Structure of Liquid Crystalline Copolyesters from Two Acetoxybenzoic Acids and Polyethylene Terephthalate

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ABSTRACT: The molecular and supermolecular structures of thermotropic liquid crystalline copolyesters from *p*-acetoxybenzoic acid (B), polyethylene terephthalate (E), and *m*-acetoxybenzoic acid (M) were studied by Fourier transform infrared spectrometer, 200-MHz ¹H-nuclear magnetic resonance (NMR), and wide-angle X-ray diffraction methods. The assignments of resonance peaks in NMR spectra are given and the effect of B/E/M molar ratio on the NMR spectra and number-average degree of polymerization of the copolyesters are discussed. The equatorial, meridional, and azimuthal scans, and their dependency on monomer mole ratio for the copolymers, are elaborated. The persistence length and orientation of the copolymer ribbons were found to increase with an increase in *p*-oxybenzoate unit content from 60 to 75 mol % at a fixed *m*-oxybenzoate unit content of 5 mol %. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2921–2925, 1999

Key words: hydroxybenzoic acid copolymer; liquid crystalline copolyester; Fourier transform infrared spectrum; proton nuclear magnetic resonance; wide-angle X-ray diffraction; meridional reflection; orientation index

INTRODUCTION

The molecular structure of the copolymers, especially their sequence and supermolecular structures, are always an important research subject in polymer science. A structural study on changing copolymer monomer ratios is of considerable theoretical and practical interest. It is known that thermotropic liquid crystalline copolyesters are one of the high-performance polymer materials. A few investigations on the molecular, sequential, supermolecular, and morphological structures and thermal property for the liquid crystalline copolyesters from *p*-acetoxybenzoic acid (B), polyethylene terephthalate (E), and several third monomers have been reported.¹⁻⁸

tion of China; contract grant number: 29804008. Journal of Applied Polymer Science, Vol. 73, 2921–2925 (1999) The main subject of this study is a thermotropic liquid crystalline copolyester based on pacetoxybenzoic acid (B), polyethylene terephthalate (E), and *m*-acetoxybenzoic acid (M). Fourier transform infrared and proton nuclear magnetic resonance spectroscopies and wide-angle X-ray diffraction are used to investigate the molecular structure and crystalline structure.

EXPERIMENTAL

A series of terpolymers in this study were synthesized from *p*-acetoxybenzoic acid, poly(ethylene terephthalate), and *m*-acetoxybenzoic acid by molten polycondensation at 270-320°C. The details of the procedure were reported previously.^{9,10} The ribbons and film for structural testing were drawn directly and uniaxially from copolycondensation melts and cooled in ambient air.

IR spectrum of the oriented film $(30-\mu m \text{ thick})$ of B/E/M (60/35/5) terpolymer was obtained on a

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Nicolet 710 Fourier transform infrared spectrometer. Groups of 32 scans were co-added for a total of 200 scans at a spectral resolution of 4 cm⁻¹.

The terpolymers were dissolved in deuterated trifluoroacetic acid (TFA) at ca. 5 wt % concentration. ¹H-NMR spectra were recorded on a Bruker AM-400 NMR spectrometer at 400 MHz for B/E/M (60/40/0) copolymer and on a Bruker AC-P 200 NMR spectrometer at 200 MHz for B/E/M (60/35/5), (65/30/5), (70/25/5), and (75/20/5) for four terpolymers. The chemical shifts were read from tetramethylsilane added as an internal standard. The peak areas were determined by spectral integration.

The equatorial and meridional reflections of wide-angle X-ray diffractograms for as-drawn ribbons of the copolymers were obtained by using a Rigaku X-ray diffractometer (40 kV, 150 mA) with nickel-filtered K α radiation at a scanning rate of 2°/min.

The width at half-height β (in degree) or β' (in radian) at the strongest meridional reflections at $2\theta = 43.5^{\circ}$ can give the length (*L*) of coherent periodicity in the draw direction (i.e., the axial direction of polymer main chain) by using one of the following two expressions¹¹:

$$L = \lambda / [2(\sin \theta_1 - \sin \theta_2)] \tag{1}$$

where $\lambda = 0.154178$ nm, $\theta_1 = 21.75 + \beta/2$, $\theta_2 = 21.75 - \beta/2$, or

$$L = \lambda / (\beta' \cos \theta) \tag{2}$$

where $\beta' = \beta \pi / 180 = 0.0174532\beta$.

The orientational index was determined from the azimuthal scans (at a scanning rate of 8° /min) of the strongest meridional peak at a diffraction angle of around 43.5° using the following equation:

Orientational index =
$$[1 - (\Delta H/180)] \times 100\%$$
(3)

where ΔH is the peak width at half maximum height.

RESULTS AND DISCUSSION

FTIR Spectrum of B/E/M Terpolymer

Figure 1 shows a representative FTIR spectrum of the oriented film with the thickness of ca. 30 μ m of the B/E/M (60/35/5) terpolymer. The spec-



Figure 1 Fourier transform infrared spectrum of oriented film with the thickness of 30 μ m for copoly[*p*-oxybenzoate (B)–ethylene terephthalate (E)–*m*-oxybenzoate (M)] B/E/M (60/35/5) terpolymer.

trum displays the characteristic C=O stretching vibration at 1725 cm⁻¹ and the C—O—C unsymmetrical stretching vibration connected with the *para*-benzene ring at 1270 and 1100 cm^{-1,10} indicating ester linkage in the terpolymer. Another weak band at 3450 cm^{-1} might be attributed to the C=O vibration. Four well-separated sharp bands at 1604, 1504, 1470, and 1410 cm^{-1} are parallel bands associated with aromatic ring vibration which is conjugated with the C=O group.¹² Three bands at 1016, 1125, and 1405 cm^{-1} may be ascribed to C—O stretching, and C-O-C and C-C=O deformations, respectively. Three medium bands associated with flexible methylene (-CH₂CH₂-) groups are located at 725 and 760 cm⁻¹. Two bands at $\sim 2910-2969$ and $\sim 3105 \text{--} 3075 \text{ cm}^{-1}$ are supposed to be mostly due to C-H stretching (and bending) vibrations in -CH₂CH₂- and benzene ring, respectively. However, the out-of-plane twisting vibration of C—H in the meta-benzene ring at 1840 and 1900 cm^{-1} does not seem to be found in the spectrum, possibly due to the low content (5 mol % M unit in the terpolymer). Note that the terpolymer hardly ever exhibits the very characteristic O-H stretching vibration in free carboxylic acid in $\sim 3560-3500 \text{ cm}^{-1}$ or a strong and broad band due to O-H stretching vibration in associating carboxylic acids of two molecules by hydrogen bonding in $\sim 3000-2500 \text{ cm}^{-1}$, which implies a high molecular weight of the terpolymer.

Assignments of ¹H-NMR Peaks in B/E/M Terpolymers

Figure 2 shows the 400- and 200-MHz ¹H-NMR spectra of the B/E/M copolymers. According to the





Figure 2 ¹H-NMR spectra with the assignments of the all resonance peaks for B/E/M (60/40/0) at 400 MHz and B/E/M (60/35/5), (65/30/5), (70/25/5), and (75/20/5) terpolymers at 200 MHz in deuterated trifluoroacetic acid.

methods proposed earlier,¹³ the assignments of ¹H-NMR peaks in four B/E/M terpolymers are listed in Table I. The chemical shifts of the all protons on B, E, and M units in the B/E/M terpolymers are almost invariant with increasing B-unit content from 60 to 75 mol % at a fixed M content of 5 mol %. Note that a_2 and b_1 protons both corresponds to two types of dyads. The two resonance peaks at ~ 8.18-8.19 and ~ 8.11-8.15 ppm could be ascribed to the E–B

$$-\operatorname{OCH}_2\operatorname{CH}_2\operatorname{OOC}\overset{\mathbf{a_2}}{\underset{\mathbf{a_2}}{\longrightarrow}} \operatorname{CO} - \operatorname{OOC} - \operatorname$$

and E–E

$$-\operatorname{OCH}_2\operatorname{CH}_2\operatorname{OOC} \bigotimes_{a_2 a_2}^{a_2 a_2} \operatorname{CO} - \operatorname{OCH}_2\operatorname{CH}_2\operatorname{OOC} \bigotimes_{a_2 a_2}^{OC} \operatorname{CO} -$$

dyads, respectively. Similarly, the two peaks at \sim 7.37–7.39 and \sim 7.28–7.32 ppm are ascribed to the B–B and B–E dyads, respectively.

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The proton peak area in acetoxyl end group could be used to calculate the DP_n of the terpolyesters if the final terpolymer compositions are the same as the feeding monomer unit content and every terpolymer chain has only one acetoxyl end group. For B/E/M (75/20/5) terpolyester,

$$\begin{aligned} \mathbf{DP}_n &= [(b_1 + b_2 + b_3 + b_4)_{\text{peak area}}] \\ &\quad \div [(d_1 + d_2)_{\text{peak area}} \times 2 \div 3] \div 0.8 \end{aligned}$$

Therefore, the average DP_n of the B/E/M (75/20/5) terpolymer was calculated to be ca. 62. The average DP_n values for four B/E/M terpolymers are listed in Table I. It appears that the average DP_n will increase with increasing B unit and reach the highest value at the B-unit content of 70 mol %.

Wide-Angle X-ray Equatorial and Meridional Diffractions for B/E/M Terpolymers

Figures 3 and 4 show the equatorial and meridional intensity profiles for four terpolymers. The quantitatively analytical results of the equatorial and meridional reflections are given in Table II. It is obvious that the B/E/M (65/30/5) terpolymer exhibits an equatorial peak that is broader than those of B/E biopolymers but sharper than those of B/E/Vanillate (V) terpolymers.² Note that there is a weaker diffuse reflection on the equator in the 2θ range from 15 to 10° for B/E/M terpolymer, which is not observed in the equatorial scans of B/E biopolymers and B/E/V terpolymers.² This indicates that lateral molecular packing in B/E/M terpolymers is poorer than B/E biopolymers because of the bending effect of meta-benzene ring on molecular chain packing.

As shown in Figures 3 and 4 and Table II, three meridional reflections with d spacings of 0.208, $\sim 0.320-0.328$, and $\sim 0.441-0.455$ nm, were observed for B/E/M terpolymers. The reflection of 0.208 nm is the strongest and almost invariant with terpolymer composition. It is reported that the strongest reflection at 0.208 nm could correspond to the third order of B unit.² The peak width at a half height of 0.208 nm appears to increase first and then decrease slightly with an increase in B-unit content from 60 to 75 mol % at a fixed M-unit content of 5 mol % and reaches a lowest value of 1.72° at B-unit content of 75 mol %. This corresponds to the largest persistence length of 5.53 nm, suggesting that the B/E/M

B/E/M (mol %)	Assignment ^a (ppm)									
	a_1	<i>a</i> ₂	<i>a</i> ₃	b_1	b_2	b_3	b_4	С	d	DP_n
60/35/5	8.33	8.18, 8.11	8.18	7.37, 7.29	7.52	7.92	7.09	4.78	2.38, 2.18	38
65/30/5	8.34	8.19, 8.14	8.19	7.39, 7.32	7.56	7.95	7.09	4.80	2.39, 2.19	76
70/25/5	8.33	8.19, 8.14	8.19	7.39, 7.32	7.54	7.91	7.08	4.80	2.38, 2.19	105
75/20/5	8.33	8.19, 8.15	8.19	7.37, 7.28	7.55	7.92	7.09	4.80	2.38, 2.19	62

Table I	Assignments of	¹ H-NMR Spectra	for Poly[p-oxybenzoate	e (B)–ethylene terephthalate (H	E) -m -
oxybenz	oate (M)] B/E/M '	Terpolymers			

^a The terpolymer chain structure is





and end groups are



(75/20/5) terpolymer chain is straightest in the four terpolymers. These results imply that the macromolecular chains in the ribbons are oriented along the direction of draw, but lack crystalline order. The same behavior has been found for B/E and B/E/V copolymers.²

Additionally, the variability of the *d* spacing of the meridional maxima and the fact that they are not orders of one another indicate an aperiodic chain structure or a random sequence of monomer units just like thermotropic liquid crystalline copolyesters.²

Orientation Index for B/E/M Terpolymer Ribbons

The orientation index for four B/E/M terpolymer ribbons was calculated by eq. (3) based on the



Figure 3 Equatorial intensity of the oriented ribbon for B/E/M (65/30/5) terpolymer.



Figure 4 Meridional intensities of the oriented ribbons for the B/E/M (60/35/5), (65/30/5), (70/25/5), and (75/20/5) terpolymers.

	First Peak			Second Peak			Third Peak			
B/E/M	$rac{2 heta^{\mathrm{a}}}{(^{\mathrm{o}})}$	d (nm)	Width (°)	$2 heta^{\mathrm{a}}$ (°)	d (nm)	Width (°)	$rac{2 heta^{\mathrm{a}}}{(^{\mathrm{o}})}$	d (nm)	Width (°)	Persistence Length (nm)
Equatorial										
65/30/5	20.2s	0.440	4.8							
Meridional										
60/35/5	19.7w	0.451		27.2m	0.328	2.2	43.5s	0.208	1.9	5.01
65/30/5	20.0w	0.441		27.4m	0.325	2.1	43.6s	0.208	1.9	5.01
70/25/5	19.6w	0.453		27.8m	0.321	1.9	43.5s	0.208	2.0	4.76
75/20/5	19.5w	0.455	_	27.9m	0.320	1.6	43.5s	0.208	1.7	5.52

Table II The Peak Position (2θ and d spacing) and Peak Width at Half Height of Wide-Angle X-ray Diffraction for Drawn Ribbon of Poly[*p*-oxybenzoate (B)-ethylene terephthalate (E)-*m*-oxybenzoate (M)] B/E/M Terpolymers

^a Relative intensities are denoted as follows: s, strong; m, medium; w, weak.

azimuthal scans of the strongest meridional peaks at the Bragg angles of 43.5°. The orientation index will increase from 86.1, 86.7, 88.3 to 90.6% with the variation in B/E/M monomer ratios from 60/35/5, 65/30/5, 70/25/5 to 75/20/5. This indicates a strong orientation ability of the B unit in the terpolymers. In fact, a highly oriented fibrillar structure in the terpolymer ribbons has been observed easily with the naked eye. This result is substantially consistent with the suggested structure of the B/E/V terpolymers by X-ray diffraction, scanning electron, and polarizing microscopies.^{2-4,14}

CONCLUSIONS

FTIR and ¹H-NMR spectra of the B/E/M terpolymers have been analyzed and the assignments of the resonance peaks in the FTIR and ¹H-NMR spectra for the four terpolymers have been determined. As-drawn ribbons for B/E/M terpolymers exhibit a diffuse equatorial scattering due to extensive lateral disorder and two strong meridional reflections owing to a paracrystalline array of oriented chain macromolecules, indicative of a lack of three-dimensional crystalline order. The most intense equatorial and meridional maxima are at *d* spacings of 0.440 and 0.208 nm, respectively, which are almost independent of the terpolymer composition. The meridional maxima are aperiodic of one another. The linearity and orientation degree of the terpolymer chains in the as-drawn ribbons would increase with increasing B unit.

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