# Triad Sequence Analysis of Poly(ethylene/butylene terephthalate) Copolymer Using $^{1}$H NMR

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ABSTRACT: The analysis of the triad sequence of a poly(ethylene/butylene terephthalate) copolymer using 600 MHz $^{1}$H NMR is reported in a solvent system of *o*-chlorophenol/deuterated chloroform mixture (75/25 v/v) at 80 °C. The well-resolved alcoholic $CH_2$ proton peak of the glycol units made the detailed sequence analysis possible. Exact peak assignment was performed with two special NMR experiments: a $^{13}$C-labeling experiment and a two-dimensional heteronuclear multiple bond correlation (HMBC) observation. The number-average sequence lengths calculated from the triad sequences by $^{1}$H NMR were in good agreement with those from the dyad sequences by $^{13}$C NMR. From the triad sequence information, it can be shown that the transesterification of the copolymer is controlled according to Bernoullian statistics.

## Introduction

The properties of copolymers depend not only on the comonomer composition but also on the sequence distribution of the constituent comonomers. The latter can range from alternating through random to blocky. NMR is the most powerful analytical method for determining the sequence distribution, and a knowledge of the relative abundances of monomer sequences provides a means of characterizing the average microstructure of a copolymer.[1,2] As an extension of such a sequence information, it has become common in practice to check for conformity of the observed sequence distribution to an appropriate statistical model.[1] The rationale for this is that, as well as providing a more complete description of copolymer microstructure, conformity to a particular model can impart important information concerning the mechanism of polymer propagation. In addition, in favorable cases, the relative reactivities of the comonomers can also be established.[3]

Polyesters, particularly poly(ethylene terephthalate) (PET), constitute an important class of polymers with widespread applications such as fibers, films, and beverage containers.[4] To overcome some undesirable properties such as poor dyeability and solubility, pilling, and brittleness, the chemical modification of PET has been intensively investigated by the copolymerization with other dicarboxylic or glycolic monomers or the transesterification with other polyesters.[5,6]

In this paper, we will report the sequence analysis of poly(ethylene/butylene terephthalate) copolymer with NMR, mainly 600 MHz $^{1}$H NMR. So far, the sequence analysis of this copolymer with $^{13}$C NMR has been reported[7,8] but was limited to the dyad level, and therefore only insufficient information on the sequence was obtained. For example, triad level sequence analyses have been performed for the poly(ethylene terephthalate-*co*-isophthalate) copolymer by NMR.[10−14] Detailed discussion was performed about stricter control of the polymerization reactions and the physical properties. Thus, it is required to analyze the microstructure of poly(ethylene/butylene terephthalate) copolymer at higher level than dyad, for further detailed analysis. In addition, it is well-known that any mechanism can be fitted but none can be tested from dyad information alone, and a Bernoulli model can be tested from triad information.[1] We used here a 600 MHz $^{1}$H NMR apparatus with high sensitivity and high resolution. At first, the NMR solvent was carefully selected in order to obtain a well-resolved spectrum. Then, two special experiments, $^{13}$C-labeling experiment and two-dimensional heteronuclear multiple bond correlation (HMBC) observation, were performed to assign the peaks at triad level exactly. The triad level sequence analysis was performed for the $^{1}$H NMR spectrum.

## Experimental Section

**Polymer Preparation.** Poly(ethylene/butylene terephthalate) copolymer, of which the ethylene to butylene monomer unit ratio was 40/60 mol %, poly(ethylene terephthalate) (PET), and poly(butylene terephthalate) (PBT) were synthesized by melt polycondensation. The weight-average molecular weights of these polymers which were determined by GPC were $4.92 \times 10^{4}$, $5.26 \times 10^{4}$, and $6.57 \times 10^{4}$ g mol$^{-1}$, respectively. Additionally, [1-$^{13}$C]-labeled PET was prepared from [1-$^{13}$C]-labeled dimethyl terephthalate (98% label enrichment).[4]

**Blend Preparation.** The blend of PET and PBT, of which the polymer ratio was 40 and 60 mol %, respectively, was prepared by dissolving two polymers in hexafluoro-2-propanol and pouring then them into a large excess of acetone. The precipitated polymer was filtered and dried under vacuum at 50 °C for 24 h.

**Transesterification between PET and PBT.** Heat treatment of the blend of PET and PBT, for the transesterification reaction, was performed on a TA Instruments 2920 differential scanning calorimeter under a 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.

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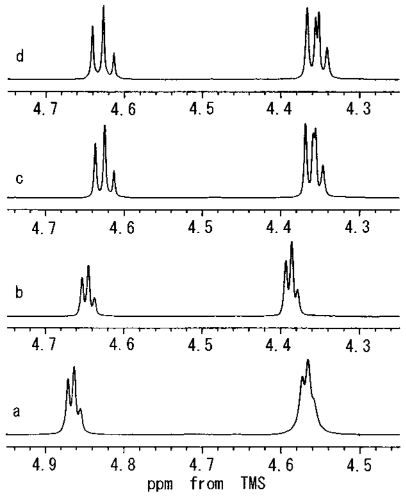

**Figure 1.** Expanded 600 MHz $^1$H NMR spectra (the alcoholic CH$_2$ proton region) of poly(ethylene/butylene terephthalate) copolymer. The solvent systems (a) 50/50 (v/v) mixture of deuterated trifluoroacetic acid/deuterated chloroform and (b) 25/75 (v/v) mixture, (c) 50/50 (v/v) mixture, and (d) 75/25 (v/v) mixture of *o*-chlorophenol/deuterated chloroform were used. The spectra were observed at room temperature in the case of spectrum (a), but 80 °C in the case of all others. The spectra were obtained under homospin decoupling of the nonalcoholic methylene protons of butylene glycol units.

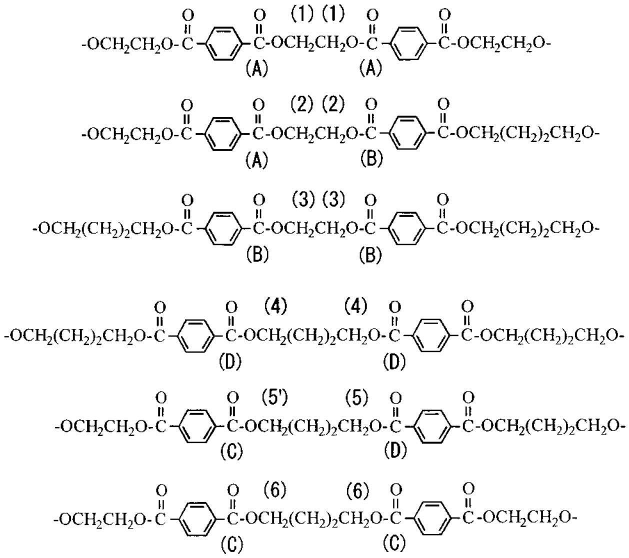

**Figure 2.** Possible triad sequences on the glycol units of poly(ethylene/butylene terephthalate) copolymer along with the notations of protons and carbonyl carbons.

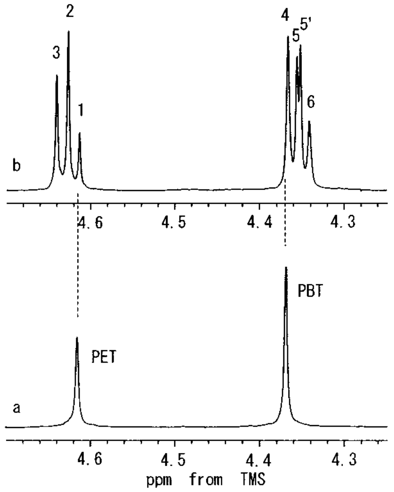

**Figure 3.** Expanded 600 MHz $^1$H NMR spectra (the alcoholic CH$_2$ proton region) of poly(ethylene/butylene terephthalate) copolymer and a blend of poly(ethylene terephthalate) and poly(butylene terephthalate) in 75/25 (v/v) mixture of *o*-chlorophenol/deuterated chloroform at 80 °C. The spectra were obtained under homospin decoupling of the nonalcoholic methylene protons of butylene glycol units.

**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*-chlorophenol/deuterated chloroform mixture (25/75, 50/50, and 75/25, 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. Homospin decoupled spectra were obtained by decoupling of the nonalcoholic CH$_2$ protons of the butylene 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. The $^1$H-selective decoupled $^{13}$C NMR spectrum of PBT homopolymer was obtained by selective decoupling of the terephthalic proton. A two-dimensional heteronuclear multiple bond correlation (HMBC) spectrum was obtained with a delay time $\tau = 160$ ms calculated for $^3J_{\mathrm{H-C}} = 3$ Hz. 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 1.88 and 1.28 kHz, respectively. The digital resolution of the spectrum was 0.95 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.

## Results and Discussion

**Selection of Solvent.** The 600 MHz $^1$H NMR spectra of poly(ethylene/butylene terephthalate) copolymer were measured in deuterated trifluoroacetic acid/deuterated chloroform mixture and *o*-chlorophenol/deuterated chloroform mixture upon the decoupling of the nonalcoholic methylene protons of the butylene glycol units. In the latter case, the relative composition was changed. As shown in Figure 1a, three peaks of the alcoholic CH$_2$ protons and three peaks of the butylene glycol units were observed in a deuterated trifluoroacetic acid/deuterated chloroform mixture. A further separation of the center peak in the latter peaks was observed in the *o*-chlorophenol/deuterated chloroform mixture, 50/50 and 75/25 (v/v) % solvents. This is likely due to the ring current effect of the aromatic ring of *o*-chlorophenol. So, the solvent system, *o*-chlorophenol/deuterated chloroform mixture, 75/25 v/v, was selected in this NMR observation. The observed temperature was 80 °C.

**Comparison of the $^1$H NMR Spectra between Copolymer and Homopolymer.** In the spectrum of the copolymer, the three peaks from 1 to 3 of the alcoholic CH$_2$ group and four peaks, 4, 5, 5′, and 6, of the butylene glycol units are considered to reflect the triad level sequences of the copolymer. The possible triad sequences of this copolymer are shown in Figure 2. To assign these peaks, the peak position was compared among the copolymer and homopolymers, PET and PBT (Figure 3). Peaks 1 and 4 in Figure 3b were clearly assigned to the protons numbered by (1) and (4) in Figure 2, respectively.

**$^{13}$C-Labeling Experiment for Exact Assignment of Peaks 5 and 5′.** In Figure 3b, peaks 5 and 5′ with

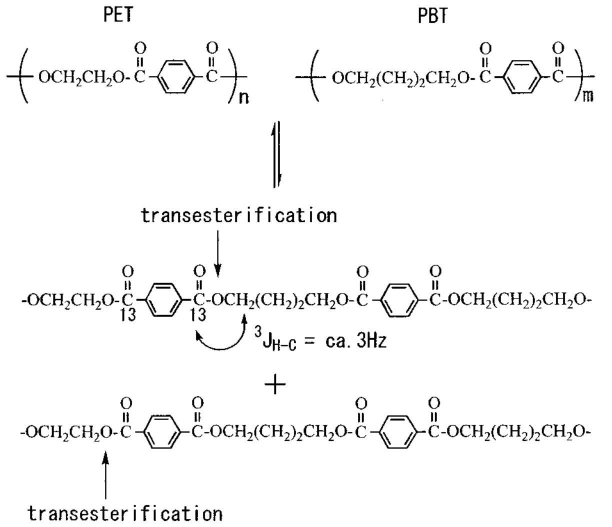

**Figure 4.** Reaction scheme of the transesterification between the carbonyl carbons of [1-$^{13}$C]-labeled poly(ethylene terephthalate) and nonlabeled poly(butylene terephthalate).

equal peak intensity can be assigned to the alcoholic butylene proton (5) or (5′) in the unsymmetrical triad sequence in Figure 2. Although the assignment of these peaks in unsymmetrical sequence has frequently been tried on the basis of the additive rule of the chemical shifts,[13–16] it is difficult to obtain exact assignment. To do exact assignment, a long-range spin-coupling NMR experiment was performed in this study. After transesterification reaction between [1-$^{13}$C]-labeled PET and nonlabeled PBT, a doublet peak with $^{3}J_{^{1}\mathrm{H}-^{13}\mathrm{C}}$ coupling constant should be observed for the alcoholic $CH_2$ protons of the butylene glycol unit adjacent to PET sequence as summarized in Figure 4. Actually, peak 5′, which was split into two peaks with $^{3}J_{\mathrm{H-C}}$ coupling constant ca. 3 Hz, was observed in Figure 5a. There still remains a single peak which did not contribute to such reaction, and therefore three peaks were finally observed. The magnitude of the spin-coupling constant, ca. 3 Hz, was reasonable because the corresponding coupling constant of PBT homopolymer was also observed to be ca. 3 Hz by $^{1}$H-selective decoupled $^{13}$C NMR experiment (data not shown). Thus, peak 5′ in Figure 3b was assigned to the butylene proton (5′) in Figure 2, and peak 5 in Figure 3b was assigned to the butylene proton (5).

**Two-Dimensional Heteronuclear Multiple Bond Correlation (HMBC) Spectrum.** To confirm the assignment, the HMBC spectrum was observed as shown in Figure 6. The cross-peaks were observed between the alcoholic $CH_2$ protons of glycol units and the carbonyl carbons of terephthalic units through $^{3}J_{\mathrm{H-C}}$ coupling. The carbonyl carbon peak D was correlated with peak 4, which was already assigned to triad sequence of PBT. Peak D was also correlated with peak 5. Therefore, peak 5 was assigned to the butylene proton (5) and peak 5′ to the proton (5′) in Figure 2. This assignment is in agreement with that by the transesterification reaction using $^{13}$C-labeled PET mentioned above. The carbonyl carbon peak C, which was correlated with peak 5′, was also correlated with peak 6. Therefore, peak 6 was assigned to the butylene proton (6) in Figure 2. Similarly, peaks 2 and 3 of the ethylene glycol units were assigned to the butylene protons (2) and (3), respectively.

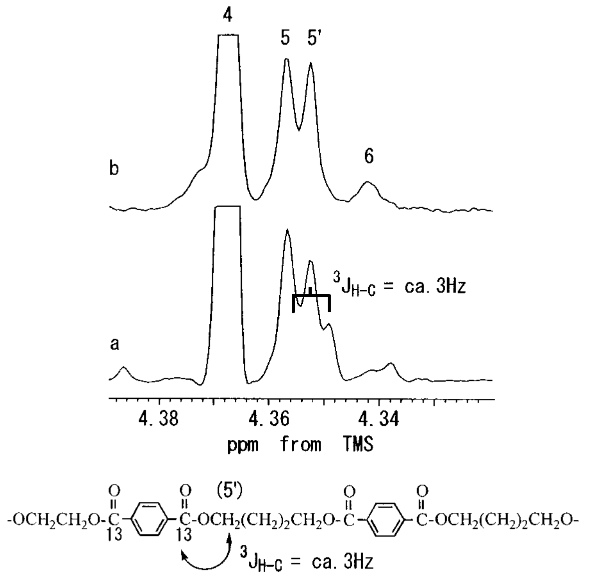

**Figure 5.** Assignment of the alcoholic $CH_2$ proton peaks of butylene glycol units in poly(ethylene/butylene terephthalate) copolymer. (a) The alcoholic $CH_2$ proton peaks of the butylene glycol units of the esterification products of nonlabeled poly(butylene terephthalate) and [1-$^{13}$C]-labeled poly(ethylene terephthalate) observed under homospin decoupling and (b) the corresponding peak of a similar sample, for nonlabeled poly(ethylene terephthalate) was used. Esterification was performed for 60 min at 300 °C.

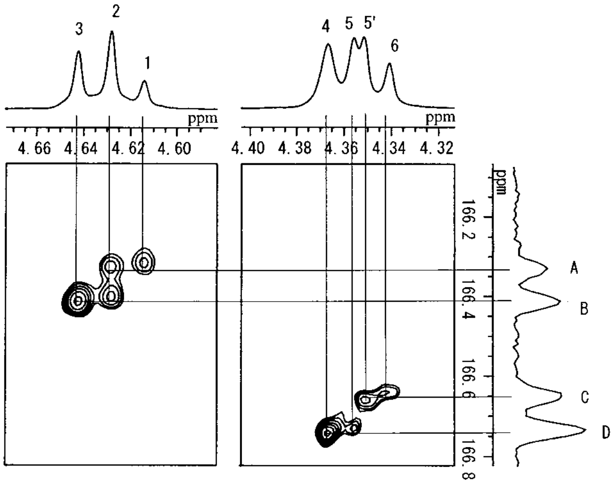

**Figure 6.** $^{1}$H−$^{13}$C HMBC spectrum of poly(ethylene/butylene terephthalate) copolymer. The delay time was $\tau = 160$ ms calculated for $^{3}J_{\mathrm{H-C}} = 3$ Hz. The time domain signals consisted of 256 $t_1$ slices, each with 1024 data points. In $t_2$ and $t_1$ dimensions the sweep width was ca. 1.88 and ca. 1.28 kHz, respectively. The digital resolution of the spectrum was 0.95 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 the both dimensions.

Conversely, by this HMBC observation, the carbonyl carbon peaks, A, B, C, and D in Figure 6, were assigned to the carbonyl carbons (A), (B), (C), and (D) in Figure 2. This assignment is in agreement with that by Backson et al.[17] Thus, all the peaks in $^{1}$H and $^{13}$C NMR spectra of poly(ethylene/butylene terephthalate) copolymer are assigned to the triad and dyad sequences of the chain, respectively.

**Comparison with Dyad Sequence Analysis.** To check whether the triad level sequence information obtained by $^{1}$H NMR coincides with the sequence information on dyad level obtained by $^{13}$C NMR, the

**Table 1. Triad Fractions Centered on Glycol Units in Poly(ethylene/butylene terephthalate) Copolymers Determined by $^1$H NMR[a]**

| | reaction time (min) | | | | |
|---|---|---|---|---|---|
| | 10 | 30 | 60 | 90 | 120 |
| EG-TA-EG-TA-EG | 0.301 | 0.241 | 0.161 | 0.151 | 0.133 |
| EG-TA-EG-TA-TMG | 0.082 | 0.125 | 0.179 | 0.186 | 0.197 |
| TMG-TA-EG-TA-TMG | 0.005 | 0.021 | 0.054 | 0.058 | 0.076 |
| TMG-TA-TMG-TA-TMG | 0.515 | 0.443 | 0.377 | 0.330 | 0.296 |
| EG-TA-TMG-TA-TMG | 0.089 | 0.149 | 0.185 | 0.224 | 0.233 |
| EG-TA-TMG-TA-EG | 0.008 | 0.021 | 0.044 | 0.051 | 0.065 |

[a] Temperature of reaction 300 °C; PET/PBT = 40/60 mole ratio.

**Table 2. Dyad Fractions in Poly(ethylene/butylene terephthalate) Copolymers Determined by $^{13}$C NMR[a]**

| | reaction time (min) | | | | |
|---|---|---|---|---|---|
| | 10 | 30 | 60 | 90 | 120 |
| EG-TA-EG | 0.339 | 0.309 | 0.256 | 0.249 | 0.232 |
| EG-TA-TMG | 0.102 | 0.183 | 0.284 | 0.308 | 0.361 |
| TMG-TA-TMG | 0.559 | 0.508 | 0.460 | 0.443 | 0.407 |

[a] Temperature of reaction 300 °C; PET/PBT = 40/60 mole ratio.

sequence distributions of several transesterification products between PET and PBT were analyzed by $^1$H NMR and $^{13}$C NMR. On the basis of the observed relative peak intensity, triad molar fractions centered on glycol units are determined by $^1$H NMR as summarized in Table 1. Similarly, the dyad molar fractions centered on terephthalic units determined by $^{13}$C NMR are summarized in Table 2. With these data, the number-average sequence lengths of PET and PBT residues, $L_E$ and $L_B$, respectively, were calculated. Here, a PET residue is denoted by a subscript E and a PBT residue by a subscript B. The number-average sequence lengths of the triad and dyad sequences were calculated according to the following equations:[14]

triad analysis

$$L_E = (F_{BEB} + F_{BEE} + F_{EEE})/(F_{BEB} + F_{BEE}/2) \quad (1)$$

$$L_B = (F_{EBE} + F_{BBE} + F_{BBB})/(F_{EBE} + F_{BBE}/2) \quad (2)$$

dyad analysis

$$L_E = (F_{EE} + F_{EB}/2)/(F_{EB}/2) \quad (3)$$

$$L_B = (F_{BB} + F_{EB}/2)/(F_{EB}/2) \quad (4)$$

where $F_i$ is the molar fraction of the sequence. As shown in Figure 7, the number-average sequence lengths, $L_E$ and $L_B$, calculated from the triad sequences by $^1$H NMR were in good agreement with those from the dyad sequences by $^{13}$C NMR.

A random copolycondensate (the degree of randomness equals 1) means that the structural unit distribution obeys Bernoullian statistics. Newmark et al.[15] proposed this Bernoullian behavior according to their finding with $^{13}$C NMR on the random copolymer of PET and PBT. To check whether the triad level sequence information obtained by $^1$H NMR for the copolymer elucidated in this paper is controlled according to Bernoullian statistics, the degrees of randomness ($R$) were calculated with the following equation:[15]

$$R = 1/L_E + 1/L_B \quad (5)$$

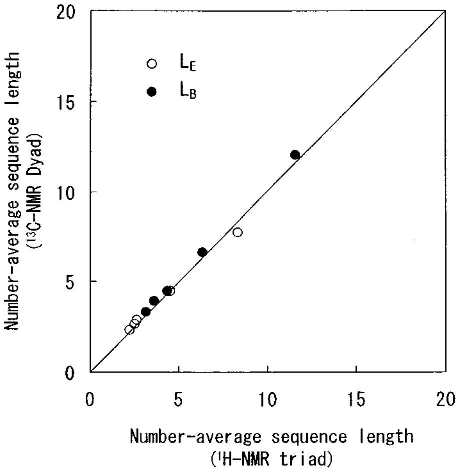

**Figure 7.** Comparison of the number-average sequence lengths of PET units ($L_E$) and PBT units ($L_B$) calculated from the triad sequences obtained from$^1$H NMR and dyad sequences obtained from $^{13}$C NMR for several poly(ethylene/butylene terephthalate) copolymers with different sequences of the comonomer.

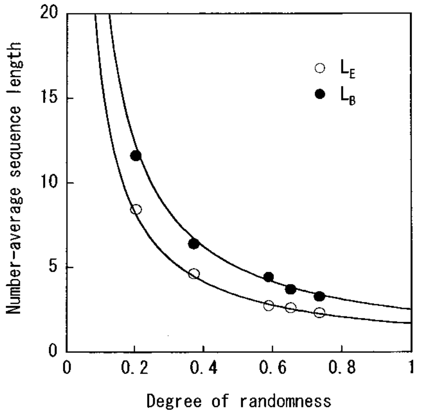

**Figure 8.** Number-average sequence length of PET units ($L_E$) and PBT units ($L_B$) as a function of degree of randomness ($R$) for a PET/PBT = 40/60 blends. Solid lines indicate the theoretical curves based on Bernoullian statistics for several poly(ethylene/butylene terephthalate) copolymers with different sequences of the comonomer.

where $L_E$ and $L_B$ are the number-average sequence lengths evaluated from eqs 1 and 2, respectively. The number-average sequence lengths vs the degrees of randomness are plotted in Figure 8. The solid lines represent the theoretical curves calculated according to the following equations by Bernoullian statistics:[15]

$$L_E = 1/(F_B R) \quad (6)$$

$$L_B = 1/(F_E R) \quad (7)$$

where $F_B = 0.60$ and $F_E = 0.40$ are the molar fractions of tetramethylene glycol unit and ethylene glycol unit in the copolymer, respectively. As shown in Figure 8, the observed data obtained by $^1$H NMR are in good agreement with the theoretical curve. Therefore, it was confirmed that the structural unit distribution of the copolymer obeys Bernoullian statistics from the triad level sequence information.

Only the dyad sequence analyses have been reported previously with $^{13}$C NMR for this copolymer or the transesterification products from PET with PBT.[15–17] The reason for the use of the $^{13}$C NMR method is to overcome the overlapping from terephthalic peaks in the $^1$H NMR spectrum. Therefore, the terephthalic peaks have been used for only the dyad sequence analysis (T-E-T-E-T, T-E-T-B-T, T-B-T-B-T equal to E-T-E, E-T-B, B-T-B, respectively, where T is terephthalic unit, E is ethylene glycol unit, and B is tetramethylene glycol unit). However, it is well-known that any mechanism can be fitted but none can be tested from dyad information alone, and a Bernoulli model can be tested from triad information.[15] Besides, Jacques et al.[16] have pointed out the limitations of the $^{13}$C NMR method for the precise quantitative determination of small transesterification levels, because of the low signal/noise ratio. Crystallization[18,19] or reactive processing with the catalyst[20] has been studied for blends of PET and PBT. Misra et al.[19] have investigated that PET−PBT block copolymers exhibit a considerably higher rate of crystallization than the corresponding random copolymers and emphasized the necessity of the investigation of the relationship between the crystallization behavior and the monomer sequences. For such a detailed analysis of the relationship between the microstructures and the physical properties, the triad sequence level information by $^1$H NMR will be also useful.

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