Longer Range Sequence Analysis of Four-Component Copolyester Using NMR

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ABSTRACT: Pentad-level sequence analysis of a copolyester derived from two diacids and two diols, poly(ethylene/trimethylene terephthalate/2,6-naphthalate), which was prepared by transesterification between poly(ethylene terephthalate) and poly(trimethylene 2,6-naphthalate), was reported in a solvent system of *o*-chlorophenol/deuterated chloroform mixture (75/25 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. Many peaks were split into the pentad sequence centered on the glycol units and could be assigned by a comparison of the spectra of the model copolymers and by a two-dimensional heteronuclear multiple bond correlation observation. The pentad sequences determined here gave more detailed information on the change in the molar fractions of the sequences with increasing the transesterification reaction time. The discrimination among the different copolymerization state was performed on the basis of the pentad sequence analysis. Furthermore, the larger percentage of transesterification of the polymers was obtained than the value determined from the triad level analysis.

Introduction

A large number of sequence analyses have been reported using nuclear magnetic resonance (NMR)[1−4] because the microstructures of copolymers are important in connection with the physical properties. The copolyesters can be classified according to the nature and number of acidic and diolic components. For examples, copolyesters derived from one diacid (usually terephthalic acid) and two diols (1/2 copolyester)[5−9] or two diacids and one diol (usually ethylene glycol or tetramethylene glycol) (2/1 copolyester)[10−16] have been well examined by NMR because the sequence variation of these copolyesters is comparatively simple. Whereas in the case of copolyesters derived from two diacids and two diols (2/2 copolyester), sequence variation becomes very complex. There are three possible triad sequences centered on the diolic component in 2/1 copolyester (A1-B-A1, A1-B-A2, and A2-B-A2, where A1 and A2 indicate the diacidic components and B the diolic component). On the other hand, there are six triad sequences centered on the diolic components in 2/2 copolyester (A1-B1-A1, A1-B1-A2, A2-B1-A2, A1-B2-A1, A1-B2-A2, and A2-B2-A2, where B1 and B2 indicate the diolic components). Recently, many complex copolyesters such as 2/2 copolyester have been developed as higher performance polyesters. Only a few sequence analyses of 2/2 copolyesters, however, have been reported, and most of them were dyad or triad level analyses using mainly ^{13}C NMR because of the limited peak splitting in the NMR spectra.[17−20]

Recent development of NMR apparatus and its technique, however, makes possible to obtain the detailed sequence information for the complex copolymers. In our previous paper, we reported the longer sequence analyses centered on glycol units of copolyesters, poly(ethylene/tetramethylene terephthalate)[21] and poly(ethylene/1,4-cyclohexanedimethylene terephthalate),[22] derived from the one acidic and two diolic components (1/2 copolyester), which was performed by careful selection of the NMR solvent and temperature and by use of high field instrument (600 MHz ^{1}H NMR).

In this paper, we will report the pentad sequence analysis of a copolyester derived from two diacids and two diols (2/2 copolyester), poly(ethylene/trimethylene terephthalate/2,6-naphthalate) copolymer, that was obtained by transesterification between poly(ethylene terephthalate) (PET) and poly(trimethylene 2,6-naphthalate) (PTN). PTN[23] as well as poly(trimethylene terephthalate) (PTT) is a remarkable polyester based on the development of the commercial procedure of trimethylene glycol monomer. Remarkable many peak splitting in the ^{1}H NMR spectrum of the 2/2 copolyester was observed due to the ring current effect from the aromatic ring of *o*-chlorophenol used as a solvent, and therefore the sequence analysis of the 2/2 copolyester was performed in pentad level. On the basis of sequence analysis, the merits of the longer sequence analysis for the copolyester derived from two diacids and two diols will be pointed out.

Experimental Section

Polymer Preparation. Poly(ethylene terephthalate) (PET), poly(ethylene 2,6-naphthalate) (PEN), poly(trimethylene terephthalate) (PTT), and poly(trimethylene 2,6-naphthalate) (PTN) were synthesized by melt polycondensation. Poly(ethylene terephthalate/2,6-naphthalate) (p(E//T/N)), the molar ratio of terephthalic unit/2,6-naphthalate unit is ca. 50/50 mol %, was also synthesized. The blend of PET and PTN, of which the polymer ratio was ca. 50/50 mol %, was prepared by dissolving two polymers in hexafluoro-2-propanol and then pouring them into a large excess of acetone. The precipitated polymer was filtered and dried under vacuum at 50 °C for 24 h. The blends of PET and PTT, PEN and PTN, PTT and PTN, and PET and PEN, of which the polymer ratio were ca. 50/50 mol %, respectively, were also prepared. The blend of p(E//T/N) and PTN was also prepared as ca. 50/50 wt % mixture. The p(E/G//T), p(E/G//N), p(E//T/N), p(G//T/N), and p(E/G//T/N) copolymers, where G indicates the trimethylene glycol unit, were obtained by the transesterification (following heat treatment) between PET and PTT, PEN and PTN, PET and PEN, PTT and PTN, and PET and PTN, respectively.

Transesterification Products. Heat treatment of the blend of PET and PTN (molar ratio ca. 50/50 mol %) was

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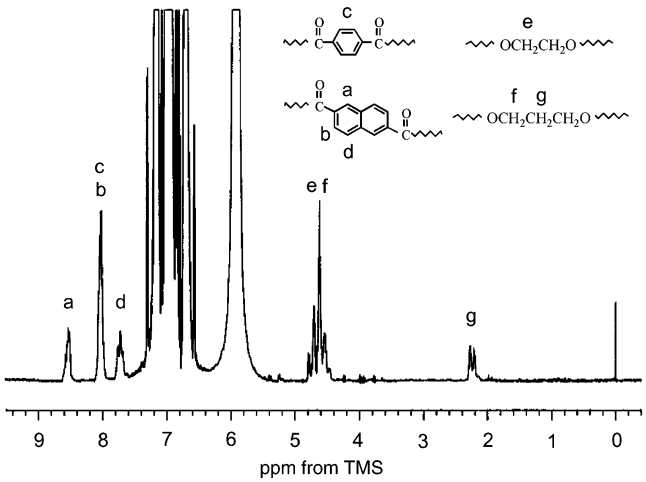

Figure 1. ^{1}H NMR (600 MHz) spectrum of the transesterification products between poly(ethylene terephthalate) and poly(trimethylene 2,6-naphthalate). The solvent is a 75/25 (v/v) mixture of *o*-chlorophenol/deuterated chloroform. The spectrum for sequence analysis was observed by homospin decoupling of the nonalcoholic CH_2 proton, g, of the trimethylene glycol unit.

performed on a TA Instruments 2920 differential scanning calorimeter under a dry nitrogen atmosphere. Samples were heated from room temperature to 310 °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 blends of PET and PTT, PEN and PTN, and PTT and PTN, p(E//T/N) and PTN were also performed.

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 (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. Homo-spin-decoupled spectra were obtained by decoupling of the nonalcoholic CH_2 protons of the trimethylene 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 heteronuclear multiple bond correlation (HMBC) spectrum was obtained with a delay time τ = 100 ms calculated for $^3J_{H-C}$ = 5 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 1.88 and 1.28 kHz, respectively. The digital resolution of the spectrum was 0.92 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 the transesterification products between PET and PTN 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 trimethylene glycol units. Figure 1 shows the spectrum in 75/25 (v/v) mixture of *o*-chlorophenol/deuterated chloroform mixture at 80 °C together with the assignment. The expanded spectra of the alcoholic CH_2 proton region are

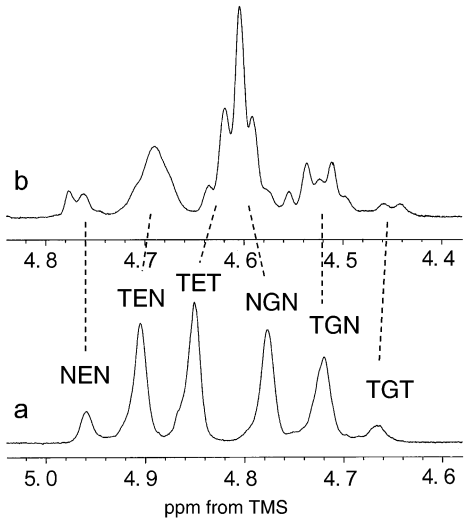

Figure 2. Expanded 600 MHz ^{1}H NMR spectra (the alcoholic CH_2 proton region) of the transesterification products between poly(ethylene terephthalate) and poly(trimethylene 2,6-naphthalate). The solvent systems are (a) a 50/50 (v/v) mixture of deuterated trifluoroacetic acid/deuterated chloroform at room temperature and (b) a 75/25 (v/v) mixture of *o*-chlorophenol/deuterated chloroform at 80 °C. The spectra were obtained under homospin decoupling of the nonalcoholic CH_2 protons of trimethylene glycol units.

shown in Figure 2. Six peaks of the alcoholic CH_2 protons were observed in 50/50 (v/v) mixture of deuterated trifluoroacetic acid/deuterated chloroform at room temperature (Figure 2a). These peaks are considered the signals reflecting triad sequences centered on the glycol units (N-E-N, T-E-N, T-E-T, N-G-N, T-G-N, and T-G-T). However, a further remarkable splitting was observed in 75/25 (v/v) mixture of *o*-chlorophenol/deuterated chloroform at 80 °C, as shown in Figure 2b. This is likely due to the ring current effect from the aromatic ring of *o*-chlorophenol as described in our previous papers,[21,22] and these peaks are considered the signals reflecting the more long-range sequences than the triad sequences mentioned above. 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.

Assignment of the ^{1}H NMR Spectra by Model Copolymers. In Figure 2b, more than 17 peaks can be observed, reflecting the pentad sequences in the chain. There are 20 possible pentad sequences centered on the glycol units of poly(ethylene/trimethylene terephthalate/2,6-naphthalate) copolymer, as shown in Figure 3. In the case of the copolyesters derived from two diols and two diacids, the sequence of B-A-B-A-B is a pentad, where A is acidic units and B is glycol units. However, in the case of the copolyesters derived from two diols and one diacid, it is triad on the glycol units. In our previous paper,[21] it was found that the glycol unit peaks of the copolyester derived from two diols and one diacid, PET/PBT copolyester, were split into the pentad sequences on the glycol units in *o*-chlorophenol/deuterated chloroform mixture at 80 °C. Therefore, for the precise assignment of the separated peaks in Figure 2b, we applied some model copolymers derived from two diols and one diacid. For example, the glycol unit peaks of the transesterification product between PET and PTT are expected to split into the pentad sequences, E-T-E-T-E, E-T-E-T-G, and G-T-E-T-G, centered on ethylene

1	E - T - E - T - E (PET)	11	G - N - G - N - G (PTN)
2	E - T - E - T - G	12	E - N - G - N - G
3	G - T - E - T - G	13	E - N - G - N - E
4	E - T - E - N - E	14	G - T - G - N - G
5	E - T - E - N - G	15	E - T - G - N - G
6	G - T - E - N - E	16	G - T - G - N - E
7	G - T - E - N - G	17	E - T - G - N - E
8	E - N - E - N - E	18	G - T - G - T - G
9	E - N - E - N - G	19	E - T - G - T - G
10	G - N - E - N - G	20	E - T - G - T - E

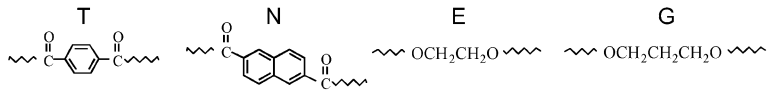

Figure 3. Possible pentad sequences centered on the glycol units of poly(ethylene/trimethylene terephthalate/2,6-naphthalate) copolymer.

glycol unit, and G-T-G-T-G, E-T-G-T-G, and E-T-G-T-E, centered on trimethylene glycol unit, where T is the terephthalic unit, E is the ethylene glycol unit, and G is the trimethylene glycol unit. These six pentad sequences are present in the possible 20 pentad sequences shown in Figure 3. Therefore, it is possible to assign the peaks to six pentad sequences by comparing the peak positions in the ^{1}H NMR spectrum between PET/PTN and PET/PTT copolymers. For the assignment of the separated peaks in Figure 2b, the transesterification products between PET and PTT, PEN and PTN, derived from two diols and one diacid, respectively, were prepared. As shown in Figure 4b,c, three peaks of the ethylene glycolic CH_2 protons and three peaks of the trimethylene glycolic CH_2 protons were observed in a 75/25 (v/v) mixture of *o*-chlorophenol/deuterated chloroform mixture at 80 °C for the transesterification products between PET and PTT, PEN and PTN, respectively. By reference of the spectra of homopolymers, the change in the peak intensity for the transesterification reactin time, and the analysis of two-dimensional HMBC spectrum as well as our previous assignment,[21] these peaks in Figure 4b,c were clearly assigned to the protons numbered by 1, 2, 3, 18, 19, and 20 in Figure 3 for the PET/PTT copolymer and 8, 9, 10, 11, 12, and 13 in Figure 3 for the PEN/PTN copolymer, respectively. The example of the pentad sequence assignment of the transesterification products between PET and PTT is shown in Figure 5, and the assignment was performed easily by the change in the peak intensity for the reaction time.

Similarly to the precise assignment of the separated peaks in Figure 2b, the model copolymer prepared by the transesterification between PTT and PTN, derived from one diol and two diacids, were also used. As shown in Figure 3d, four peaks of the alcoholic CH_2 protons were observed and assigned to the protons numbered by 11, 14, and 18 in Figure 3. Two peaks were observed for 14 in Figure 3 reflecting the unsymmetrical pentad sequence.

By comparison of peak position among Figure 4a and Figures 4b−d, the peaks of the transesterification product of PET/PTN were assigned as shown in Figure 4a. Here, the small differences in the chemical shifts of the each peak were observed between Figure 4a and

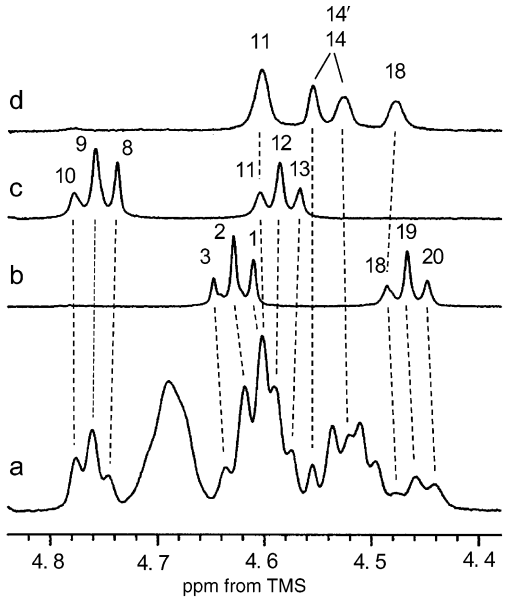

Figure 4. Assignment of the alcoholic CH_2 proton peaks of glycol units in the transesterification products between poly(ethylene terephthalate) and poly(trimethylene 2,6-naphthalate) using the model copolymer. Transesterification product between (a) poly(ethylene terephthalate) and poly(trimethylene 2,6-terephthalate), (b) poly(ethylene terephthalate) and poly(trimethylene terephthalate), (c) poly(ethylene 2,6-naphthalate) and poly(trimethylene 2,6-naphthalate), and (d) poly(trimethylene terephthalate) and poly(trimethylene 2,6-naphthalate). The ratio of the polymer blend was 50/50 mol %. Transesterification was performed for 120 min at 310 °C. The solvent systems are a 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 trimethylene glycol units.

Figures 4b−d. This is considered due to the influence of longer range sequences than pentad. For example, G-T-G-T-G (pentad) is equal to T-G-T-G-T-G-T (heptad) for the central trimethylene glycol unit G in PTT homopolymer. However, in PET/PTT copolymer, there are three heptad sequences, T-G-T-G-T-G-T, T-G-T-G-T-G-N, and N-G-T-G-T-G-N, for the G-T-G-T-G segment. This results in the change of the peak top and broadening of the peak of G-T-G-T-G. Indeed, in Figure 4a,

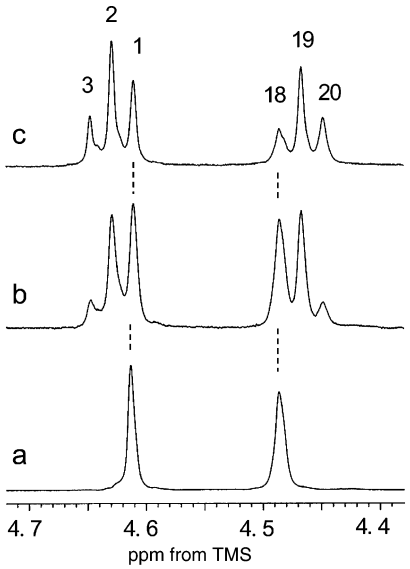

Figure 5. Expanded 600 MHz ^{1}H NMR spectra (the alcoholic CH_2 proton region) of the transesterification products between poly(ethylene terephthalate) and poly(trimethylene terephthalate). The solvent systems are 75/25 (v/v) mixture of *o*-chlorophenol/deuterated chloroform at 80 °C. Transesterification was performed (a) 0, (b) 30, and (c) 120 min at 310 °C. The spectra were obtained under homospin decoupling of the nonalcoholic CH_2 protons of trimethylene glycol units.

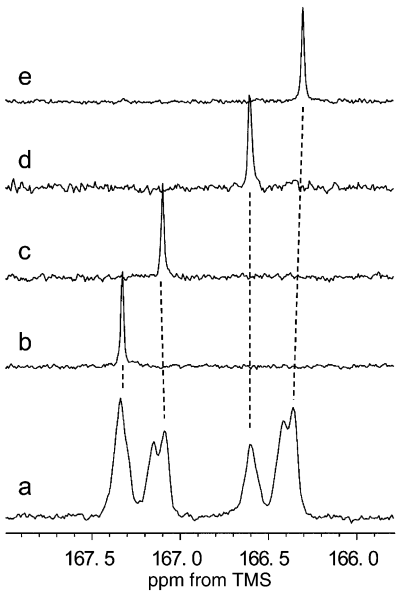

Figure 6. Expanded 150 MHz ^{13}C NMR spectra (the carbonyl carbon region) of (a) the transesterification products of poly(ethylene terephthalate) and poly(trimethylene 2,6-naphthalate), (b) poly(ethylene terephthalate), (c) poly(trimethylene terephthalate), (d) poly(ethylene 2,6-naphthalate), and (e) poly(trimethylene 2,6-naphthalate) in 75/25 (v/v) mixture of *o*-chlorophenol/deuterated chloroform at 80 °C.

broadenings of the peaks were observed in addition to the changes of the peak tops.

The 150 MHz ^{13}C NMR spectrum of the transesterification products between PET and PTN was measured in the *o*-chlorophenol/deuterated chloroform mixture as in the case of ^{1}H NMR. Although ^{13}C NMR is generally superior to ^{1}H NMR in viewpoint of the peak separation because of its inherent wide chemical shift range, the peak separation of the carbonyl carbons reflecting long-range sequence was inferior to the ^{1}H NMR when there are large ring current effect of the solvent, *o*-chlorophenol, as shown in Figure 6. It was considered that the carbonyl peaks were separated in mostly triad level, E-T-E, E-T-G, G-T-G, E-N-E, E−N-G, and G-N-G, by comparing the peak position of the spectra of homopolymers.

Two-Dimensional Heteronuclear Multiple Bond Correlation (HMBC) Spectrum. For further assignment and confirmation of the above assignment, the HMBC spectrum was observed, as shown in Figure 7. The cross-peaks were observed between the alcoholic CH_2 protons of the glycol units and the carbonyl carbons of the terephthalic and 2,6-naphthalic units through $^3J_{H-C}$ coupling. The cross-peak A originates from N-E-N triad sequences. Similarly, the cross-peaks B, C, D, E, and F originate T-E-N, T-E-T, N-G-N, T-G-N, and T-G-T triad sequences, respectively. Important information concerning the unsymmetrical triad sequences was obtained from the HMBC spectrum. In this copolymer, there are four pentad sequences centered on trimethylene glycol unit, as shown in Figure 7. Although the clear distinction between the protons 14 and 14′ was not established in the one-dimensional ^{1}H NMR spectrum (Figure 4d), it was established by the HMBC spectrum, as shown in Figure 7. That is, the protons 14 and 14′ were assigned by the cross-peaks between the proton peak 14 and the carbonyl carbon peak (A) and between the proton peak 14′ and carbonyl carbon peak (A*), respectively. Similarly, the protons 15 and 15′ were also assigned by the cross-peaks between the proton peak 15 and carbonyl carbon peak (B) and between the proton peak 15′ and carbonyl carbon peak (B*), respectively. Here, the distinction between the protons 14 and 15, and between the protons 14′ and 15′, was performed by the ^{1}H NMR spectrum of the initial product of the transesterification between PET and PTN (Figure 8). The pentad sequence E-T-G-N-G is formed earlier than G-T-G-N-G by the transesterification reaction between PET and PTN. Therefore, the peaks observed at 4.51 and 4.54 ppm in the ^{1}H NMR spectrum (Figure 8b) of the product by heat treatment of the blend of PET and PTN at 310 °C for 10 min were assigned to the peaks 15 and 15′, respectively, and not the peaks 14 and 14′. On the other hand, distinction between the protons 16 and 17, and between the protons 16′ and 17′, could not be performed because of the overlapping of the proton peaks, as shown in Figure 7. Similarly, the broad peaks from ca. 4.65 ppm to ca. 4.73 ppm could not be assigned to the detailed pentad sequences because of the peak overlapping. The assignment of ^{1}H NMR peaks of the PET/PTN copolymer is summarized in Figure 9.

Total correlation spectroscopy (TOCSY) is also considered to be useful for the assignment of the unsymmetrical sequences. Therefore, we tried the TOCSY experiment, but the well-resolved cross-peaks among the alcoholic CH_2 protons of the glycol units could not be obtained. Thus, a further analysis using TOCSY spectrum was not included in this paper.

Analysis of Sequence Distribution. To obtain the pentad sequence information, several transesrerification products between PET and PTN at 310 °C were measured by ^{1}H NMR, as shown in Figure 8. The pentad molar fractions centered on glycol units were determined on the basis of the observed relative peak area. Figure 10 shows the comparison between the pentad and triad sequences. In the case of the triad sequence information, TET and NGN sequences simply decrease

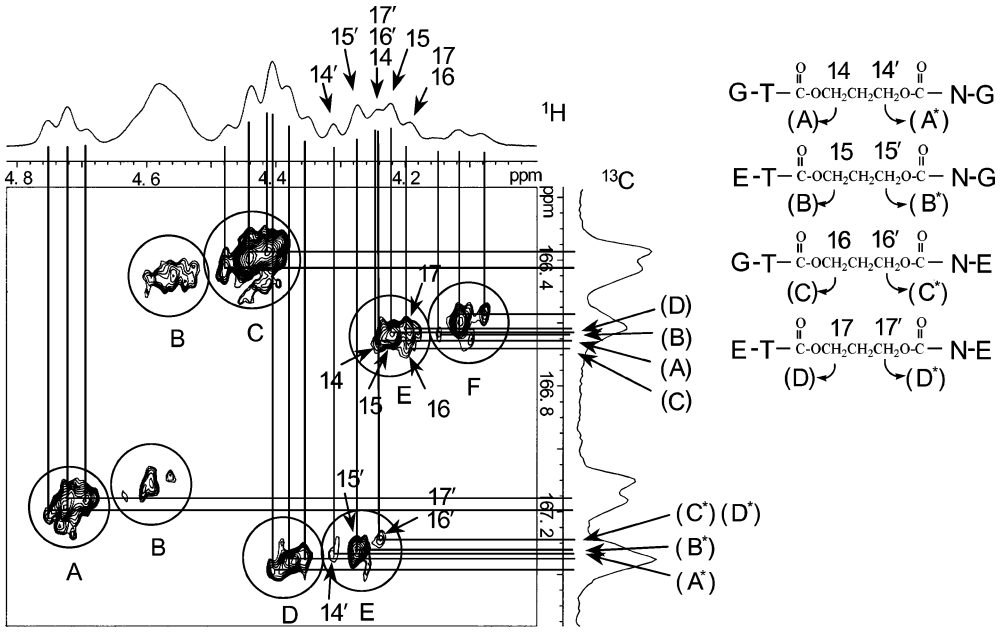

Figure 7. ^{1}H−^{13}C HMBC spectrum of the transesterification product of poly(ethylene terephthalate) and poly(trimethylene 2,6-naphthalate) together with the possible unsymmetrical pentad sequences centered on the trimethylene glycol unit. The delay time was $\tau = 100$ ms. The time domain signals consisted of 256 t_1 slices, each with 1024 data points. In t_2 and t_1 dimensions the sweep width was ca. 1.88 kHz and ca. 1.28 kHz, respectively. The digital resolution of the spectrum was 0.92 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.

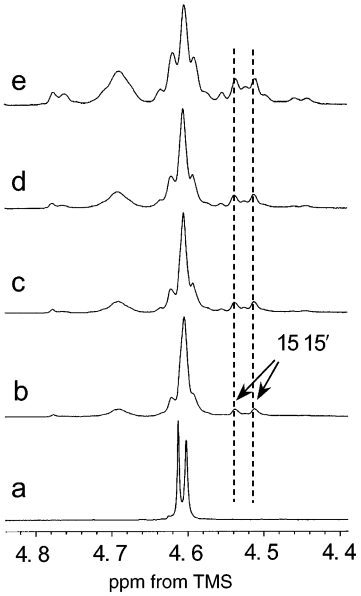

Figure 8. Spectra of the transesterification products of poly(ethylene terephthalate) and poly(trimethylene 2,6-naphthalate); the blend ratio was 50/50 mol %. Transesterification was performed (a) 0, (b) 10, (c) 20, (d) 30, and (e) 45 min at 310 °C.

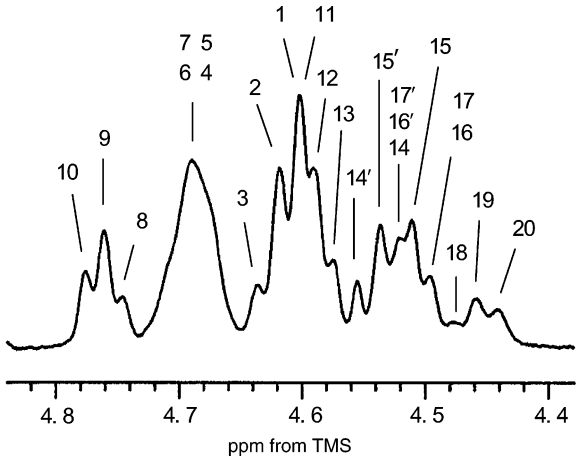

Figure 9. Assignment of the alcoholic CH_2 proton peaks of the transesterification products of poly(ethylene terephthalate) and poly(trimethylene 2,6-naphthalate).

with increasing the transesterification reaction time. However, the pentad sequences can give more detailed information. That is, the molar fractions of the sequences of ETETG and ENGNG increase at the first stage of the transesterification reaction time and decrease at the latter stage. This is the reason that these sequences react and change to GTETG, ENGNE, and the other pentad sequences with increasing the transesterification reaction time.

So far, a number of the sequence analyses of copolyesters have been performed by NMR. Most of those, however, were copolyesters derived from one diacid and two diols, or two acids and one diol, because of lack of the peak separation and complexity of the sequences in the case of copolyesters derived from two diacids and two diols. Only a few sequence analyses of copolyesters derived from two diacids and two diols have been reported. Most of those were the copolyesters derived from one aromatic and one aliphatic diacid, that is, copolyesters derived from terephthalic acid, adipic acid, ethylene glycol, 1,6-hexanediol, etc.,[17] copolyesters derived from terephthalic acid, azelaic acid, ethylene glycol, and 1,4-butanediol,[19] and copolyesters derived from isophthalic acid, adipic acid, neopentyl glycol, and trimethyrolpropane.[20] It is considered that those copolyesters are superior to the copolyesters derived from two aromatic diacids in our present paper for the peak separation because of more heterogeneity on the acidic residues. Therefore, Russell et al.[19] pointed out the possibility of the pentad sequence analysis by ^{13}C NMR. However, analyses of only the dyad sequences, A-B, or triad sequences centered on glycol units, A-B-A, or centered on acidic units, B-A-B, where A is the acidic unit and B is the glycol unit, have been mainly inves-

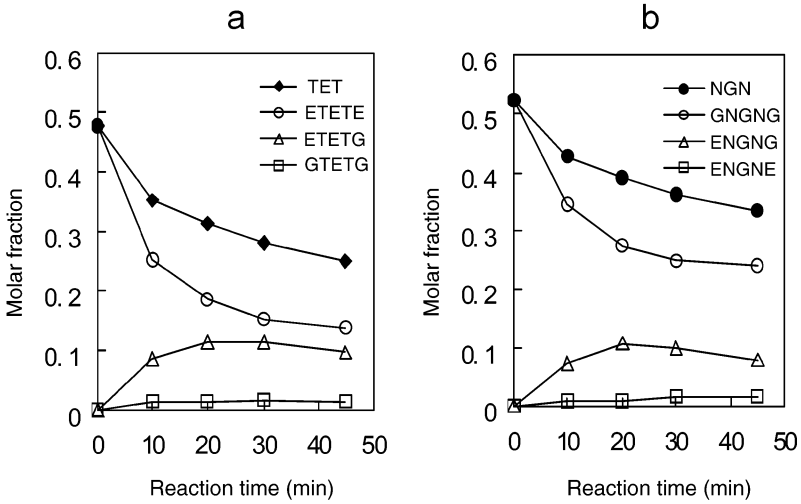

Figure 10. Change of the triad sequences (TET, NGN) and pentad sequences (ETETE, ETETG, GTETG, GNGNG, ENGNG, and ENGNE) centered on (a) ethylene glycol units and (b) trimethylene glycol units in the transesterification products of poly(ethylene terephthalate) and poly(trimethylene 2,6-naphthalate)in Figure 8.

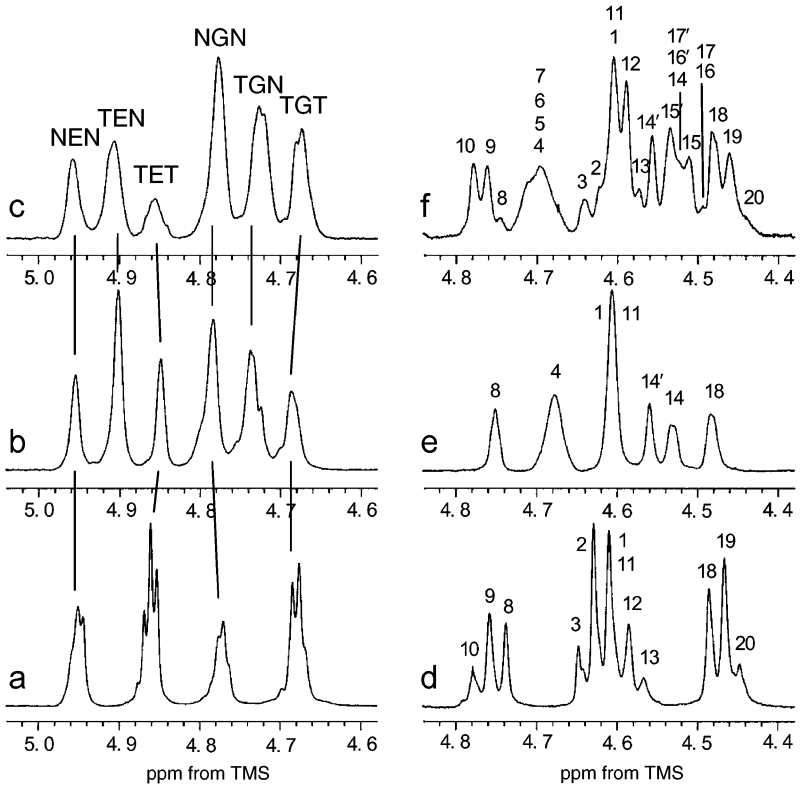

Figure 11. Comparison of the spectra of the alcoholic CH_2 proton region of (a) the blend of p(E/G//T) and p(E/G//N), (b) the blend of p(E//T/N) and p(G//T/N), and (c) p(E/G//T/N) copolymer, where T is the terephthalic unit, N is the 2,6-naphthalic unit, E is the ethylene glycol unit, and G is the trimethylene glycol unit. p(E/G//T), p(E/G//N), p(E//T/N), p(G//T/N), and p(E/G//T/N) were obtained by the transesterification between PET and PTT, PEN and PTN, PET and PEN, PTT and PTN, and PET and PTN, respectively. The solvent systems are (a−c) a 50/50 (v/v) mixture of deuterated trifluoroacetic acid/deuterated chloroform at room temperature and (d−f) a 75/25 (v/v) mixture of *o*-chlorophenol/deuterated chloroform at 80 °C.

tigated by ^{13}C NMR because of lack of the peak separation and complexity of the sequences. For copolyester derived from terephthalic acid, succinic acid, ethylene glycol, and poly(ethylene glycol), Maeda et al.[24] have reported the sequence analysis by ^{1}H NMR. However, only dyad or triad sequences have been reported. Also in the case of copolyamides derived from two diacids and two diamines,[25,26] it has been performed by dyad level using ^{13}C NMR.

Merits of Longer Range Sequence Information. We will point out the merits of longer sequence analysis in addition to the example shown in Figure 10. ^{1}H NMR spectra of the E/G//T/N copolymer, the blend of the E//T/N copolymer and the G//T/N copolymer, and the blend of the E/G//T copolymer and the E/G//N 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 trimethylene glycol units. Here, T indicates terephthalic unit, N indicates 2,6-naphthalic unit, E indicates ethylene glycol unit, and G indicates trimethylene glycol unit. As shown in Figure

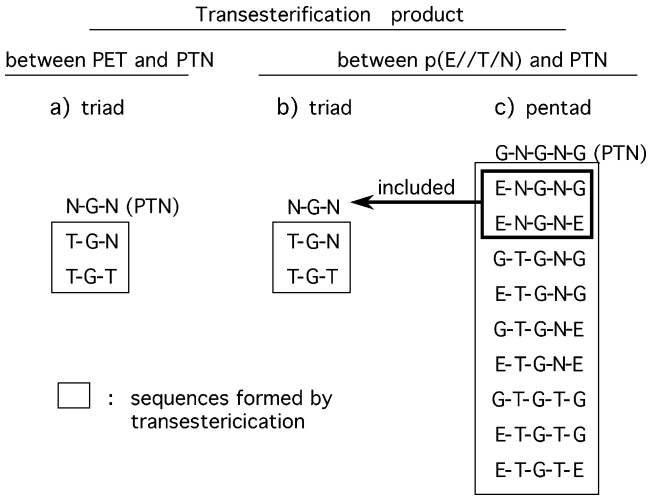

Figure 12. Comparison of the triad and pentad sequences centered on trimethylene glycol unit formed by transesterification between PET and PTN, p(E//T/N) and PTN.

11a−c, when a deuterated trifluoroacetic acid/deuterated chloroform mixture was used as solvent, the blend of the E/G//T copolymer and the E/G//N copolymer (Figure 11a) is possible to be distinguished from the other two polymers (Figure 11b,c) in the ^{1}H NMR spectrum. However, discrimination between the E/G//T/N copolymer (Figure 11c) and the blend of the E//T/N copolymer and the G//T/N copolymer (Figure 11b) is difficult as long as the use of deuterated trifluoroacetic acid/deuterated chloroform mixture as a solvent because these polymers have the same triad sequences centered on glycol units and provide the similar ^{1}H NMR spectra reflecting only the triad sequences. On the other hand, in the case of *o*-chlorophenol/deuterated chloroform mixture, discrimination among the three polymers is possible because these polymers have the different pentad sequences centered on the glycol units and provide the different ^{1}H NMR spectra reflecting the pentad sequences, as shown in Figure 11d−f. Thus, the longer sequence analysis provides the detailed information on the copolymerization.

We can determine the percentage of transesterification precisely as the merit of longer sequence analysis. In the case of the transesterification product between homo-PET and homo-PTN, the percentage of transesterification is able to be precisely evaluated by triad sequence analysis centered on the glycol units, as shown in Figure 12a. However, in the case of the transesterification product between poly(ethylene terephthalate/2,6-naphthalate), p(E//T/N), copolymer, and homo-PTN, the matter becomes different. The T-G-N and T-G-T sequences as the triad sequences centered on G unit are formed by the transesterification between the E-T sequence in p(E//T/N) and homo-PTN. These sequences are possible to be dealt with as Figure 12a. However, the N-G-N sequence as the triad sequence centered on the G unit, which is formed by the transesterification between the E-N sequence in p(E//T/N) and homo-PTN, is not able to be distinguished with the N-G-N sequence in homo-PTN because the peaks of these N-G-N sequences overlap with each other. Therefore, in the case of the triad sequence analysis, the percentage of transesterification will be evaluated smaller than the real value because of neglect of the amount of the N-G-N sequence formed by the transesterification. In the case of the pentad sequence analysis, however, N-G-N sequences formed the transesterification between the E-N sequence in the p(E//T/N) and homo-PTN are able to be distinguished as the E-N-G-N-G and E-N-G-N-E sequences. As described in the present paper, the ^{1}H NMR peaks of these pentad sequences are able to be observed by the use of *o*-chlorophenol/deuterated chloroform mixture. Therefore, the pentad sequence analysis is superior to the triad sequence analysis for the more precise evaluation of the percentage of transesterification (Figure 12b,c). Parts a and b of Figure 13 show the ^{1}H NMR spectra of the transesterification product between p(E//T/N), the molar ratio of E//T/N is 100//50/50, and homo-PTN at 300 °C for 120 min in deuterated trifluoroacetic acid/deuterated chloroform mixture and *o*-chlorophenol/deuterated chloroform mixture, respectively. The peak 1 reflecting the triad sequence N-G-N in Figure 13a is separated into the peaks 11, 12, and 13, reflecting the pentad sequence G-N-G-N-G, E-N-G-N-G, and E-N-G-N-E, respectively, in Figure 13b. The triad and pentad molar fractions in Figure 13a,b were determined on the basis of the observed relative peak area as shown in Tables 1 and 2. The percentage of transesterification (Φ) was calculated by the following equation:

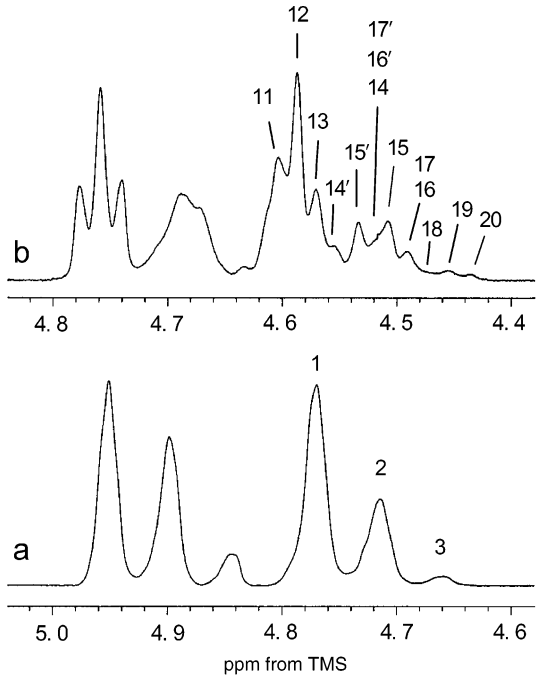

Figure 13. Comparison of the spectra of the alcoholic CH_2 proton region of the transesterification product between p(E//T/N), the molar ratio is 100//50/50, and PTN for 90 min at 300 °C. The blend ratio of p(E//T/N)/PTN was ca. 50/50 wt %, final molar ratio of T/N was 25.3/74.7, and E/G was 52.3/47.7. The solvent systems are (a) 50/50 (v/v) mixture of deuterated trifluoroacetic acid/deuterated chloroform at room temperature and (b) 75/25 (v/v) mixture of *o*-chlorophenol/deuterated chloroform at 80 °C.

$$\Phi = (F_{obs}/F_{random}) \times 100\ (\%) \qquad (1)$$

where F_{obs} indicates the sum of the observed molar fractions except the PTN sequence, and F_{random} indicates the sum of the theoretical molar fractions except the PTN sequence at completely random sequence. The percentage of transesterification obtained from the pentad sequence analysis (Figure 13b) was larger than that obtained from the triad sequence analysis (Figure

Table 1. Triad Fractions (*F*) and Percentage of Transesterification (Φ) Centered on Trimethylene Glycol Unit in the Transesterification Product between Poly(ethylene terephthalate/2,6-naphthalate) and Homo-Poly(trimethylene 2,6-naphthalate) Determined by ^{1}H NMR[a]

peak no.	dyad sequence	F_{obs}[b]		F_{random}[c]	Φ (%)
1	N-G-N	0.647		0.558	
2	T-T-N	0.311	0.353[d]	0.442[d]	79.9
3	T-G-T	0.042			

[a] Blend ratio: p(E//T/N)/PTN = ca. 50/50 wt % (molar ratio of E//T/N = 100//50/50 in p(E//T/N), final molar ratio: T/N = 25.3/74.7, E/G = 52.3/47.7), transesterification reaction: 300 °C, 90 min, solvent: *o*-chlorophenol/deuterated chloroform = 50/50 (v/v). [b] Observed molar fractions. [c] Theoretical molar fractions at completely random sequence. [d] Sum of molar fractions except PTN sequence.

Table 2. Pentad Fractions (*F*) and Percentage of Transesterification (Φ) Centered on Trimethylene Glycol Unit in the Transesterification Product between Poly(ethylene terephthalate/2,6-naphthalate) and Homo-Poly(trimethylene 2,6-naphthalate) Determined by ^{1}H NMR[a]

peak no.	triad sequence	F_{obs}[b]		F_{random}[c]	Φ (%)
11	G-N-G-N-G	0.194		0.115	
12	E-N-G-N-G	0.311			
13	E-N-G-N-E	0.142			
14	G-T-G-N-G	0.044			
15	E-T-G-N-G	0.079			
16	G-T-G-N-E	0.083	0.806[d]	0.885[d]	91.1
17	E-T-G-N-E	0.069			
18	G-T-G-T-G	0.043			
19	E-T-G-T-G	0.009			
20	E-T-G-T-E	0.007			

[a] Blend ratio: p(E//T/N)/PTN = ca. 50/50 wt% (molar ratio of E//T/N = 100//50/50 in p(E//T/N), final molar ratio: T/N = 25.3/74.7, E/G = 52.3/47.7), transesterification reaction: 300 °C, 90 min, solvent: *o*-chlorophenol/deuterated chloroform = 50/50 (v/v). [b] Observed molar fractions. [c] Theoretical molar fractions at completely random sequence. [d] Sum of molar fractions except PTN sequence.

13a). Thus, the percentage of transesterification obtained from the longer sequence analysis is larger than that obtained from the shorter range sequence analysis and becomes more close to the true value.

Conclusion

The well-resolved ^{1}H NMR spectrum of copolyester derived from two diacids and two diols, poly(ethylene/trimethylene terephthalate/2,6-naphthalate), was observed in *o*-chlorophenol/deuterated chloroform mixture (75/25 v/v) at 80 °C using 600 MHz NMR and could be assigned at the pentad level. The pentad sequence analysis provides more detailed information on the change in the molar fractions of the sequences with the transesterification reaction and on the copolymerization or blend state of the copolymers. Furthermore, the percentage of transesterification obtained from such a longer sequence analysis is larger than that obtained from the shorter range sequence analysis and becomes more close to the true value.

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References and Notes

(1) Bovey, F. A. *High-Resolution NMR of Macromolecules*; Academic Press: New York, 1972.
(2) Matsuzaki, K.; Uryu, T.; Asakura, T. *NMR Spectroscopy and Stereoregularity of Polymers*; Japan Scientific Societies Press: Tokyo, 1996.
(3) Herbert, I. R. Statistical analysis of copolymer sequence distribution. In *NMR Spectroscopy of Polymers*; Ibbett, R. N., Ed.; Blackie Academic & Professional: Glasgow, 1993.
(4) Fakirov, S. *Transreactions in Condensation Polymers*; Wiley-VCH: Germany, 1999.
(5) Newmark, R. A. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 559.
(6) Lee, S. C.; Yoon, K. H.; Park, I. H.; Kim, H. C.; Son, T. W. *Polymer* **1997**, *38*, 4831.
(7) Backson, S. C. E.; Kenwright, A. M.; Richards, R. W. *Polymer* **1995**, *36*, 1991.
(8) Jacques, B.; Devaux, J.; Legras, R.; Nield, E. *J. Polym. Sci., Polym. Chem. Ed.* **1996**, *34*, 1189.
(9) Kint, D. P. R.; Wigström, E.; Martínez de Ilarduya, A.; Alla, A.; Muñoz-Guerra, S. *J. Polym. Sci., Polym. Chem. Ed.* **2001**, *39*, 3250.
(10) Montaudo, G.; Montaudo, M. S.; Scamporrino, E.; Vitalini, D. *Macromolecules* **1992**, *25*, 5099.
(11) Spera, S.; Pó, R.; Abis, L. *Polymer* **1993**, *34*, 3380.
(12) Yoshie, N.; Inoue, Y.; Yoo, H. Y.; Okui, N. *Polymer* **1994**, *35*, 1931.
(13) Ha, W. S.; Chun, Y. K.; Jang, S. S.; Rhee, D. M.; Park, C. R. *J. Polym. Sci., Polym. Phys. Ed.* **1997**, *35*, 309.
(14) Kint, D. P. R.; Martínez de Ilarduya, A.; Muñoz-Guerra, S. *J. Polym. Sci., Polym. Chem. Ed.* **2000**, *38*, 1994.
(15) Kint, D. P. R.; Martínez de Ilarduya, A.; Muñoz-Guerra, S. *J. Polym. Sci., Polym. Chem. Ed.* **2000**, *38*, 3761.
(16) Kint, D. P. R.; Martínez de Ilarduya, A.; Muñoz-Guerra, S. *J. Polym. Sci., Polym. Chem. Ed.* **2001**, *39*, 1994.
(17) Kricheldorf, H. R. *Macromol. Chem.* **1978**, *179*, 2133.
(18) Henrichs, P. M.; Hewitt, J. M.; Russell, G. A.; Sandhu, M. A.; Grashof, H. R. *Macromolecules* **1981**, *14*, 1770.
(19) Russell, G. A.; Henrichs, P. M.; Hewitt, J. M.; Grashof, H. R.; Sandhu, M. A. *Macromolecules* **1981**, *14*, 1764.
(20) Hvilsted, S. *Macromol. Chem., Macromol. Symp.* **1991**, *52*, 199.
(21) Matsuda, H.; Asakura, T.; Miki, T. *Macromolecules* **2002**, *35*, 4664.
(22) Matsuda, H.; Nagasaka, B.; Asakura, T. *Polymer* **2003**, *44*, 4681.
(23) Stier, U.; Oppermann, W. *J. Polym. Sci., Polym. Chem. Ed.* **2001**, *39*, 620.
(24) Maeda, Y.; Maeda, T.; Yamaguchi, K.; Kubota, S.; Nakayama, A.; Kawasaki, N.; Yamamoto, N.; Aiba, S. *J. Polym. Sci., Polym. Chem. Ed.* **2000**, *38*, 4478.
(25) Aerdts, A. M.; Eersels, K. L. L.; Groeninckx, G. *Macromolecules* **1996**, *29*, 1041.
(26) Aerdts, A. M.; Eersels, K. L. L.; Groeninckx, G. *Macromolecules* **1996**, *29*, 1046.

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