

Effects of Catalyst on Sequence Distribution and Transparency of Poly(tetramethylene terephthalate)–Poly(tetramethylene ether) Segmented Copolymers

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SYNOPSIS

Polyether-polyester segmented copolymer based on hard segments of tetramethylene terephthalate (PBT) and soft segments of poly(tetramethylene ether glycol) (PTMG) was synthesized by four kinds of catalyst: tetrabutyl titanate and magnesium acetate (Ti-Mg); tetrabutyl titanate and triethanolamine; tetra(isopropyl) titanate; and isopropoxy(triethanolaminate) titanate, respectively. Their segment sequence distributions were analyzed by ¹³C-NMR, based on different chemical shifts of aromatic quaternary carbons in the three different triad sequences. The effects of catalyst on sequence distribution and transparency were investigated. It was found that the copolymer has lower probability of B-T-B when Ti-Mg was used as catalysts, and results in higher transparency. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Polyether–polyester segmented copolymer is a class of thermoplastic elastomers that display many excellent properties, such as high strength, impact resistance, chemical resistance, and low temperature flexibility. The synthesis, mechanical properties, and morphology of the copolymers have been extensively studied. However, for such a crystalline heterophase structure of polyester elastomer, the correlation between structure and transparency have been little studied. Several reports indicate that the haze of poly(tetramethylene terephthalate)–poly(tetramethylene ether glycol) segmented copolymer (PBT–PTMG) could be decreased by selecting suitable catalysts.¹ The aim of this work is to use four kinds of catalysts for synthesis of PBT–PTMG in an attempt to increase the transparency and understand the relationship between transparency and sequence distribution.

Nuclear magnetic resonance (NMR) spectroscopy is a powerful technique for the quali-

tative and quantitative analysis of polyester composition.² Quantitative analysis of ¹³C-NMR spectra is limited by the fact that different carbons have different relaxation times and nuclear Overhauser enhancements. The aromatic quaternary carbons of terephthalate have different chemical shifts but identical relaxation times and nuclear Overhauser enhancements in the three different triad sequences.³ Newmark reported that ¹³C-NMR of polyethylene/tetramethylene terephthalate copolyesters could be used to determine the sequence distribution of the copolyester.³ In previous articles^{4,5} we described the application of ¹³C-NMR spectroscopy for the characterization and sequence analysis of poly(ethylene terephthalate)–PTMG segmented copolymer (PET–PTMG). PBT–PTMG is a typical and commercial polyether-polyester segment copolymer; however, the sequence distribution of PBT–PTMG has not been determined by ¹³C-NMR, owing to the structural similarity of these two diols.

This article describes use of 500-MHz high resolution ¹³C-NMR to investigate the sequence distribution of PBT–PTMG synthesized by different catalysts.

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EXPERIMENTAL

Materials

PTMG having a number-average molecular weight of 981 (Terathane^R 1000), tetra(isopropyl) titanate, and isopropoxy (triethanolamino) titanate were obtained from the DuPont company. Dimethyl terephthalate (DMT) was obtained from the Toyobo Company. 1,4-Butanediol (4G), tetrabutyl titanate (Ti(OBu)₄), and triethanolamine were purified by vacuum distillation. Magnesium acetate (Mg(OAc)₂) was dried at 134°C for 6 h. Irganox 1010 was practical-grade material and used without further purification.

Polymer Preparation

The polyether-polyester segmented copolymers were prepared by a standard melt condensation technique. The starting reaction mixture contained DMT, PTMG, and 4G, the total diol present in 50% molar excess above the stoichiometric amount required. The reactions were carried out in the presence of catalysts and antioxidant Irganox 1010. The mixture was heated to 180–190°C for transesterification under an argon atmosphere. After removing methanol, the stirred reaction mass was gradually heated to 250°C in 0.5 h, and finally reducing the pressure below 0.1 mm Hg and removing excess diol by distillation from the viscous reaction mass in about 2 h.

Four segmented polyether-polyester copolymers, based on PBT as the hard segment and PTMG as the soft segment, were synthesized. The mole ratio of the starting components was equivalent and selected to result in copolymers with constant hard : soft segment weight ratio (30 : 70). The catalysts were tetra(isopropyl)titanate (TPT), isopropoxy (triethanolamino) titanate (TE), tetrabutyl titanate and triethanolamine (Ti-N), tetrabutyl titanate and magnesium acetate (Ti-Mg).

Gel permeation chromatography indicated that the copolymers had the expected geometric molecular weight distribution with M_n being about 3.0×10^4 .

Polyether-polyester segmented copolymer structure was ascertained by ¹H-NMR spectrum. The copolymers synthesized were extracted by ethanol to remove the trace unreacted polyether and low molecular weight oligomer and then dissolved in CDCl₃ for NMR analysis.

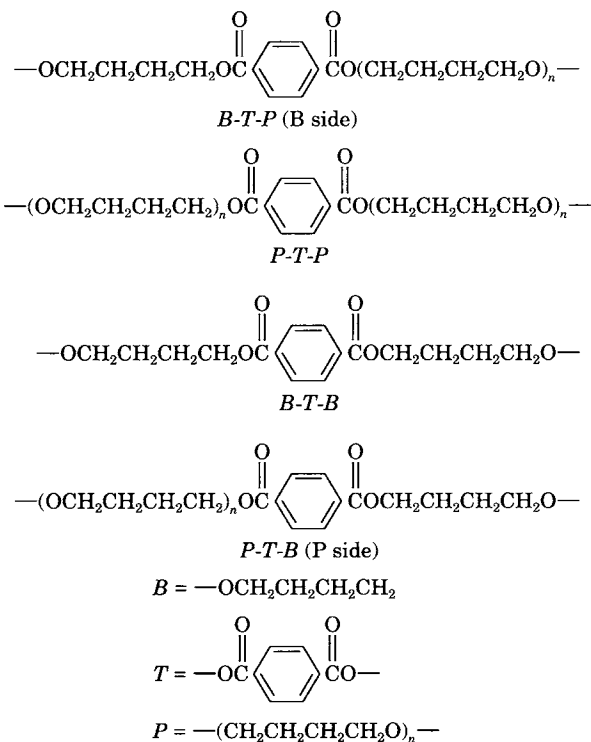
The DSC traces exhibited only one melting peak at 156.5°C of the hard segments attributed to the PBT crystalline segment in the PBT-PTMG copolymers, indicating no PBT homopolymers were formed.

Characterization Methods

The spectra were recorded on a Bruker WH-500 NMR spectrometer at room temperature. Deuteriochloroform was used as solvent and chemical shifts are reported for the δ value (in ppm) relative to tetramethylsilane as an internal standard. Fourier transform proton-noise decoupled ¹³C-NMR spectra were obtained on 22,727.273-Hz sweeps that used a 1.442-s acquisition time and 4.4- μ s RF pulse. The transparency of the copolymer films was determined by using a TD-528 transmission densitometer.

RESULTS AND DISCUSSION

A typical ¹³C-NMR spectrum of PBT-PTMG expanding the NMR spectrum in the region of 133–135 ppm are shown in Figure 1. As can be seen from the figure, there are four peaks in these regions for each sample, assignable to four possible triad sequences as follow:



For the sake of convenience in subsequent discussions, the four peaks are numbered as 1, 2, 3, 4 from upfield to downfield. The relaxation times and nuclear overhauser enhancements (NOEs) of aromatic quaternary are the same within experimental error and showed that quantitative comparisons of the integrated peak intensities of the quaternary

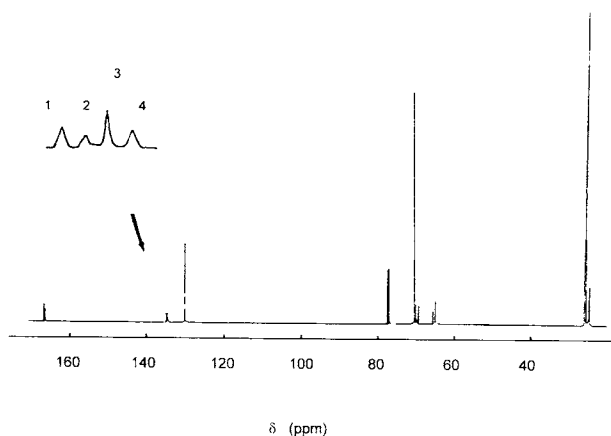


Figure 1 ^{13}C -NMR spectrum of PBT-PTMG.

carbons are valid in these copolymers.³ The chemical shifts and integrated peak intensities of the quaternary aromatic carbons for three different copolyester compositions are listed in Table I.

Degree of randomness B is calculated from the contents of the three possible triad sequences⁴:

$$B = q(B-T-P)/2q(B) \cdot q(P)$$

where $q(B)$, $q(P)$ is the probability of tetramethylene terephthalate and poly(tetramethylene glycol) terephthalate, respectively.

$$q(B) = q(B-T-B) + \frac{1}{2}q(B-T-P),$$

$$q(P) = q(P-T-P) + \frac{1}{2}q(B-T-P).$$

Values of B calculated for the four PBT-PTMG range from 0.98 to 1.03, with an experimental error of 1.0, indicating that the PBT-PTMG prepared by a standard melt condensation yields a random copolymer.

From the probabilities it could be calculated that the number-average sequence length of $B-T-B$ (L_{nB}) and $P-T-P$ (L_{nP}) units,

$$L_{nB} = 2q(B)/q(B-T-P),$$

$$L_{nP} = 2q(P)/q(B-T-P).$$

The ratios of the different triad sequence were then calculated directly and compiled in Table II. Values presented in Table II show that the L_{nB}/L_{nP} ratio was in good agreement with the hard/soft segment ratio determined ^1H -NMR.

The transparency of copolymer films prepared by casting from solution and melt-injected methods are summarized in Table III. As can be seen from Table III, when Ti-Mg was used as catalyst, the probability of $B-T-B$ is the lowest, and the transparency is the highest. When Ti-N was used as catalyst, the $B-T-B$ is the highest, and the transparency is lowest. It has been shown from the previous work⁶ that polyether-polyester segmented copolymer with lower

Table I Chemical Shifts of Aromatic Quaternary Carbons and Sequence Distribution of Segments

Catalysts	Peaks	Triad	δ (ppm)	Relative Intensity	Probability (%)
Ti-Mg	3	$B-T-B$	133.86	0.7379	42.68
	1	$B-T-P$ (B side)	134.11	0.4231	24.47
	4	$P-T-B$ (P side)	133.74	0.3798	21.97
Ti-N	2	$P-T-P$	133.97	0.1880	10.87
	3	$B-T-B$	133.88	0.6120	47.85
	1	$B-T-P$	134.13	0.3830	21.41
TE	4	$P-T-B$	133.75	0.3455	22.24
	2	$P-T-P$	134.00	0.1736	8.50
	3	$B-T-B$	133.91	0.7542	45.54
TPT	1	$B-T-P$	134.15	0.3830	23.12
	4	$P-T-B$	133.78	0.3455	20.86
	2	$P-T-P$	134.02	0.1736	10.48
TPT	3	$B-T-B$	133.98	0.6948	43.91
	1	$B-T-P$	134.25	0.3428	21.66
	4	$P-T-B$	133.86	0.3542	22.38
	2	$P-T-P$	134.13	0.1906	12.04

Table II Randomness Parameter (B), Number-Average Sequence Lengths (L_n), and Mole Ratios (L_{nB}/L_{nP})

Catalysts	Determined by $^{13}\text{C-NMR}$				Determined by $^1\text{H-NMR}$
	B	L_{nB}	L_{nP}	L_{nB}/L_{nP}	L_{nB}/L_{nP}
Ti-Mg	1.03	2.83	1.47	1.93/1	2.10/1
Ti-N	1.03	3.19	1.39	2.29/1	2.21/1
TE	1.00	3.07	1.48	2.07/1	2.16/1
TPT	0.98	2.99	1.55	1.93/1	2.11/1

crystallinity has higher transparency and the transparency can be improved by decreasing the crystallinity of the copolymer. As only the hard segment has crystalline forms in the studied copolymers, the copolymer with higher hard segment fraction has higher crystallinity and lower transparency. Thus the sample with high content of B - T - B should have high crystallinity and result in low transparency.

CONCLUSION

The effects of catalysts on the transparency of polyether-polyester thermoplastic elastomers resulting

Table III Transparency of PBT-PTMG Synthesized by Different Catalysts

Catalysts	Transparency (%)	
	CHCl_3 SC	MI
Ti-Mg	89.1	65.0
Ti-N	76.0	40.0
TE	81.3	59.0
TPT	83.1	60.0

CHCl_3 SC, chloroform solution cast film; thickness is about 0.10 mm. MI, melt-injected film; thickness is about 1.0 mm.

from the changes of composition uniformity and segment sequence distribution were studied by means of $^{13}\text{C-NMR}$. The probability of B - T - B of copolymers synthesized by different catalysts is in the order: Ti-N > TE > TPT > Ti-Mg; the transparency is in the order: Ti-Mg > TPT > TE > Ti-N.

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