Synthesis and Characterization of Liquid Crystalline Polymers from *p*-Hydroxybenzoic Acid, Poly(ethylene terephthalate), and Third Monomers

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ABSTRACT: Eight new *p*-hydroxybenzoic acid (PHB) and poly(ethylene terephthalate) (PET) copolymers containing vanillic acid (VA), *p*-aminobenzoic acid, *m*-hydroxybenzoic acid, hydroquinone/terephthalic acid (TPA), bisphenol A/TPA, 1,5-naphthalenediol/TPA, 2,7-naphthalenediol/TPA, and 1,4-dihydroxyanthraquinone/TPA as eight third monomers with a variety of structural features were synthesized by melted-state copolycondensation and were characterized through a thermal analyzer, proton nuclear magnetic resonance, wide-angle X-ray diffraction (WAXD), and a scanning electron microscope (SEM). The experimental results show that PHB/PET/VA copolymers exhibit a faster polycondensation rate, lower melting temperature, and higher thermostability than do the other seven copolymers and third monomer-free PHB/PET polymers. The as-spun fibers derived from the PHB/PET/VA copolymers with different VA contents show tensile strengths, Young's moduli, and break elongations of 0.6–1.5 GPa, 28–67 GPa, and 7–9%, respectively. A highly oriented fibrillar structure in the PHB/PET/VA copolymer fibers was observed using WAXD and SEM. The most effective third monomer of the eight third monomers for an enhancing polycondensation rate and molecular weight of the PHB/PET polymers and for improving their thermal and mechanical properties is found to be vanillic acid (VA). © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 2129–2138, 1997

Key words: thermotropic liquid crystal; liquid crystalline polymer; copolyester; vanillic acid; synthesis; characterization; fiber

INTRODUCTION

Thermotropic liquid crystalline polymers are one of the most promising classes of new polymeric materials. They have exhibited the ability to be prepared into a high Young's modulus, high ten-sile strength fibers and biaxially oriented films as a result of rigid rod-like macromolecular chains with largely aromatic repeat units.[1–5] Among the well-known thermotropic liquid crystalline polymers such as Vectra, Xydar, Ultrax, and X7G, the X7G polymers based upon *p*-hydroxybenzoic acid (PHB)/poly(ethylene terephthalate) (PET) are considered to be the cheapest and the easiest to process at a relatively low melt temperature. It should be noted that the molten polycondensation reaction of *p*-acetoxybenzoic acid with PET has low rate and is also accompanied with a greater

Table I The Third Monomers Employed and the Resulting Constituent Units in the Copolymers

| Third Monomer	Constituent Unit	Abbreviation
p-Acetoxyvanillic acid	p-Oxy-m-methoxybenzoyl	VA
p-Acetaminobenzoic acid	p-Benzamide	PBA
m-Acetoxybenzoic acid	m-Oxybenzoyl	MHB
Hydroquinone diacetate	1,4-Phenylenedioxy	HQ
Bisphenol A diacetate	4,4′-Dioxydiphenylpropane	BPA
1,5-Diacetoxynaphthalene	1,5-Dioxynaphthalene	1,5-DHN
2,7-Diacetoxynaphthalene	2,7-Dioxynaphthalene	2,7-DHN
1,4-Diacetoxyanthraquinone	1,4-Dioxyanthraquinone	DHAQ
Terephthalic acid	Terephthaloyl	TPA

escape of oligomers from the polycondensate melts. These will result in the difficulty of controlling the polycondensation processes, the composition variation, and the relatively low molecular weight of the resulting PHB/PET polymers. There are many detailed studies concerning the PHB/PET polymers.[6,7] However, there are few reports concerning the copolycondensation modification of PHB/PET polymers through introducing third monomers with different structural features.

By copolymerizing the PHB/PET polymers with third monomers in order to accelerate the polycondensation reaction of p-acetoxybenzoic acid with PET, to enhance the molecular weight of the resulting polymers and thus to improve their properties, the eight readily available monomers having a variety of structural features listed in Table I were carefully selected as the third mono-

mers in this article. The copolycondensation time, structure, and properties of the resulting PHB/PET/third-monomer copolymers, such as molecular structure, supermolecular structure, thermal behavior, and mechanical property, are discussed.

EXPERIMENTAL

The copolymers were prepared in a three-neck glass flask on a 0.6 mol scale by melt copolycondensation following the procedure described previously.[8,9] During polycondensation, the acetic acid as a byproduct of polycondensation was collected volumetrically. The copolymers have the general structure
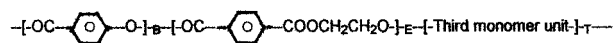
Table II Characterization of PHB/PET/Third Monomer (60/35/5) and PHB/PET (60/40) Copolymers

Third Monomer	Polycondensation Time (h)[a]	$[\eta]$ (dL/g)	Appearance	Spinnability	Fibrillarity[b]
VA	4.1	0.76	Milk white, luster	Very good	Very strong
PBA	5.3	0.67	Golden yellow	Medium	Strong
MHB	6.5	0.5[c]	Yellowish	Medium	Medium
HQ–TPA	5.5	0.71	Yellowish, luster	Good	Strong
BPA–TPA	7.0	0.38	Milk white, lusterless	Bad	Weak
DHAQ–TPA	7.5	0.35	Brown, lusterless	Good	Weak
1,5-DHN–TPA	4.5	0.97	Golden yellow, luster	Medium	Strong
2,7-DHN–TPA	4.6	0.81	Brownish, lusterless	Medium	Strong
PHB/PET (60/40)	6.0	0.60	Yellowish, luster	Medium	Medium

[a] Polycondensation time is the entire period which the polycondensation underwent in a vacuum.
[b] Strong fibrillarity is good or bad, depending on the specific case. The highly oriented fine fibrils might directly serve as a reinforcing short fiber in a fiber-reinforced composite system.
[c] Partially soluble.

Table III   Characterization of PHB/PET/Third Monomer Copolymers and PHB/PET Polymers with Higher PHB Contents

Copolymer	Polycondensation Time (h)	$[\eta]$ (dL/g)	Spinnability	Fibrillarity
PHB/PET/VA				
65/30/5	4.0	0.87	Very good	Very strong
70/25/5	3.8	1.02	Good	Very strong
PHB/PET/PBA				
65/30/5	5.1	0.83	Good	Strong
70/25/5	4.7	0.88[a]	Good	Strong
PHB/PET/MHB				
65/30/5	6.3	0.72[a]	Medium	Medium
70/25/5	6.0	0.82[a]	Good	Strong
PHB/PET				
65/35	5.5	0.60	Medium	Medium
70/30	5.0	0.91	Good	Strong
75/25	4.7	0.88	Good	Strong

[a] Partially soluble.

For high-resolution nuclear magnetic resonance (NMR) spectra, 2 wt % solutions of the copolymers in deuterated trifluoroacetic acid (TFA) were made. ^{1}H-NMR spectra were measured at 25°C on a Bruker AM-400 NMR spectrometer operating at 400 MHz. The intrinsic viscosity $[\eta]$ of
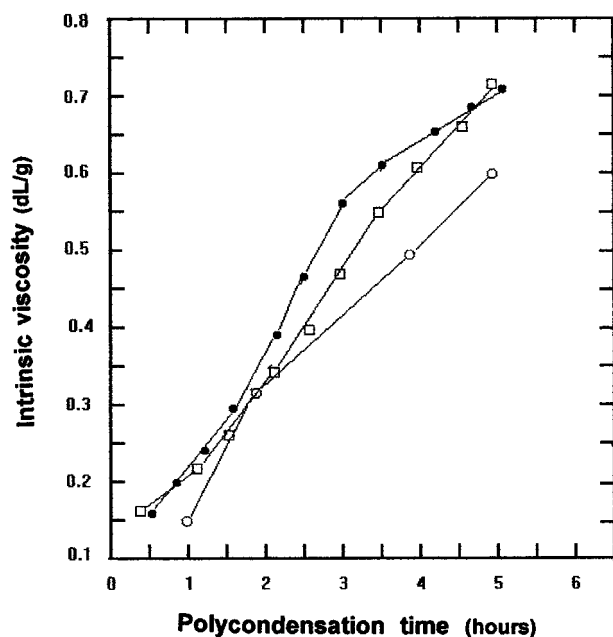

Figure 1 Intrinsic viscosity vs. copolycondensation time relationship for the copolymers with PHB/PET/VA molar ratios: (○) 6/40/0; (●) 60/39/1; (□) 60/36.5/3.5.

the copolymers was measured with an automated Ubbelohde viscometer thermostatted at 30°C with a concentration of 5 g/L in phenol/symtetrachloroethane (50/50 vol).

Thermal behavior experiments were performed using a DuPont Instrument 9900 computer/thermal analyzer. Thermal transitions were determined in the temperature range from 25 to 400°C with a heating rate of 20°C/min at a nitrogen flow of 50 mL/min. Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves were obtained under the following conditions: The nitrogen flow was kept constant at 50 mL/min; the sample size was about 25 mg and the heating rate was 5°C/min.

An Instron universal tester Model 1122 was used to investigate the stress–strain behavior of the copolymer fibers. A gauge of 20 mm, a strain rate of 500 mm/min, and a temperature of 20°C were used for this study. The tear section of the oriented as-spun fibers was observed by scanning electron microscopy (SEM) in a Cambridge Stereoscan type 4. The wide-angle X-ray diffraction (WAXD) measurements of the as-spun fibers were performed on a Rigaku 3015 X-ray diffractometer with Ni-filtered CuKα radiation at a scanning rate of 4°/min. The orientation index (OI) was calculated from azimuthal scans of the meridional peak at a diffraction angle of 43.5° using the following equation:
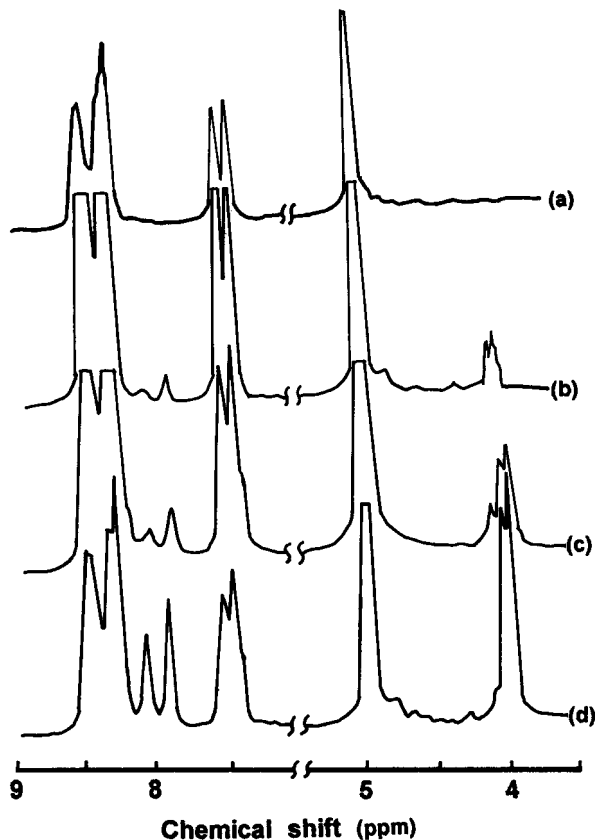
$$OI = [(180 - H)/180] \times 100\%$$

Figure 2 ^{1}H-NMR spectra at 400 MHz in trifluoro-acetic acid for the copolymers with the following PHB/PET/VA molar ratios: (a) 60/40/0; (b) 60/35/5; (c) 50/35/15; (d) 33/33/34.

where the H is the peak width at half-maximum of the scanning curves. WAXD patterns of the oriented fibers were taken with a flat-plate camera.

RESULTS AND DISCUSSION

Synthesis of Third Monomer-Containing Copolymers

The vanillic acid (VA), p-aminobenzoic acid (PBA), m-hydroxybenzoic acid (MHB), hydroquinone terephthalic acid (HQ–TPA), bisphenol A (BPA)–TPA, 1,5-dihydroxynaphthalene (1,5-DHN)–TPA, 2,7-dihydroxyanphthalene (2,7-DHN)–TPA, and 1,4-dihydroxyanthraquinone (DHAQ)–TPA polycondensation monomers with different structural features shown in Table I were selected as the third monomers for modifying the PHB/PET polymers. The content of the third monomers in the copolymers was kept at

5 mol %. Apparently, the third monomers may replace 5 mol % PET or 5 mol % PHB in the PHB/PET polymers. All the aforementioned copolymers exhibit a typical stir opalescence and color nematic liquid crystal texture upon melting an elevated temperature on a polarizing microscope,[8] i.e., the copolymers containing the third monomer units, as expected, are thermotropic liquid crystalline polymers, just like the PHB/PET polymers. The copolycondensation time and properties of the copolymers are listed in Tables II and III. In spite of the deterioration of the properties of some copolymers, most of the third monomers, such as VA, 1,5-DHN–TPA, 2,7-DHN–TPA, PBA, and HQ–TPA, can be used to effect the improvement of the properties of the PHB/PET polymers. Note that the VA shows the best effect. The detailed changes of the properties with the introduction of the third monomers are as follows:
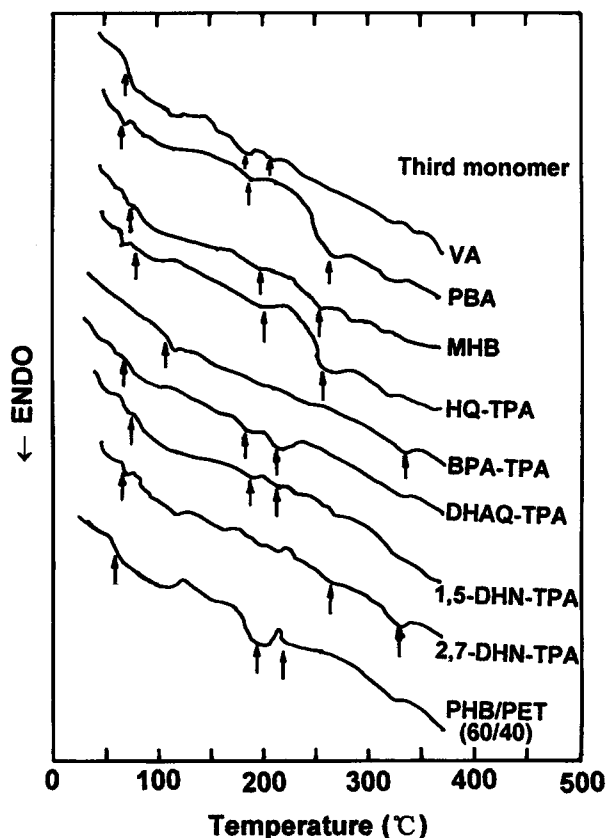
(i) Incorporating 5 mol % MHB, especially

Figure 3 DSC scans taken at the heating rate of 20°C/min for the copolymers containing 60 mol % PHB unit and different third monomers of 5 mol %.
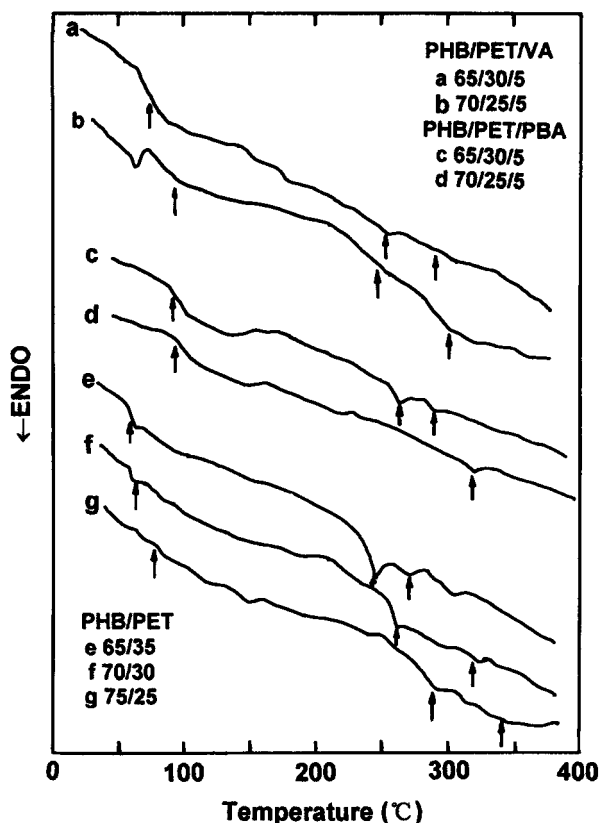
Figure 4 DSC scans at 20°C/min heating rate for the copolymers with higher PHB contents.

incorporating 5 mol % BPA–TPA or DHAQ–TPA in the PHB/PET (60/35) and (70/25) polymers, will prolongate the time when the Weissenberg effect occurs and will decrease the copolycondensation rate and the intrinsic viscosity [η] of the copolymers as compared with the PHB/PET (60/40) and (70/30) polymers, which brings about the dull lusters and low tensile strength of the copolymers.

The lower reactivity of the MHB may be due to the inductive effect, the shared effect, and the spatial hindrance between the carboxyl and the *meta*-acetoxyl groups in the MHB, which causes the break of the —CO—O— bond, which results in the difficulty to copolymerize. The lowest reactivity of the DHAQ and BPA is probably due to the huge spatial hindrance of the anthraquinone structure around the acetoxyls in the DHAQ and of the isopropyl group in the BPA.

It was found from the synthetic experiments with unaided eyes that many of the oligomers escaped from the copolycondensate melts during the initial stage of the PHB/PET/MHB or PHB/PET/DHAQ–TPA copolycondensation, just like the 60/40 PHB/PET binary copolycondensation, resulting in the composition changes of the copolymers. Note that the incorporation of 5 mol % MHB in the PHB/PET (65/30) polymer will increase the intrinsic viscosity compared with the PHB/PET (65/35) polymer, as listed in Table III.

(ii) The incorporation of 5 mol % PBA or HQ–TPA in the PHB/PET (60/35) and (65/30) polymers may accelerate slightly the copolycondensation of the copolymers and even increase slightly the intrinsic viscosity of the resulting copolymers as compared with the PHB/PET (60/40) and (65/35) polymers listed in Tables II and III. Differing from the PHB/PET/MHB or PHB/PET/DHAQ–TPA systems, only a few of the oligomers escape from the copolycondensate melts during the copolycondensation of the PHB/PET/PBA or PHB/PET/HQ–TPA.

(iii) Adding 5 mol % 1,5-DHN–TPA or 2,7-DHN–TPA to the PHB/PET (60/35) polymers will accelerate the copolycondensation

Table IV Thermal Transition of PHB/PET/Third Monomer (60/35/5) Copolymers and PHB/PET (60/40) Polymer

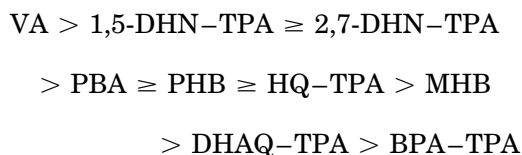| Third Monomer	VA	PBA	MHB	HQ–TPA	BPA–TAP	DHAQ–TPA	1,5-DHN–TPA	2,7-DHN–TPA	PHB/PET (60/40)
T_g (°C)	69	68	73	76	100	69	75	70	64
T_m (°C)	183	190	200	201	344	188	194	264	196
	207	261	253	257		215	215	340	220
ΔHm (J/g)	0.94	2.21	0.99	2.76		2.97	0.65	1.0	4.4

Table V   Thermal Transition of PHB/PET/VA and PHB/PET/PBA Copolymers and PHB/PET Polymers with Higher PHB Contents

Copolymer	PHB/PET/VA		PHB/PET/PBA		PHB/PET		
	65/30/5	70/25/5	65/30/5	70/25/5	65/35	70/30	75/25
T_g (°C)	74	86	78	79	65	71	77
T_m (°C)	255, 286	249, 301[a]	263, 285	319[a]	243, 270	260, 319[a]	280, 340[a]

[a] Very weak endotherm.

and also increase the intrinsic viscosity of the resulting copolymers compared with the PHB/PET (60/40) polymer as shown in Table II, which may be attributed to the changes of the chain rigidity of the copolymers in which bigger DHN–TPA units replace partially the PET or PHB units. These 1,5-DHN and 2,7-DHN unit-containing copolymers exhibit very strong fibrillarity and high tensile strength.[10] Like the PHB/PET/PBA copolymers system, there is an escape of only a few oligomers during the entire copolycondensation process of the PHB/PET/DHN–TPA. It is apparent that 1,5-DHN–TPA and 2,7-DHN–TPA are both better third monomers, improving the PHB/PET polymers.

(iv) The incorporation of 5 mol % VA into the PHB/PET (60/35), (65/30), and (70/25) polymers has several advantages in that the copolycondensation rate is significantly speeded up, the escape of the oligomers from the copolycondensate melts is largely reduced, and the intrinsic viscosity of the resulting copolymers is increased, as compared with the PHB/PET (60/40), (65/35), and (70/30) polymers listed in Tables II and III. This may be due to the interaction between the acetoxyl and *ortho*-methoxyl groups in the *p*-acetoxy-*m*-methoxybenzoic acid. These VA-containing copolymers show better solvancy in the organic solvents, better fluidity of liquid crystalline melts, higher orientation of the molecular chains, better fiber-forming ability, higher fibrillarity, and higher tensile strength.

(v) Summarizing, the order of the copolycondensation reactivity of the above-mentioned eight third monomers in the PHB/PET polymer system is

$$VA > 1,5\text{-DHN–TPA} \geq 2,7\text{-DHN–TPA}$$

$$> PBA \geq PHB \geq HQ\text{–TPA} > MHB$$

$$> DHAQ\text{–TPA} > BPA\text{–TPA}$$

It can be concluded that the VA is the best third monomer for improving the PHB/PET binary polymers.

Copolycondensation Kinetics of the PHB/PET/VA Copolymer System

To investigate the copolycondensation kinetics, the mixtures of the PHB/PET/VA monomers were maintained at 275°C under a dry nitrogen flow for about 30 min and then under a vacuum (20 Pa). It was found that the byproduct of copolycondensation, i.e., acetic acid, began to liberate after the copolycondensation time of 9 min under nitrogen. When a vacuum was applied, a large amount of acetic acid and a small amount of the oligomers would be liberated rapidly and the molecular weight of the copolymers increased rapidly, suggesting that the copolycondensation in the PHB/PET/VA system is similar to the typical polycondensation. The variation of the intrinsic viscosity of the PHB/PET/VA copolymers with copolycondensation time under a vacuum is shown in Figure 1. It can be seen that the intrinsic viscosity of the VA-containing copolymers increases with a higher speed than that of the VA-free copolymers with increasing the copolycondensation time from 2 to 5 h. Furthermore, the intrinsic viscosity of the PHB/PET/VA (60/36.5/3.5) copolymer with the largest VA content increases at the highest speed for the latter period (3–5 h) of the copolycondensation as a result of the higher reactivity of the VA monomer.
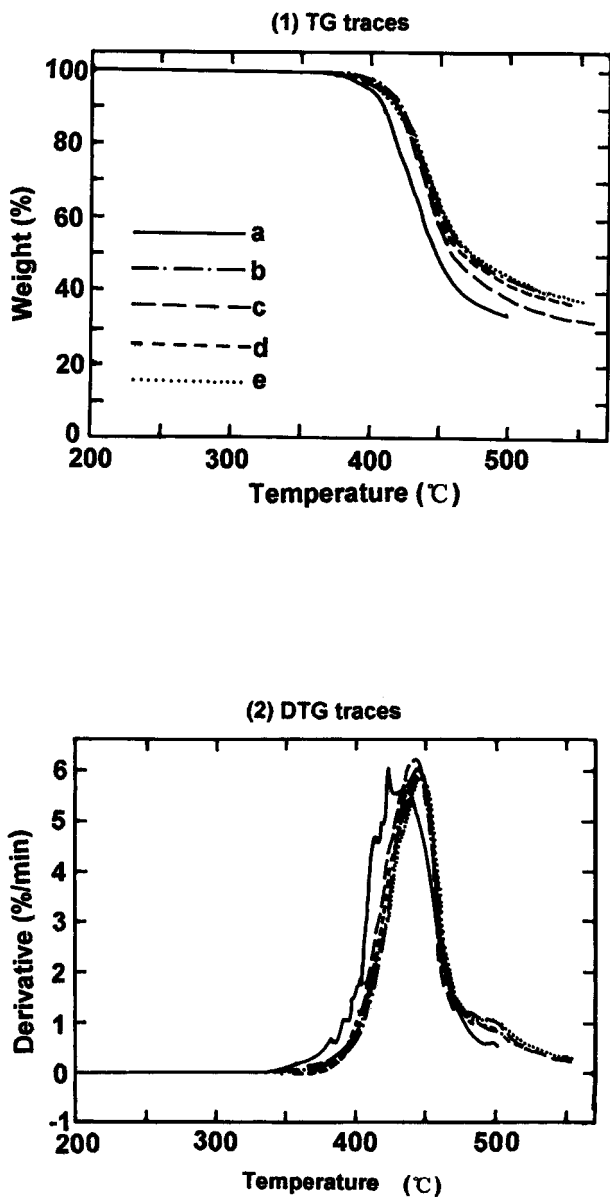
(1) TG traces

(2) DTG traces

Figure 5 (1) TG traces and (2) DTG traces at the heating rate of 5°C/min for the copolymers with the following PHB/PET/VA molar ratios: (a) 60/40/0; (b) 60/39.95/0.05; (c) 60/38.5/1.5; (d) 60/37.5/2.5; (e) 60/35/5.

^{1}H-NMR Characteristics of the PHB/PET/VA Copolymers

^{1}H-NMR spectra of all the obtained PHB/PET/VA copolymers are similar. Typical ^{1}H-NMR spectra for the copolymers are shown in Figure 2. Most signals of three comonomer units are well separated and allow a more accurate assignment of the signals. The signals at 4.0–4.1, 4.9, 7.3–7.4, and 8.3–8.5 ppm are assigned to the CH$_3$O— protons in the VA unit, —OCH$_2$CH$_2$O— protons in the PET unit,
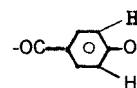
protons in the PHB unit, and
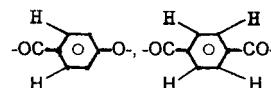
protons in the PHB and PET units, respectively.[8,11] By comparing the ^{1}H-NMR spectra of the PHB/PET/VA copolymers with those of the PHB/PET polymers, it can be concluded that the signals appearing at 7.9 and 8.1 ppm are probably due to the phenyl protons in the VA unit because their peak intensities become stronger with increasing the VA content in the copolymers. The doublet splitting of the phenyl proton signals is the result of the PHB–PHB and PHB–PET sequence isomerism, indicating the expected randomness of the copolymer sequences. It can be found from Figure 2 that the peaks corresponding to the protons in the carboxyl and acetoxyl groups of the PHB and VA monomers are absent in the ^{1}H-NMR spectra of the copolymers. The absence of these protons confirms the formation of the copolymers having a higher molecular weight.

Thermal Transition of the Eight Copolymers

The DSC thermograms of the eight copolymers in the first heating cycle are shown in Figures 3 and

Table VI   TG and DTG Results at 5°C/min Heating Rate in Nitrogen for the PHB/PET/VA Copolymers

PHB/PET/VA	60/40/0	60/39.95/0.05	60/38.5/1.5	60/37.5/2.5	60/35/5
T_d (°C)[a]	403	417	416	417	417
$T_{d_{max}}$ (°C)[b]	426	445	443	444	445
Char residue[a] at 450°C (wt %)	50	60	59	59	63

[a] From the TG curves.
[b] From the DTG curves.

Table VII   Orientation Index (OI) and Tensile Properties of the As-spun fibers for the PHB/PET/VA Copolymers with Different VA Contents

PHB/PET/VA	$[\eta]$ (dL/g)	OI (%)	Tenacity (GPa)	Modulus (GPa)	Elongation (%)
60/40/0	0.57	84	0.32	30	7
60/39.95/0.05	0.64	88	0.89	28	8
60/39.5/0.5	0.60	89	1.21	34	7
60/39/1	0.70	87	0.61	42	8
60/38.5/1.5	0.73	89	1.50	48	9
60/37.5/2.5	0.71	88	0.60	33	8
60/35/5	0.75	86	1.35	67	9

4. Eight DSC curves of the copolymers containing the third monomer units show very small exotherms above the glass transition region and also show very small endotherms coinciding with the onset of the flow and formation of nematic mesophases, but two PHB/PET polymers show small endotherms arising from the crystallite melting, which coincided with the onset of the flow. Obviously, the third monomers will reduce the crystallinity of the PHB/PET polymers even at their content of no more than 5 mol %, as shown in Tables IV and V. The introduction of BPA–TPA, HQ–TPA, and 2,7-DHN–TPA to the PHB/PET (60/35) polymer and of PBA to the PHB/PET (65/30) and (70/25) polymers will enhance the glass transition and melting temperatures compared with the PHB/PET (60/40), (65/35), and (70/30) polymers. This might be attributable to the enhancements of the copolymer chain rigidity or spatial hindrance as a result of the incorporation of the BPA, HQ, 2,7-DHN, or PBA units. On the contrary, incorporating VA to PHB/PET (60/35) and (70/25) polymers will lower their melting temperatures, as shown in Tables IV and V, probably owing to the increase of the polymer chain flexibility as a result of the incorporation of the methoxyl groups on the VA units. Apparently, this is of benefit to the melt processing of the copolymers. A study on the systematic influence of the third monomers on the thermal properties of the PHB/PET polymers is being carried out in our laboratory.

Thermostability of the PHB/PET/VA Copolymers

Figure 5 shows the TG and DTG traces for the PHB/PET/VA copolymers. The corresponding numerical data are listed in Table VI. It is noted that all the copolymers exhibit a similar pattern

of decomposition with no significant weight loss below 416°C under nitrogen. The thermostability of the copolymers will increase slightly with increase of the VA content from 0 to 5 mol %. This enhancement of the thermostability is probably due to the enhancement of macromolecular chain rigidity as a result of the increase of the VA content. It follows that the VA-containing copolymers have good thermostability for melt processing below 410°C. Note that these copolymers are somewhat less thermostable than are wholly aromatic
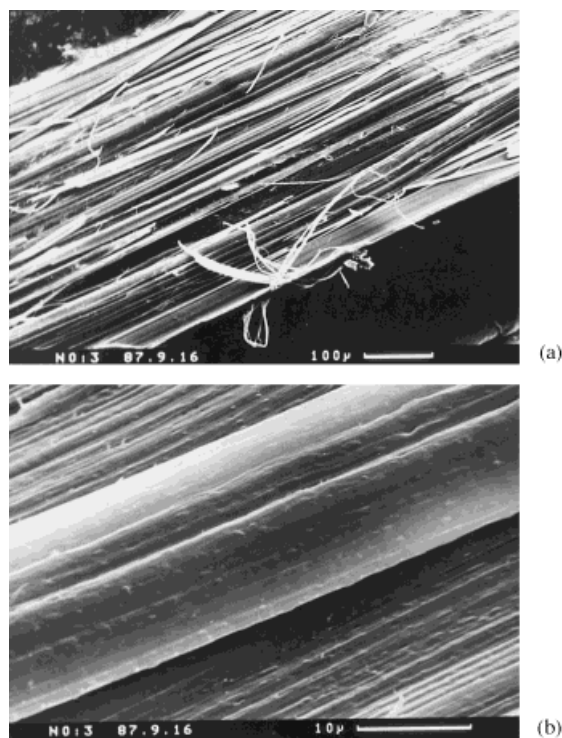

Figure 6   SEM micrographs of the highly oriented fibrillar texture of the PHB/PET/VA (60/35/5) copolymer at magnifications indicated by the scale markers.

PHB/2,6-hydroxynaphthoic acid binary copoly-mers and the PHB homopolymer.[12,13]

Mechanical Properties and Structure of PHB/PET/Third Monomer Copolymer Fibers

The five copolymers with VA, PBA, HQ–TPA, 1,5-DHN–TPA, and 2,7-DHN–TPA as the third monomer exhibit better spinnability, higher fibrillarity, and higher tensile strength in comparison with the copolymers containing MHB, DHAQ–TPA, BPA–TPA, or PHB/PET (60/40) polymers, probably due to the difference in their molecular weights. Typically, Table VII summarizes the tensile properties of the as-spun fibers from PHB/PET/VA copolymers. The fibers have a tensile strength of 0.6–1.5 GPa, Young's modulus of 28–67 GPa, and elongation at break of 7–9%. Apparently, the copolymers containing a VA unit of no more than 5 mol % exhibit higher mechanical properties than those of the VA unit-free PHB/PET polymers, which is attributed to the changes of the sequence distribution and chain rigidity of the copolymers after the incorporation of the VA unit. On the other hand, the methoxyl group with a certain movability will endow the copolymer liquid crystalline melts with higher fluidity and better processability. Consequently, the VA unit-containing copolymers with these features will be easily processed into high-performance fibers, showing a higher chain orientation, as shown in Table VII and Figures 6 and 7. The fibers of the VA-containing copolymers exhibit a higher orientation index (Table VII), which is confirmed by the typical highly oriented fibrils with about a 16 μm diameter observed in Figure 6. X-ray diffraction patterns for PHB/PET/VA (60/40/0) and (60/35/5) copolymer fibers are clearly anisotropic, which is characteristic of an oriented nematic phase.[14] Two meridional reflections can also be seen from Figure 7, indicating that the fibers are highly oriented.[15,16]

CONCLUSIONS

A series of copolymers have been prepared by melt copolycondensation of p-acetoxybenzoic acid (PHB) and poly(ethylene terephthalate) (PET) with eight third monomers, respectively. Most of the third monomers selected in this study can effectively improve the properties of PHB/PET polymers, presumably due to the increase in the molecular weight and orientation of the copolymers as a result of the the incorporation of the third monomers. The copolymers containing vanillic acid (VA) as the third monomer require a shorter copolycondensation time and also exhibit a lower melting temperature, higher thermostability, better spinnability, stronger fibrillarity, and higher tensile strength and modulus than those of the other copolymers. The VA is the third monomer suitable for accelerating the copolycondensation reaction and for improving the properties of the PHB/PET polymers.
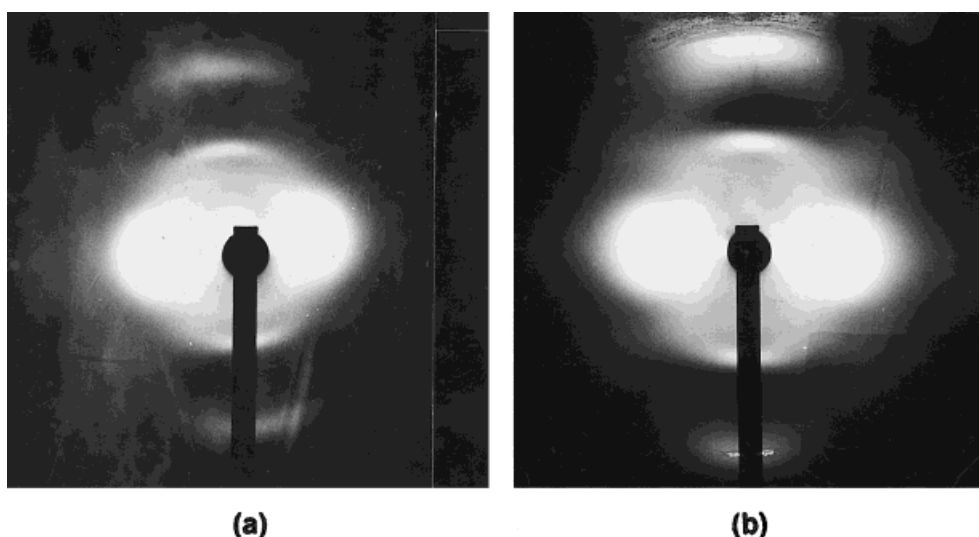

Figure 7   Wide-angle X-ray fiber diagrams of the as-spun fibers for the copolymers with the following PHB/PET/VA molar ratios: (a) 60/40/0; (b) 60/35/5.

REFERENCES

1. H. Sugiyama, D. N. Lewis, J. L. White, and J. F. Fellers, *J. Appl. Polym. Sci.,* **30,** 2329 (1985).
2. Tong Sun, Y. G. Lin, H. H. Winter, and R. S. Porter, *Polymer,* **30,** 1257 (1989).
3. X.-G. Li, G.-H. Guan, and T. Sun, *J. China Text. Univ. (Engl. Ed.),* **8**(1), 1 (1991).
4. S. S. Kim and C. D. Han, *J. Polym. Sci. Part B Polym. Phys.,* **32,** 371 (1994).
5. S. D. Hudson and A. J. Lovinger, *Polymer,* **34,** 1123 (1993).
6. W. J. Jackson, Jr. and H. F. Kuhfuss, *J. Polym. Sci. Polym. Chem. Ed.,* **14,** 2043 (1976).
7. V. A. Nicely, J. T. Dougherty, and L. W. Renfro, *Macromolecules,* **20,** 573 (1987).
8. X.-G. Li, PhD Dissertation, China Textile University, Shanghai, China, 1988.
9. X.-G. Li, M.-R. Huang, G.-H. Guan, and T. Sun, *Angew. Makromol. Chem.,* **227,** 69 (1995).
10. X.-G. Li, Z.-L. Zhou, X.-G. Wu, and T. Sun, *J. Appl. Polym. Sci.,* **51,** 1913 (1994).
11. H. J. Lader and W. R. Krigbaum, *J. Polym. Sci. Polym. Phys. Ed.,* **17,** 1661 (1979).
12. M. Y. Cao and B. Wunderlich, *J. Polym. Sci. Polym. Phys. Ed.,* **23,** 521 (1985).
13. X.-G. Li, M.-R. Huang, G.-H. Guan, and T. Sun, *Chin. J. Polym. Sci.,* **11,** 230 (1993).
14. R. J. Alonso, J. A. Puertolas, P. Davison, B. Martinez, J. I. Martinez, L. Oriol, and J. L. Serrano, *Macromolecules,* **26,** 4304 (1993).
15. X.-G. Li, M.-R. Huang, G.-H. Guan, and T. Sun, *Chin. Chem. Lett.,* **3,** 207 (1992).
16. X.-G. Li, M.-R. Huang, G.-H. Guan, and T. Sun, *J. Appl. Polym. Sci.,* **59,** 1 (1996).