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An NMR study on sequence distributions of block copolymers of poly(butylene terephthalate) and poly(tetramethylene glycol

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Summary

The analytical methods to characterize the exact chemical composition and sequence distributions of block copolymers of poly(butylene terephthalate) and poly(tetramethylene glycol) (PBT/ PTMG) were reinvestigated by NMR spectroscopy. To obtain accurate information, the choice of the solvents, NMR experimental conditions, ^{1}H and ^{13}C peak assignments and the methods of calculating various sequence parameters were closely examined. For phenol-d_6/tetrachloroethane(TCE) solutions of two copolymers having the hard segment (PBT) contents of 20 and 35wt.%, various sequence parameters were extracted from NMR spectra. In addition to that, we could accurately measure the actual number average molecular weight of PTMG segments within the copolymer by NMR. Measured average molecular weight of PTMG segments was used to calculate theoretical sequence distributions. The experimental and theoretical sequence parameters as well as chemical compositions were compared with each other.

Introduction

Block copolymers of poly(butylene terephthalate) and poly(tetramethylene glycol) (PBT/ PTMG) belong to thermoplastic elastomers. As in the case of other thermoplastic elastomers, PBT/PTMG consists of hard and soft segments. In these materials, it is well known that hard segments tend to form semicrystaline domains whereas soft segments play as the matrix of rubbery amorphous regions(1-3). Generally, the resulting morphology such as crystal size is crucial in the manifestation of the desired mechanical properties. Among the various factors that determine morphological properties, the importance of sequence distributions and resulting blokiness have been widely accepted(4-7). Of course, a major factor controlling sequence distributions is the chemical composition of the copolymer. The simple calculation using Bernoullian statistics can provide theoretical parameters relevant to sequence distributions including segment length at given hard segment contents(HSC). However, one can also expect that there are some variations in the sequence distributions owing to the different preparation and processing conditions. Moreover, the degradation of the constituents, such as PTMG can influence the microstructures of the polymers. Therefore, to correlate the chemical compositions and the properties of PBT/PTMG copolymers, it is essential to characterize the real microstructures of the copolymers.

In this study, PBT/PTMG copolymers with relatively low hard segment contents were

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closely characterized by NMR spectroscopy. The NMR studies of these copolymers have been previously reported by Higashiyama et al.(8). However, we found that the conventional method(8-10) adopted by them was inadequate for the detailed examination of the experimental results as pointed by other authors(9). In the present study, to overcome the limitations, a modified method was used with revised ^{1}H and ^{13}C NMR peak assignment and subsequent calculation.

To perform NMR study, one crucial factor was the choice of NMR solvent. In previous reports, NMR spectra of PBT/PTMG copolymers were measured in CDCl3 over relatively wide range of HSC. However, we found that $CDCl_3$ hardly or partly dissolve the samples with high HSC which may lead to misunderstanding real systems. In this study, phenol-d_6/TCE was chosen as the adequate solvent and relevant experiments were performed.

Experimental

Samples

The methods of synthesizing PBT/PTMG block copolymers have been reported elsewhere by several other authors(11-13). In a little detail, the two samples were prepared by two stages melt polymerization method including ester interchange and polycondensation reaction. The relative amounts of starting materials were adjusted for HSC of the polymer to be 20 and 35wt.% (sample 1 and 2). The prepared polymer was used without further purification. For starting materials, commercial grade dimethyl terephthalate(DMT), butanediol(BD) and PTMG-2,000 were purchased from SK Chemicals Co., GAF Corporation and E.I. duPont de Nemours & Co. respectively. The number average molecular weight($\overline{M}_n$) of poly(tetramethylene glycol)(PTMG) was claimed to be 2,000 by the maker and it could be confirmed by end-group analysis using acetic anhydride and successive titration with alcoholic KOH.

NMR experiments

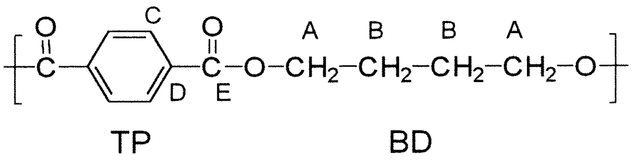
Bruker DRX-300 NMR spectrometer equipped with a temperature controller was utilized for all NMR experiments. All NMR experiments were made on the solution of which concentrations were adjusted to be 10wt.%. Phenol-d_6/TCE(50:50 in volume)(13, 15) were mainly used to collect NMR data. For comparison, $CDCl_3$ was also used. For the solution in phenol-d_6/TCE, the temperature was elevated up to 80°C during all the experiments for the purpose of good resolution. ^{1}H NMR experiments were conducted using 30° pulse with long relaxation delays more than 5 sec. ^{13}C NMR spectra were obtained under the condition of suppression of NOE with long relaxation delay(14 sec). Proton noise decoupling was applied during the acquisition (inverse gated decoupling). Pulse width of 8.0 μs and number of scans of about 10,000 were used for the ^{13}C NMR experiments. For the confirmation of molecular weight of starting PTMG, the same ^{13}C NMR experiments were performed and the intensities of NMR signals of terminal carbons were compared with the main signal of PTMG to evaluate $\overline{M}_n$. Then the results were compared with those from previous wet analysis. For the detailed evaluation of the accuracy of the method in this study, 5 independent NMR samples were prepared and the same experiments were performed for all the samples. To perform clear assignments of ^{1}H and ^{13}C NMR spectra, ^{1}H -^{1}H COSY, ^{1}H -^{13}C COSY(HETCOR) and other 2D experiments detecting ^{1}H and ^{13}C long-range couplings were conducted. For the last experiments, we used indirect experiment (HMBC) because of low sensitivity of long-range couplings in the polymers. To obtain 2D spectra with good digital resolution, narrow range spectral widths were used for both axes to result in FID resolution of 0.4 Hz for proton and 4 Hz for carbon.

Results and discussion

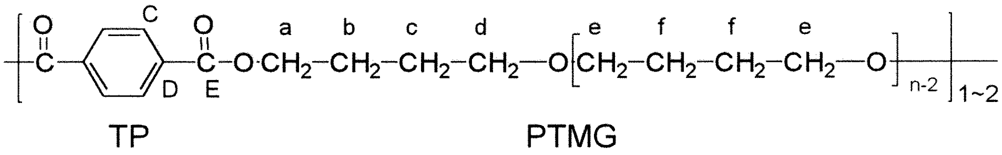
^{1}H *and* ^{13}C *NMR peak assignment*

Many works related to the characterizations of copolyesters have based on the assignment and analysis of NMR spectra(8, 12, 14, 15). Especially, for the investigation concerning the sequence distributions, several authors mainly used the four lines of phenyl quaternary carbons in terephthaloyl (TP) units(8-10). In the case of PBT/PTMG, Higashiyama et al. suggested that those four peaks are attributed for the quaternary carbons in four possible triads; BD-TP-BD, BD-TP-PTMG(BD site), PTMG-TP-BD(PTMG site), PTMG-TP-PTMG; abbreviated as BB, BP, PB and PP.

Hard Segment (PBT unit)



Soft Segment (TP- PTMG unit)



From the integration of four peaks of the quaternary carbons, they could extract the information relevant to the probability of four possible triads, though we found that there were some mistakes in the peak assignment and calculation of sequence lengths. For our samples, in the case of $CDCl_3$ solutions, we could find similar patterns of the spectrum as those in the previous paper(8). However, as previously stated, we mainly used phenol-d_6/TCE as the solvent because of lower solvating power of $CDCl_3$ for our samples. Unfortunately, in phenol-d_6/TCE, the resonance lines of those carbons split into only three (D in Figure 1). Of course, it is impossible to extract full information relevant to the probabilities of four possible triads from only three lines. We could overcome the difficulties by making use of additional resonance lines, such as phenyl proton and carbonyl carbon peaks that also split into three lines respectively(Figure 1). Actually, the comparison of the integral values of these nine peaks revealed that all these peaks had some relationship with triad probabilities or their linear combinations. Clearer assignment could be obtained through 2D HMBC spectra. In Figure 2-a, we presented 2D spectrum of sample 1 representing long-range couplings between phenyl protons and quaternary carbons. In that spectrum, four cross peaks are shown, which means that there are four different heteronuclear long-range couplings between phenyl protons and quaternary carbons. In that 2D spectrum, we can see that the middle peak of quaternary carbon shows two cross peaks with two outer peaks of the phenyl proton, and the middle peak of phenyl proton has also two cross peaks with two side peaks of quaternary carbons. Another 2D HMBC(Figure 2-b) spectrum shows the long-range couplings between phenyl protons and carbonyl carbons. Each line of three peaks of carbonyl carbons corresponds to

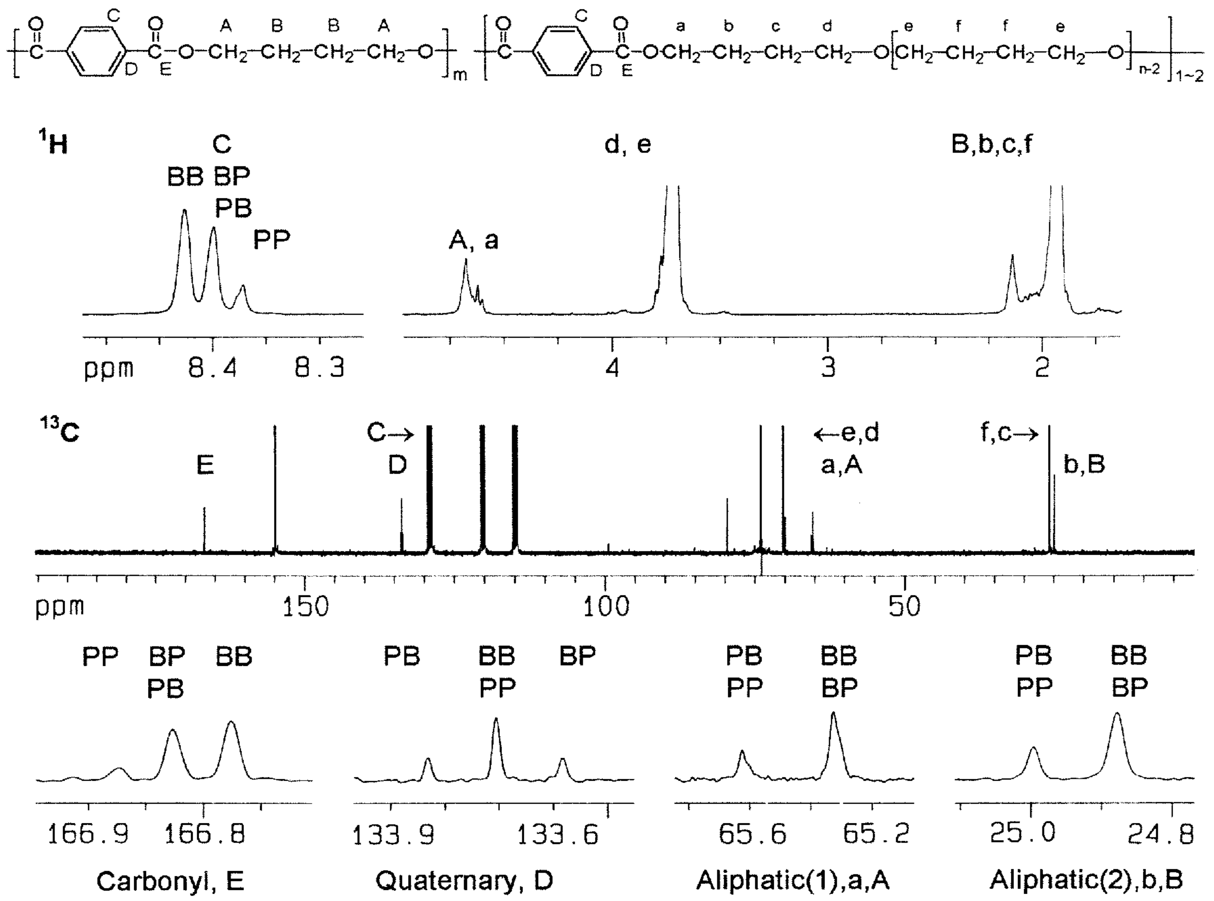


Figure 1. Peak assignment of ^{1}H and ^{13}C NMR spectra according to the chemical structure and microstructures of PBT/PTMG(sample 1).

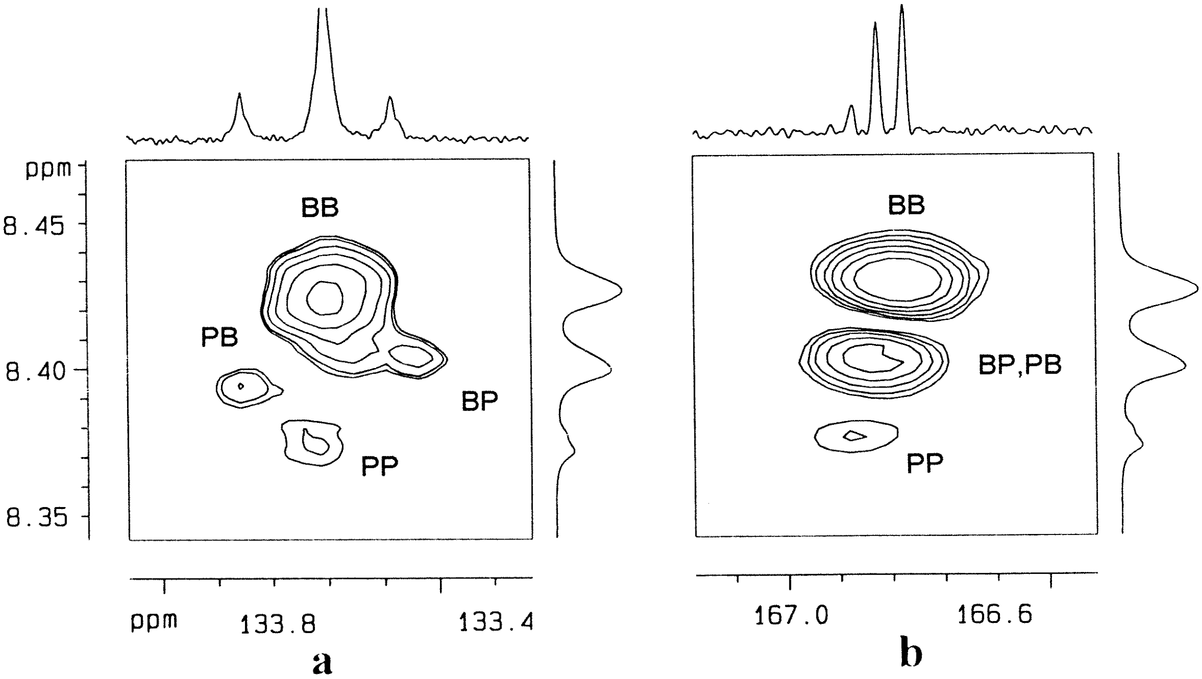


Figure 2. Selected regions of HMBC spectra of PBT/PTMG(coupling between a: phenyl proton and phenyl quaternary carbon, b: phenyl proton and carbonyl carbon).

each single line of phenyl protons, which means that the respective three lines of protons and carbons originate from the same microstructures of the polymer. Above results of 2D HMBC experiments and integral intensity analyses allow us assign above nine peaks as follows; for phenyl protons, left peak to BB, middle peak to BP and PB, right peak to PP; for quaternary carbon, left peak to PB, middle peak to BB and PP, right peak to BP; for carbonyl carbon, left peak to PP, middle peak to BP and PB, right peak to BB.

Besides above nine peaks in phenyl and carbonyl regions, the peaks in aliphatic region also gave us useful information associated with triad sequences. First, we focused overlapped small peaks beside main peaks in the aliphatic regions of ^{1}H NMR spectra. According to the close examinations of chemical shifts, coupling patterns and ^{1}H-^{1}H COSY spectra, the small peaks could be assigned to terminal tetramethylene group of PTMG that directly attached to the TP unit(a ~ d in the previous structure). Then, the analysis of ^{1}H-^{13}C COSY enabled us to assign easily the small peaks in aliphatic regions of ^{13}C NMR spectra. As a result, we could see that the carbon peaks at 65.62 and 25.00 ppm originated from terminal tetramethylene group of PTMG(a, b in previous structure) that had direct linkage to TP unit in the polymer chain. Therefore both the peaks could be considered to contain the combined information about two triad; PP and PB. Also, because the peaks at 65.33 and 24.88 ppm were attributed to the tetramethylene group of BD portion(A, B in the structure), both of them are considered to have sum of the information of two triads; BB and BP. The assignment of all the lines of split peaks corresponding to above 5 kinds of nuclei according to chemical structures and microstructures were summarized in Figure 1 and Table 1.

Extraction of probabilities of triads

As previously described, each NMR peak corresponding to the five kinds of nuclei that were assigned in the previous section has manifestly different aspects in the points of view of triad sequences. Therefore, it is very promising to use all these peaks to obtain the

Table 1. Assignment of ^{1}H and ^{13}C NMR spectra (from phenol-d$_6$/TCE solution of sample 1) according to probabilities of triad sequences and their linear combinations

^{1}H NMR peaks vs. triad sequences

Nuclei	Phenyl			Aliphatic(1)		Aliphatic(2)	
δ (ppm)	8.43	8.40	8.37	4.68	4.62	2.14	2.08
Structure [a]	BB	BP+PB	PP	BB+BP	PB+PP	BB+BP	PB+PP

^{13}C NMR peaks vs. triad sequences

Nuclei	Carbonyl			Phenyl quaternary			Aliphatic(1)		Aliphatic(2)	
δ (ppm)	166.87	166.83	166.78	133.83	133.71	133.58	65.62	65.33	25.00	24.88
Structure [a]	PP	BP+PB	BB	PB	BB+PP	BP	PB+PP	BB+BP	PB+PP	BB+BP

[a] Abbreviations, BB: BD-TP-BD, BP: BD-TP-PTMG, PB: PTMG-TP-BD, PP: PTMG-TP-PTMG.

information associated with the probabilities of four possible triad sequences. Of course, that method is more accurate than that of other authors (8 - 10) because we can use simultaneously five independent sets of experimental data. A simple FORTRAN 77 program that performs least square fitting through simplex algorithm was used to fit experimental data. First, the probabilities of four triads sequences were assumed and the intensities of NMR peaks were calculated, then the intensities of NMR peaks from experiments and calculations were compared. Simplex algorithm(in Numerical Recipe) automatically changed the values for probabilities of triads to minimize the sum of square of error ratio; $\Delta^2 = \Sigma[S(exp)-S(cal)]^2 /S(exp)^2$. The fitting was continued up to the point at which the error ratio did not vary at constant level. For our two samples, the calculated sum of square of error ratios were less than $1x10^{-4}$ for most experiments.

Calculation and comparison of sequence parameters

The main purpose of this study is to obtain the exact knowledge of the sequence distributions of PBT/PTMG that have two different chemical compositions. This may be partly attained by making use of interpretation of probabilities of triads sequences(Table 2). In addition to those ones, there are other parameters giving detailed microstructural information of the copolymers. From the probabilities of triad sequences, average sequence lengths of hard and soft segments can be calculated as follows; hard segment length, *HSL=([BB]+[BP])/[BP]*; soft segment length, *SSL=([PB]+[PP])/[PB]*, where [AB] is the probability of AB sequence. Because [BP] must be the same as [PB] assuming infinite chain, we used average values in real calculation for simplicity. Practically, the

Table 2. Observed and theoretical parameters of sequence distributions of two PBT/PTMG copolymers (using phenol-d_6/TCE as the solvent)

Samples		Probabilities of triad sequences(%)				Sequence length		$\overline{M}_n$[c] of PTMG	Segment molecular weight		HSC[f] (%)
		BB	BP	PB	PP	HSL[a]	SSL[b]		HMW[d]	SMW[e]	
1	Exp.[g]	48.7 (0.27)	21.1 (0.30)	19.8 (0.21)	10.4 (0.13)	3.38 (0.04)	1.50 (0.04)	1,888 (16)	744 (9)	3,054 (62)	19.60 (0.30)
	The.[h]	48.7	21.1	21.1	9.1	3.32	1.44	1,888	729	2,917	20.00
2	Exp.[g]	69.1 (0.22)	14.2 (0.21)	13.8 (0.11)	2.9 (0.26)	5.94 (0.08)	1.21 (0.02)	1,880 (20)	1,309 (17)	2,455 (38)	34.78 (0.34)
	The.[h]	69.3	13.9	13.9	2.9	5.96	1.20	1,880	1,312	2,437	35.00

[a] Sequence length of hard segment.
[b] Sequence length of soft segment.
[c] Number average molecular weight of PTMG in copolymer calculated from NMR spectra.
[d] Number average molecular weight of hard segment calculated from NMR spectra.
[e] Number average molecular weight of soft segment calculated from NMR spectra.
[f] Comparison of calculated and fed hard segment contents.
[g] Averages of five independent experimental results and standard deviations(in parenthesis).
[h] Theoretical parameters calculated from feed ratio and measured $\overline{M}_n$ of PTMG.

extracted probability of triad sequences was also used to calculate the molecular weight of PTMG in block copolyester. As in the case of starting PTMG, the calculation of number average molecular weight of PTMG could be performed by the comparison of the integral values of NMR peaks of terminal with those of central part of tetramethylene group of PTMG chain. Because direct comparison of small and large peaks might give significant errors in obtaining the ratio of the intensities, we used fitted values for terminal peaks(PP+PB) instead of direct integral values of a - d peaks in NMR spectra. Then we found that our method gave us very accurate number average molecular weight of PTMG within real copolymers(see standard deviations in Table 2). Conceptually, the product of segment length and molecular weight of unit segment produces the average molecular weight of each segmented block. For example, average molecular weight of soft segmented block was calculated through production of SSL by molecular weight of PTMG added by 148.12(corresponding to TP unit) and so on. Finally, under the assumption of infinite chain, hard and soft segment contents were easily obtained from such average molecular weights of each segment on the basis of schematic picture of alternation of hard and soft segments in block copolymer.

Despite versatile uses of the NMR method in quantification of sequence distributions, we found the large errors and deviations between the data in previous works(8-10). In this study, as previously described, we found that aromatic protons of PBT/PTMG gave well resolved NMR lines in phenol-d_6/TCE and the simultaneous fitting of several groups of carbon signals could overcome, in part, poor S/N ratio of ^{13}C NMR. Therefore we think that the errors in measurement have been greatly reduced compared to the previous studies. To evaluate the accuracy of this method, five sets of above parameters were independently calculated from five measurements. Then, for each parameter, average and standard deviation were evaluated. We could see that the standard deviations(the values in parenthesis in Table 2) were very low for most parameters which meant that the method was very accurate in elucidation of the real microstructures of the polymers.

Generally, when one designs and prepares the copolyesters, the theoretical sequence distributions as well as chemical compositions of the polymers can be known from feed ratio. However, to calculate theoretical parameters, the molecular weight of PTMG in real copolymer is indispensable because, for given HSC, sequence distributions depend on the $\overline{M}_n$ of PTMG. As mentioned in the experimental section, we measured the number average molecular weight of starting PTMG by two methods (end-group analysis by titration and NMR method). As a result, we could see good agreement of both the measurements with maker's specification; $\overline{M}_n$=2,004(31) by end-group analysis and 2,015(35) by NMR where the values in parenthesis were the standard deviations of five independent experiments. However, for the PTMG in the real copolymer, the observed $\overline{M}_n$'s have found to be lower than those from the specification: 1,888(16) for sample 1 and 1,880(20) for sample 2(Table 2). Though these values were not so greatly different from those of starting ones, we could see that it affected the theoretical microstructural parameters for given HSC. Moreover, statistical significance test showed that there were true differences between the molecular weights of starting PTMGs and those within the copolymer with more than 95% certainty. This means that there exist certain extent of degradation in PTMG during the preparation of the copolymer as reported by other authors(14, 16). When we used the observed $\overline{M}_n$ of PTMG, theoretical sequence length and chemical compositions, were found to be rather close to the observed ones(Table 2).

We think that the imposed condition of the polymerization process is sufficient for all ingredients of the starting materials to be randomly copolymerized. In that point of view, good agreement of various parameters between theory and experiment confirm the suitability of this method for exact analysis of the chemical composition and microstructures of the PBT/PTMG and other relevant copolyester.

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