

NMR Characterization of Segment Sequence in Polyester–Polyether Copolymers

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ABSTRACT: The poly(butadiene terephthalate) (PBT)–poly(tetramethylene glycol) (PTMG) segmented copolymers synthesized both by ordinary monomeric method (M method) and polymeric method (P method) have been studied by NMR. By using ^{13}C NMR based on the chemical shifts of aromatic quaternary carbons, the segment sequence and the compositions of segmented copolymers are able to be precisely determined, even with unpurified samples. In contrast, only the apparent composition was obtained using ^1H NMR, because the formation of long sequence of soft segment and the effect of polyester are not taken into account in ^1H NMR measurement. Formation of long sequence of soft segment is more likely in PBT–PTMG with lower hard segment content (PBT %).

KEY WORDS ^{13}C NMR / Aromatic Quaternary Carbons / Polyester–Polyether Segmented Copolymers / Segmented Sequence Distribution / Thermoplastic Elastomer/

Polyester–polyether segmented copolymers composed of poly(butylene terephthalate) (PBT) as hard segment and poly(tetramethylene glycol) (PTMG) as soft segment are thermoplastic elastomers, which were first commercialized by E. I. Du Pont de Nemours & Company. In these thermoplastic elastomers, rubberlike elasticities are attributed to rubbery matrices of soft segments bonded by physical cross-linkings of aggregated hard segments.

Hardness, elastic modulus, and other physical properties of the elastomers have generally been controlled by the content of the hard segment and molecular weight, M_c , between cross-linking. Coupling of two polyether segments themselves is through a terephthaloyl group. As a result, M_c is doubled, leading to heterogeneity of M_c and reduction of hard segment content due to consumption of some terephthalic acid in the formation of long sequence soft segments.

The determination and control of the composition and segment sequence length of these heterophase materials are of paramount importance. The composition of PBT–PTMG was already determined with the aid of ^1H NMR by one of the present authors and her colleagues.¹

In this paper we show that ^{13}C NMR is more powerful and precise method for the determination of both the composition and the segment sequence distribution of PBT–PTMG than ^1H NMR.

EXPERIMENTAL

Samples

PBT–PTMG samples were synthesized by two methods; ordinary “monomeric method” and so-called “polymeric method.” The former method is generally used in industry using monomers of dibasic acids and glycols, and

Table I. Homogeneity and some properties of PBT-PTMG samples

Sample No.	Hard segment ^a	Method of preparation ^b	MW of PTMG	[η]	CHCl ₃ -insoluble	C ₂ H ₅ OH-soluble	mp °C
	wt%			100 cm ³ g ⁻¹	%	%	
1	21	P	2263	1.20	0	5.70	172—175
2	25	M	2035	1.33	0	4.10	181—184
3	40	P	2263	1.73	0	1.37	207—211
4	40	M	2059	1.61	0	1.40	209—212

^a Hard segment wt% calculated by feed ratio.

^b P, polymeric method; M, monomeric method.

polyether oligomers as starting materials. In the latter method, the PBT polyester is used instead of the monomers as starting material. The experimental details were reported elsewhere.^{1,2}

Purification of PBT-PTMG

Purification was conducted by using ethanol as extraction solvent to remove the ethanol-soluble fraction and then the sample was solved in CHCl₃ and filtered out of the CHCl₃-insoluble fraction. This CHCl₃-soluble fraction is cited as the purified sample.

NMR measurements

NMR measurements were carried out using JEOL GSX-270 spectrometer operating at a resonance frequency of 270 MHz for protons and using JEOL GSX-500 spectrometer operating at 125 MHz for ¹³C nuclei. The concentration of each sample was about 5 wt% in C²HCl₃. A 5 mm diameter glass tube was used for measurements. Temperature was maintained at 30 or 40°C within $\pm 0.1^\circ\text{C}$ during the measurements. ¹H NMR spectra were obtained with spectral width of 3 kHz, rf pulse width of 5 μs and pulse delay time of 3 s. ¹³C NMR spectra were obtained under proton decoupling conditions using a spectral width of 27 kHz, rf pulse width of 10 μs and pulse delay time of 3 s. For typical ¹H NMR and ¹³C NMR spectra, 64 and 300 to 1500 scans were accumulated, respectively. ¹H-¹³C shift correlated spectroscopy (¹H-¹³C COSY) was

Table II. Chemical shift of ¹H NMR in PBT-PTMG

Segment	Proton	Chemical shift
		δ/ppm
PBT	Aromatic proton	8.09
	$\text{O}=\text{C}-\text{O}-\text{CH}_2-$	4.40
	$-\text{CH}_2-\text{CH}_2-$	1.60
PTMG	$-\text{CH}_2-\text{O}-\text{CH}_2-$	3.4
	$-\text{CH}_2-\text{CH}_2-$	1.6
	$\text{O}=\text{C}-\text{O}-\text{CH}_2-$	4.4

recorded using the standard pulse sequence. The data matrix was apodized with a sine bell function in both dimensions and the spectrum is presented in the absolute value mode. Chemical shifts are presented in ppm downfield from tetramethylsilane for both ¹H and ¹³C spectra.

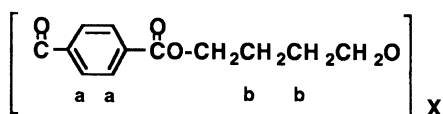
RESULTS AND DISCUSSION

In Table I are listed the homogeneity and some properties of virgin PBT-PTMG samples. The homogeneity of PBT-PTMG can be estimated from solubility test. The CHCl₃-insoluble fraction is attributed, by IR, to copolymers having much higher content of hard segments than the average or unreacted

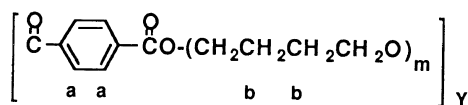
homopolyesters. The ethanol-soluble fraction is attributed to low molecular weight copolymers with higher polyether content³. The existence of these two fractions in ethanol-insoluble, but CHCl₃-soluble, fraction is the origin of inhomogeneity.

To investigate the effects of inhomogeneity, the compositions of PBT-PTMG were determined from ¹H NMR. In Table II are listed the chemical shifts of protons in PBT-PTMG. The composition and molar ratio of the hard to the soft segments are calculated by the following equations:

Hard segment:



Soft segment:



$$4X + 4Y = a \text{ (aromatic protons)} \quad (1)$$

$$4X + 4mY = b \text{ (protons of } -\text{CH}_2-\text{CH}_2-) \quad (2)$$

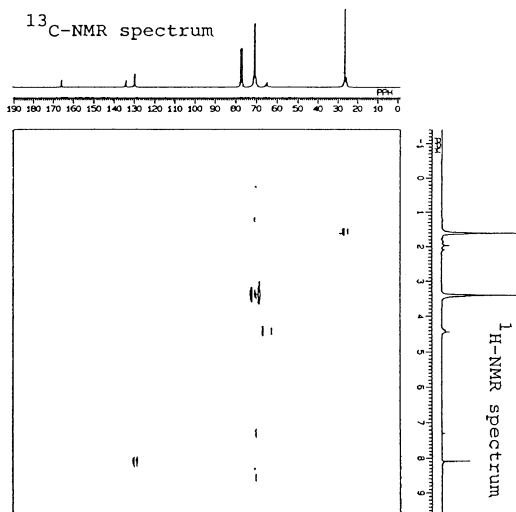
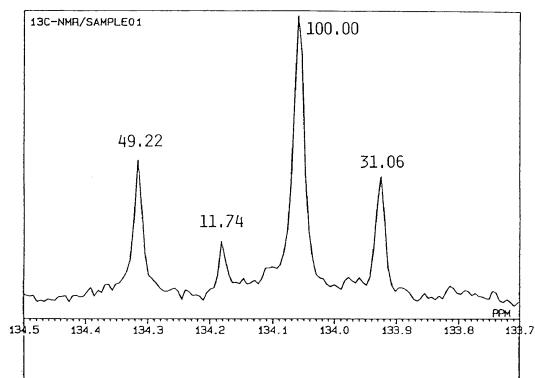
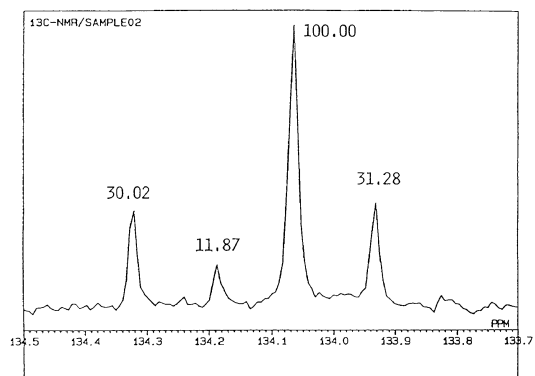


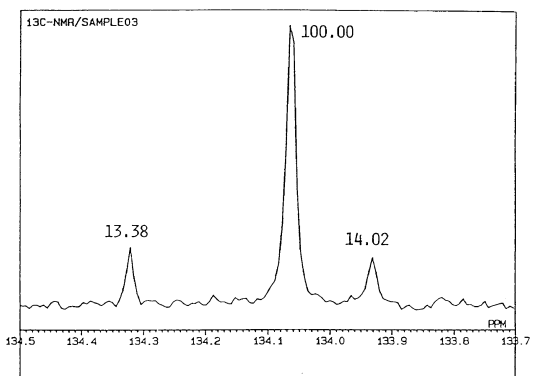
Figure 1. ¹H-¹³C COSY NMR spectrum of sample 1 in C²HCl₃ at 30°C.



(a)



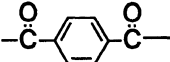
(b)



(c)

Figure 2. Expanded ¹³C NMR spectra in the region of 133.7–135.4 ppm of the samples 1(a), 2(b), and 3(c). Numbers in the spectra indicate signal intensities (heights) relative to the intensity of the peak at 134.06 ppm, normalized to 100.

where $m=31.4$ for PTMG with molecular weight of 2263. The molecular weight of the soft segment should be equal to the sum of molecular weight of PTMG and 132 (molecular

weight of.  We can obtain

information on composition, such as X and Y from ^1H NMR. Results will be shown later in Table IV.

In Figure 1 is shown ^1H - ^{13}C COSY NMR spectrum of the sample 1. There are a lot of peaks in ^{13}C NMR compared with ^1H NMR. Assignment was done by information on ^1H - ^{13}C COSY and a comparison of relative intensities between peaks. Expanding the NMR spectrum in the region of 133.7–135.4 ppm, we get Figure 2. All the peaks in the figure originate from the aromatic quaternary carbons. As can be seen from the figure, these regions are composed of four peaks for each sample, assignable to four possible triad sequences as follows:

A	B-T-P (P side)	133.92 ppm
B	B-T-B	134.06
C	P-T-P	(trace)

D P-T-B (B side) 134.18
Based on the relative intensities of these four peaks, we can determine the fraction of each triad and number average sequence length. The results are summarized in Table III. The number average sequence length, $\langle B \rangle_n$, of hard segments were calculated from

$$\langle B \rangle_n = [\text{B-T-B}] / \text{Min}\{[\text{B-T-P}], [\text{P-T-B}]\} \quad (3)$$

because an excess amount $|[\text{B-T-P}] - [\text{P-T-B}]|$ is located in the chain end. $\text{Min}\{p, q\}$ means the minimum among p and q . Polyesters having asymmetric monomers were already analyzed with the aid of NMR.⁴ However, sequence length of polyesters having asymmetric quaternary carbon has not been analysed yet. The composition of PBT-PTMG is also calculated from the values in Table III by usual method. The results are summarized in Table IV.

Since the composition determined by ^{13}C NMR is based on the probability of triad, it will be free from peaks due to impurities and inhomogeneity. This enables us to use unpurified samples for determination. PBT wt% determined by ^{13}C NMR with unpurified samples is in good agreement with that by ^1H

Table III. The probability of triad sequence and number average sequence length determined by ^{13}C NMR

Sample No.	B-T-B	B-T-P (P side)	P-T-B (B side)	P-T-P	$\langle B \rangle_n$
1(P)	52.1	16.2	25.6	6.1	3.24
2(M)	57.7	18.1	17.3	6.9	3.34
3(P)	78.5	11.0	10.5	trace	7.48

Table IV. Compositions (PBT wt%) of purified and unpurified samples

Sample No.	By feed ratio	^1H NMR	^1H NMR	^{13}C NMR ^a
		(Purified)	(Unpurified)	(Unpurified)
1	21(P)	19.0	23	18.2
2	25(M)	23.4	28	23.0
3	40(P)	39.6	46	40.3
4	40(M)	—	34.8	40.18

^a Based on aromatic quaternary carbon and calculated from eq 3.

NMR with purified samples. This is the other advantage of ^{13}C NMR compared with ^1H NMR.

Both samples 1 and 3 were synthesized by the "P" method. The former with higher polyether content in feed ratio induced a 6.7% of "C" peak, while only a trace was found in the latter. This suggests that the probability of long sequence formation of soft segments is dependent upon the concentration of polyether soft segment in the reaction. Since the composition of PBT-PTMG was controlled by the feed ratio of DMT and polyether, we can imagine that the PBT-PTMG of lower content in hard segment may contain a longer sequence of soft segments.

A comparison of the "P" method with the "M" method is interesting. Tensile strength of the former is often slightly larger than that of the latter¹. From Table IV, the sample made by the "P" method exhibits lower probability of long sequence formation of soft segments than that of a sample made by the "M" method. Perhaps this leads to difference in tensile strength. The formation of a long sequence of the soft segments leads to reduction of the hard segment content. Thus, tensile strength may be reduced. This possibility must be clarified in future. This kind of reduction cannot be detected by ^1H NMR.

In the "M" method, during the ester-exchange reaction, DMT may react with butylene glycol and polyether glycol. So the formation of a long sequence of soft segments is easier than that in the "P" method. In the

latter, the polyester was used as starting material and was alcoholized by the OH group of PTMG. Therefore, the probability of the formation of long sequence of soft segments becomes much smaller.

CONCLUSION

1. The probability of segment sequence, especially the presence of long sequence of soft segments, was detected from ^{13}C NMR and quantitatively determined.

2. Based on the probability of segment sequence, the real compositions of segmented copolymers were determined even with unpurified samples.

3. The probability of forming long sequence of soft segments in PBT-PTMG with lower PBT content is more likely than that with higher PBT content.

4. The correlation between segment sequence distribution and properties should be determined.

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