Since the peak (C) was also correlated with the peaks (4) and [4], these peaks were assigned to the protons (4) and [4] in Fig. 3, respectively. Similarly, the carbonyl carbon peak (A), which was already assigned to dyad sequence, E−T−E, was correlated with peaks (5) and (6) of ethylene glycol units. The peak (5) was also assigned to the proton (5) of the ethylene glycol units by comparison of homopolymer, PET (data not shown). The carbonyl carbon peak (B) was correlated with peaks (6) and (7) of the ethylene glycol units. Therefore, the peaks (6) and (7) were assigned to the protons (6) and (7) in Fig. 3, respectively. Thus, all of the alcoholic CH_2 proton peaks in ^1H NMR spectrum of P(ET/CT) copolymer in Fig. 6 were assigned to the triad sequences in the chain. Conversely, by this HMBC observation, the carbonyl carbon peaks, (A), (B), (C), and (D) in Fig. 6, were also assigned to the carbonyl carbons (A), (B), (C), and (D) in Fig. 3, respectively.

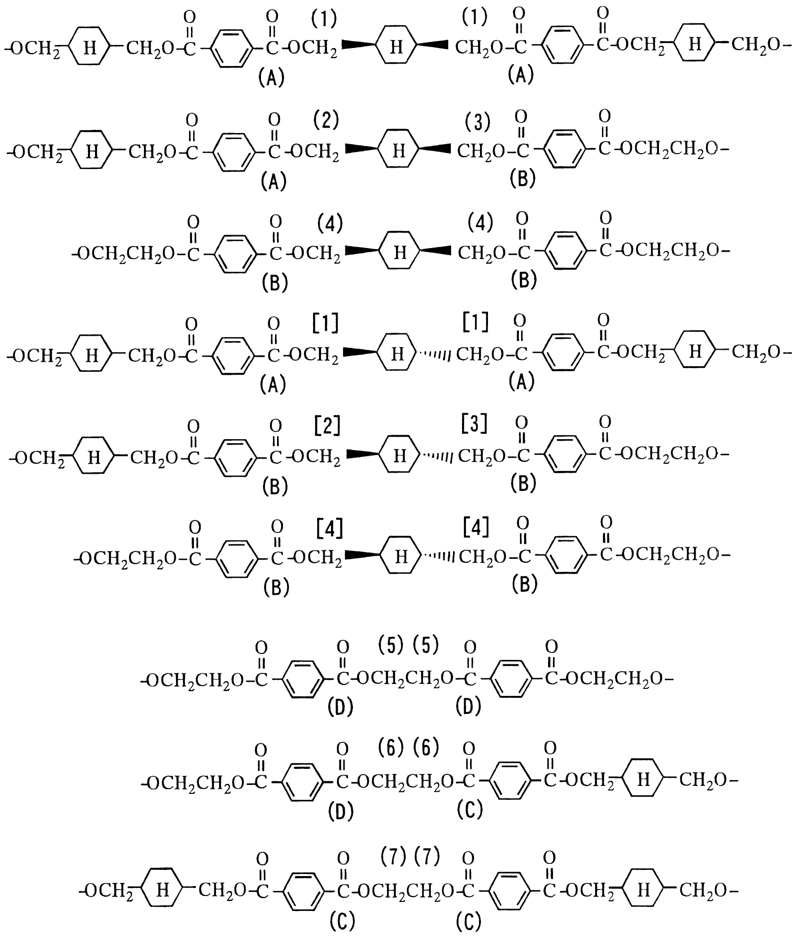

Fig. 3. Possible triad sequences on the glycol units of P(ET/CT) copolymer along with the notations of protons and carbonyl carbons.

3.3. Sequence distribution analysis of the copolymer

To estimate the degree of randomness of P(ET/CT) copolymer, the triad molar fractions centered on glycol units were determined on the basis of the observed relative peak area. The degrees of randomness (R) were calculated with the following equation [18]:

$$R_E = (f_{EEC}/2)/F_E + (f_{EEC}/2)/F_C \quad (1)$$

$$R_{Cc} = (f_{ECcC}/2)/F_E + (f_{ECcC}/2)/F_C \quad (2)$$

$$R_{Ct} = (f_{ECtC}/2)/F_E + (f_{ECtC}/2)/F_C \quad (3)$$

where R_E, R_{Cc}, and R_{Ct} are the degrees of randomness around E, Cc, and Ct, respectively. Subscript E, C, Cc, and Ct indicates ethylene glycol unit, 1,4-cyclohexanedimethylene glycol unit, *cis*- and *trans*-forms of 1,4-cyclohexanedimethylene glycol unit, respectively. f_{EEC}, f_{ECcC}, and f_{ECtC} indicate the molar fractions of the triad sequences, E–T–E–T–C, E–T–Cc–T–C, and E–T–Ct–T–C, respectively. $F_E = 0.668$ and $F_C = 0.332$ are the molar fraction of the ethylene glycol unit and the 1,4-cyclohexanedimethylene glycol unit in the copolymer, respectively. As shown in Table 1, $R_E = 1.04$, $R_{Cc} = 1.04$, and $R_{Ct} = 1.08$ were obtained. Therefore, it was made clear that the sequential unit distribution in P(ET/CT) copolymer is random and obeys Bernoullian statistics. It has been reported that the sequence distribution of the ethylene glycol unit and 1,4-cyclohexanedimethylene glycol unit (non-discrimination for two isomers, *cis*- and *trans*-forms) in this copolymer is statistically random [3,4]. From this study, the sequence information for individual *cis*- and *trans*-forms of the 1,4-cyclohexanedimethylene glycol unit could be obtained.

Table 1
Triad fractions (f) and degree of randomness (R) centered on glycol units in poly(ethylene/1,4-cyclohexanedimethylene terephthalate) copolymer determined by ^{1}H NMR

	f	R
C–T–Cc–T–C	0.070	
C–T–Cc–T–E	0.463	1.04
E–T–Cc–T–E	0.467	
E–T–E–T–E	0.419	
E–T–E–T–C	0.463	1.04
C–T–E–T–C	0.118	
C–T–Ct–T–C	0.007	
C–T–Ct–T–E	0.478	1.08
E–T–Ct–T–E	0.445	

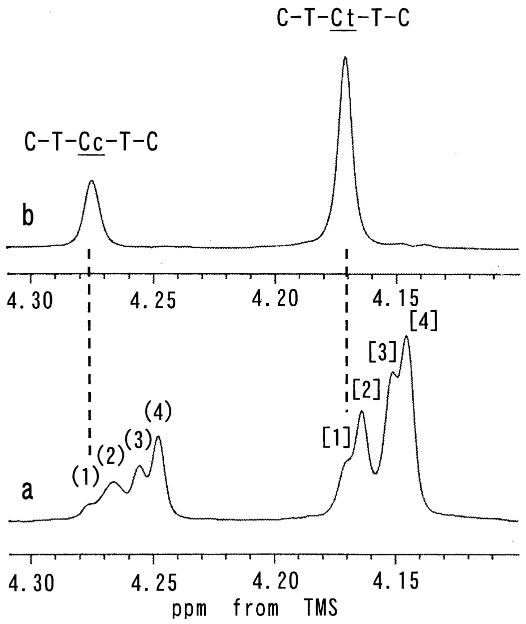

Fig. 4. Expanded 600 MHz ^{1}H NMR spectra (the alcoholic CH$_2$ proton region of the 1,4-cyclohexanedimethylene glycol units) of (a) poly(ethylene/1,4-cyclohexane dimethylene terephthalate) copolymer and (b) poly(1,4-cyclohexanedimethylene terephthalate) homopolymer in 50/50 (v/v) mixture of *o*-chlorophenol/deuterated chloroform at 80 °C. The spectra were obtained under double homospin decoupling of the non-alcoholic CH protons of 1,4-cyclohexanedimethylene glycol units.

3.4. Sequence distributions analysis of transesterification products

To confirm the randomness, the sequence distributions of several transesterification products between PET and PCT were analyzed by ^{1}H NMR. Triad molar fractions centered on glycol units were determined on the basis of the observed relative peak area. The changes in the triad molar fractions centered on the *cis*- and *trans*-forms of the 1,4-cyclohexanedimethylene glycol unit are plotted in Fig. 7, where $f_{\mathrm{CCcC}}+f_{\mathrm{CCcE}}+f_{\mathrm{ECcE}}=1$, and $f_{\mathrm{CCtC}}+f_{\mathrm{CCtE}}+f_{\mathrm{ECtE}}=1$. The change in the triad molar fractions, f_{CCcC}, f_{CCcE}, and f_{ECcE} was in good agreement with that of f_{CCtC}, f_{CCtE}, and f_{ECtE}, respectively, in the range of transesterification reaction time. In Fig. 8, the change in the degrees of randomness for E, Cc, and Ct, calculated with the above Eqs. (1)–(3), are plotted against reaction time. As the transesterification reaction proceeds, the degrees of randomness, R_{E}, R_{Cc}, and R_{Ct} increased toward $R=1$, which is in good agreement with each other. From the above triad sequence data by ^{1}H NMR, it was confirmed that P(ET/CT)

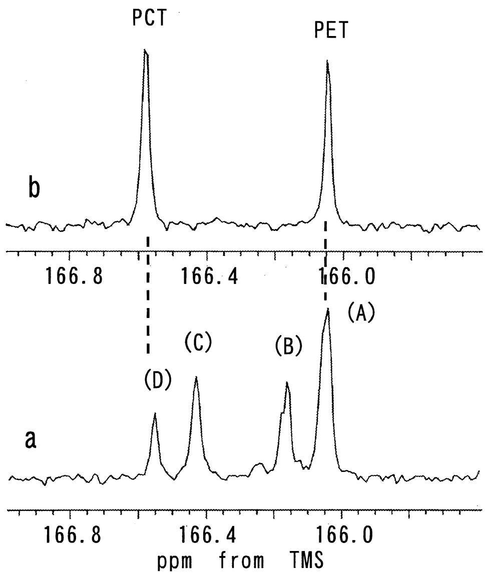

Fig. 5. Expanded 150 MHz ^{13}C NMR spectra (the carbonyl carbon region of the terephthalic units) of (a) P(ET/CT) copolymer and (b) a blend of PET and poly(1,4-cyclohexanedimethylene terephthalate) in 50/50 (v/v) mixture of *o*-chlorophenol/deuterated chloroform at 80 °C.

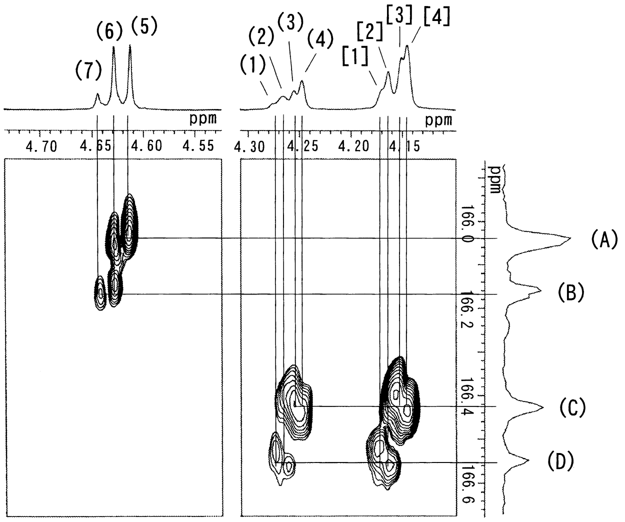

Fig. 6. ^{1}H–^{13}C HMBC spectrum of P(ET/CT) copolymer. The delay time was $\tau = 160$ ms. The time domain signals consisted of 256 t_1 slices, each with 1024 data points. In t_2 and t_1 dimensions the sweep width was ca. 2.56 and 1.28 kHz, respectively. The digital resolution of the spectrum was 1.25 Hz/point in the F_2 dimension and 1.25 Hz/point in the F_1 dimension after zero-filling. The window function used was sine-bell in both the dimensions.

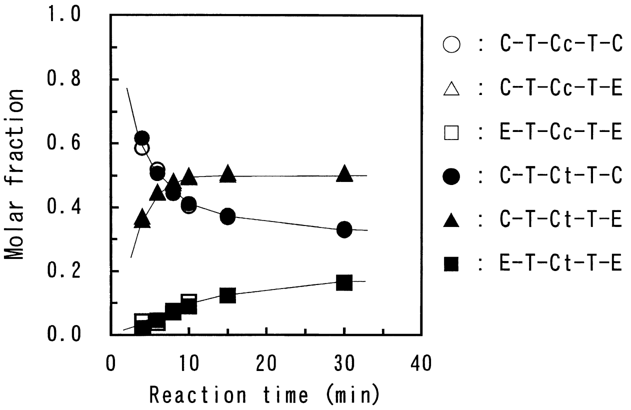

Fig. 7. Change in the molar fractions determined from the triad sequences obtained from ^{1}H NMR with the reaction time at 300 °C for a blend of PET and poly(1,4-cyclohexanedimethylene terephthalate).

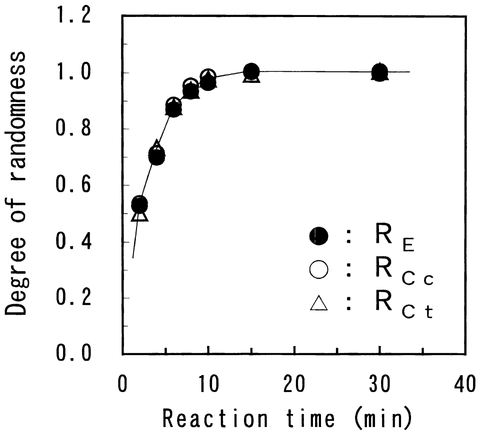

Fig. 8. Change in the degree of randomness calculated from the triad sequences obtained from ^{1}H NMR with the reaction time at 300 °C for a blend of PET and poly(1,4-cyclohexanedimethylene terephthalate).

copolymer is statistically random, and the triad sequence distributions centered on the 1,4-cyclohexanedimethylene glycol units are independent of the *cis*- and *trans*-forms of the units.

3.5. Sequence distribution analysis of PCT homopolymer using shift reagent

As shown in Fig. 4(b), only two CH_2 proton peaks of the 1,4-cyclohexanedimethylene glycol unit in PCT homopolymer were observed in 50/50 (v/v) mixture of *o*-chlorophenol/deuterated chloroform. Therefore, it was impossible to analyze the sequence distribution of the *cis*- and *trans*-forms of the 1,4-cyclohexanedimethylene glycol unit in PCT homopolymer from the spectrum. To analyze the sequence distribution of the *cis*- and *trans*-forms of the 1,4-cyclohexanedimethylene glycol unit in PCT homopolymer, tris[3-(trifluoromethylhydroxymethylene)-d-camphorato]europium, Eu(tfc)$_3$, was used as a shift reagent for ^{1}H NMR measurement of PCT homopolymer in 50/50 (v/v) mixture of *o*-chlorophenol/deuterated chloroform. Consequently, as shown Fig. 9(b), three terephthalic proton peaks were observed. From the composition of the *cis* and *trans* isomers of the 1,4-cyclohexanedimethylene glycol unit in PCT homopolymer, these separated peaks are considered to reflect the dyad sequences on the 1,4-cyclohexanedimethylene glycol units centered on the terephthalic units, Cc–T–Cc, Ct–T–Cc and Ct–T–Ct. To estimate the degree of randomness of PCT homopolymer, dyad molar fractions were determined on the basis of the observed relative peak area in Fig. 9(b). The values were determined to be $f_{CtCt} = 0.500$, $f_{CtCc} = 0.417$, $f_{CcCc} = 0.083$. Here, the ^{1}H NMR spin-lattice relaxation times were almost equal in the presence and the absence of Eu(tfc)$_3$. The degrees of randomness (R) were calculated with the following equation [18]:

$$R = (f_{CtCc}/2)/F_{Cc} + (f_{CtCc}/2)/F_{Ct} \qquad (4)$$

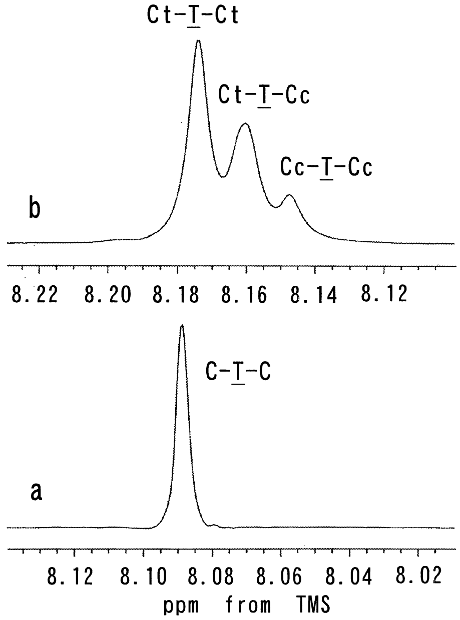

Fig. 9. Expanded 600 MHz ^{1}H NMR spectra (the terephthalic proton region) of poly(1,4-cyclohexanedimethylene terephthalate) homopolymer in 50/50 (v/v) mixture of *o*-chlorophenol/deuterated chloroform at 80 °C. (a) Without addition of shift reagent, (b) addition of shift reagent, [Eu(tfc)3] to the solution, where the concentration of the shift reagent is 0.03 M in 50/50 (v/v) mixture of *o*-chlorophenol/deuterated chloroform at 80 °C.

where f_{CtCt}, f_{CtCc}, f_{CcCc} indicate the molar fractions of the dyad sequences, Ct–T–Ct, Ct–T–Cc, Cc–T–Cc, respectively. $F_{Cc} = 0.291$ and $F_{Ct} = 0.709$ are the molar fraction of the *cis* and *trans* isomers of the 1,4-cyclohexanedimethylene glycol unit in PCT homopolymer, respectively. From Fig. 9(b), $R = 1.01$ was obtained. Therefore, it is clear that the sequence distribution of *cis*- and *trans*-forms of 1,4-cyclohexanedimethylene glycol unit in PCT homopolymer is random and obeys Bernoullian statistics. This coincides with the above results of the triad sequence analyses in P(ET/CT) copolymer and transesterification products between PET and PCT, that is, the sequence distribution on the 1,4-cyclohexanedimethylene glycol unit is independent of the *cis*- and *trans*-forms of the unit.

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References

[1] Aspy PA, Denison EE. Mod Plast 1983;August:74.
[2] Chen LP, Yee AF, Goetz JM, Schaefer J. Macromolecules 1998;31: 5371.
[3] Yoo HY, Umemoto S, Kikutani T, Okui N. Polymer 1994;35:117.
[4] Yoshie N, Inoue Y, Yoo HY, Okui N. Polymer 1994;35:1931.

[5] Bovey FA. High resolution NMR of macromolecules. New York: Academic Press; 1972.

[6] Matsuzaki K, Uryu T, Asakura T. NMR spectroscopy and stereoregularity of polymers. Tokyo: Japan Scientific Societies Press; 1996.

[7] Herbert IR. Statistical analysis of copolymer sequence distribution from NMR spectroscopy of polymers. Glasgow: Blackie; 1993.

[8] Fakirov S. Transreactions in condensation polymers. Germany: Wiley-VCH; 1999.

[9] Porter RS, Wang LH. Polymer 1992;33:2019.

[10] Pó R, Cioni P, Abis L, Occhiello E, Garbassi F. Polym Commun 1991; 32:208.

[11] Montaudo G, Montaudo MS, Scamporrino E. Macromolecules 1992; 25:5099.

[12] Ha WS, Chun YK, Jang SS, Rhee DM, Park CR. J Polym Sci: Polym Phys Ed 1997;35:309.

[13] Backson SCE, Kenwright AM, Richards RW. Polymer 1995;36:1991.

[14] Matsuda H, Asakura T, Miki T. Macromolecules 2002;35:4664.

[15] Amari T, Nishimura K, Minou K, Kawabata A, Ozaki Y. J Polym Sci: Polym Chem Ed 2001;39:665.

[16] Liu Y, Ranucci E, Lindblad MS, Albertsson AC. J Polym Sci: Polym Chem Ed 2001;39:2508.

[17] Fox B, Moad G, Diepen G, Willing I, Cook WD. Polymer 1997;38: 3035.

[18] Devaux J, Godard P, Mercier JP. J Polym Sci: Polym Phys Ed 1982; 20:1875.