Syntheses and Characterization of Poly(ethylene terephthalate) Modified with *p*-Acetoxybenzoic Acid

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ABSTRACT: Though the structure and properties of a copolyester of 40 mole % of polyethylene terephthalate (PET) and 60 mole % p-hydroxybenzoic acid (PHB) (PET/ 60PHB) and their blends have been well documented, no work has been reported in an open literature on the systematic investigation of the PET copolymers modified with broad range of *p*-acetoxybenzoic acid (PABA) composition as yet. In this study, several PETA-x copolyesters having various PABA compositions from 10 to 70 mole % were prepared by the melt reaction of PABA and PET without a catalyst, where x denotes the mole % of PABA. And the modified polyesters obtained were characterized by ¹H-NMR spectrophotometry, X-ray diffraction pattern, polarizing microscopy, thermal analysis, and rheometry. The anisotropic phase appeared when x is above 50 mole % of PABA, and especially for the x's of 60 and 70 mole %, the nematic liquid crystalline texture appeared clearly on the whole matrix. As the mole % of PABA increased, melting temperature, heat of fusion, crystalline temperature, degree of crystallinity, and the glass transition temperature of the modified PET were decreased, but the thermal stabilities of those copolyesters were increased. The dependence of melt viscosity on the shear rate for PETA-50 \sim 70 followed the typical rheological behavior of liquid crystalline polymers. Finally, it was concluded that the PETA-x copolyesters having compositions of higher than 50 mole % of PABA exhibit the behavior of thermotropic liquid crystalline polymers. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1707-1719, 1999

Key words: modified poly(ethylene terephthalate); copolyester; *p*-acetoxybenzoic acid; thermotropic liquid crystalline polymer

INTRODUCTION

Thermotropic liquid crystalline polyesters (LCPs) are reputed to be the second-generation engineering plastics and many kinds of LCPs have been reported and developed.¹⁻⁵ The molecules of LCPs are easily oriented by shear strain and elongational flow during processing, and form multi-

layer structures whose layers have various orientation states.^{6,7} Moreover, LCPs have been studied because of their inherent high stiffness and strength, high use temperature, excellent chemical resistance, low melt viscosity, and low coefficient of expansion. Because of these excellent properties, the blending of LCP with conventional polymers could result in materials that can be used as an alternative for short fiber reinforced thermoplastic composites; the in situ composites have many potential advantages as compared with short fiber reinforced polymers.⁸

These LCPs can be prepared by conventional techniques, i.e., solution condensation, interfacial

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Materials	Structure	Melting Point (°C)	M_w	Source
		015 017	190 10	A11.:.1
<i>p</i> -nyuroxy benzoic acia	0	$210 \sim 211$	136.12	Alunch
Acetic anhydride		-73 (bp: 140) ^a	102.09	Aldrich
Acetic acid	O ∥ CH₃−C−OH	16 (bp: 117)	60.05	Janssen
Sulfuric acid	$\mathrm{H}_2\mathrm{SO}_4$	3 (bp: 280)	98.08	Kukje Chem.
<i>n</i> -Butyl acetate	$\rm CH_3COO(\rm CH_2)_3\rm CH_3$	bp: 127	116.16	Janssen

Table I The Structure and Specification of Materials Used to Synthesize p-Acetoxybenzoic Acid

^a bp, boiling point (°C).

condensation, or melt condensation processes. For example, one of the well-known methods to prepare thermotropic polyesters is to modify polyethylene terephthalate (PET). Its processing is by the reaction of p-acetoxybenzoic acid (PABA) with PET. The first indication of the liquid crystalline character in polyesters comes from Jackson and Kufuss at Tennessee Eastman, who synthesized copolyesters from PET and *p*-hydroxy benzoic acid (PHB).⁹⁻¹¹ PABA is the same category with PHB in a sense because PABA is prepared by acetylation of PHB with acetic anhydride. The liquid crystalline character of the copolyesters also has been published by other workers.¹²⁻¹⁶ Most of the LCPs, obtained by the melt reaction of PET and PABA or PHB, contain 60 mole % of PABA or PHB (designated here as PET/60PABA or PET/60PHB). The structure of the PET/ 60PABA copolymer, though expected to be a block copolymer, was found to be random by NMR spectrophotometry⁹ and X-ray diffraction studies.¹⁷ Though the structure and properties of PET/ 60PABA or PET/60PHB and their blends have been well documented,¹⁸⁻²⁵ no work has been reported in an open literature on the systematic investigation of the PET copolymers modified with broad range of PABA composition as yet. The object of the present work was, therefore, to synthesize several copolyesters having various PABA compositions from 10 to 70 mole % and to systematically characterize the structure, thermal behaviors, and rheological behaviors of the copolyesters.

EXPERIMENTAL

Materials

The modified polyesters were prepared by reaction of PABA and PET as described in solid state polymerization by Jackson and Kufuss in 1974.¹¹ PABA was prepared by acetylation of *p*-hydroxybenzoic acid with acetic anhydride in acetic acid, followed by recrystallization from *n*-butyl acetate. The structures of materials used to synthesize PABA are listed in Table I. The structure of PABA was identified by the ¹H-NMR spectrum. PET of commercial grade was supplied by Sunkyung Industry Co. (Korea). Their characteristics are tabulated in Table II. Thermal properties were measured by Perkin-Elmer differential scanning calorimetry (DSC7). Inherent viscosity (IV) was obtained by the Ubbelohde viscometer at 150°C, in ortho-chlorophenol at the concentration of 0.5 g/dL.

Material	PET	<i>p</i> -Acetoxybenzoic Acid
T_{m} (°C)	250	189
$T_{c}^{m}(^{\circ}\mathrm{C})$	167	_
T_{q}° (°C)	80	_
$\tilde{M_n}$ M_{\cdots}	26,000 52,000	$180.16(M_w)$
IV (dL/g)	0.82	—

Table IIThe Characteristics of p-Acetoxybenzoic Acid and PET

Table III	The Sample Notation and Recipe of
Preparati	on of <i>p</i> -Acetoxybenzoic Acid
Modified 1	PET

Sample Notation	Mole % of PABA	PABA (g)	PET (g)
PETA-10	10	15.1	144.9
PETA-20	20	30.4	129.6
PETA-30	30	45.9	114.1
PETA-40	40	61.5	98.5
PETA-50	50	77.4	82.6
PETA-60	60	93.5	66.5
PETA-70	70	109.8	50.2

Preparation of PET Modified with PABA

A mixture of *p*-acetoxybenzoic acid (10-70 mole %) and PET particles (90-30 mole %) was placed in a 500-mL flask equipped with a stainless steel stirrer and a short head with an inlet and an outlet for nitrogen. It is very important to maintain the reaction temperature and pressure so that the setup for these reactions needs high temperature and vacuum state endurance materials. The nitrogen outlet was connected to a glass tube (distillation column), which led to a receiver with provision for applying vacuum. After the reaction flask was evacuated and purged with nitrogen three times to remove all the air, it was heated under reduced pressure (0.1 mm Hg) in a metal bath at 110°C to dry the reactants. The flask was removed from the bath, and the bath was heated to 275°C. The flask was then placed back in the bath; while the contents was stirred in a nitrogen atmosphere, acetic acid was slowly distilled out. After about 30 min when the system becomes viscous, a vacuum of 0.1 mm Hg was applied with stirring for about 4 h at 275°C. The mechanism expected for this reaction is summarized in Figure 1.The sample notation and the mole % of the prepared modified polyesters are listed in Table III. The copolyesters obtained in this study con-



where, (x+x') is the mole% of PET, (y+y') is the mole% of PABA

Figure 1 The expected reaction mechanism of PET with p-acetoxybenzoic acid.



Figure 2 ¹H- NMR spectrum of PETA-60.

sist of poly(*p*-acetoxybenzoic acid) (PPABA), PET, and PABA/PET units in the main-chain structure. The PABA/PET unit is raised up by the transesterification reaction, that is, the condensation reaction by vacuum between PABA and PET moieties, shown in Figure 1. For convenience, the copolyesters are designated as PETA-*x*, where *x* means the mole % of PABA.

Characterization

NMR Spectrophotometry

¹H-NMR spectra were recorded on trifluoroacetic acid solutions of the modified copolyesters with a Bruker 300 MHz NMR spectrophotometer. For the measurement, a 1.5-mg sample was dissolved in 0.5-mL solvent (deutriated fluoroacetic acid) in a 5-mL tube at 25°C. The sequence distribution for the PABA-modified copolyester can be described in terms of a probability model by the proton spectra of a solution. Typically, Figure 2 illustrates ¹H-NMR spectrum of the PETA-60 copolyester.

X-ray Diffraction

X-ray diffraction patterns were obtained with the Rigaku Denki X-ray diffractometer using Nickelfiltered CuK α radiation (30 kV, 20 mA). The modified copolyesters were ground to form a powder sample. The crystallinities of samples were calculated using the following equation^{26,27}:

% crystallinity =
$$\frac{I_c}{I_a + I_c} \times 100$$

where I_c is the intensity of the crystalline component and I_a is the intensity of the amorphous component.

Optical Microscope

The optical observation was made with the Leitz Ortholux Polarizing Microscope equipped with a heating stage (Mettler FP-2) in the temperature range 20–300°C. The sample was prepared by heating a piece of the glass plate 18×18 mm in size at 270°C, and then pressing the melts with another piece of hot glass plate, so that it was formed into a sandwich, keeping the thin film inside. The sandwich was then quenched at the atmosphere condition. The photographs of the films were taken by increasing the temperature of the hot stage under the polarizing microscope with incident polarizing light at 90° (magnification 320).

Thermal Analysis

The thermal analysis was performed under nitrogen with a heating rate of 10°C/min using a Perkin Elmer DSC and a Perkin Elmer Thermal Analyzer. In the TGA measurement, the weight change of a material was measured at a heating rate of 10°C/min. Glass transition temperatures (T_g) were determined with a Thermal Stimulated Current (TSC) Spectrometer (Solomat). Films of about 0.2 mm thick were pressed by hand at elevated temperatures using aluminum foil and the released films were cut to about 10-mm² area for TSC measurements. The TSC spectra were obtained by polarizing the film from polarizing temperature T_p (generally above T_g) and continuing to polarize down to the quench temperature. The depolarization was then measured at a heating rate of 7°C/min.

Dynamic Mechanical Measurement

Viscoelastic properties were measured on a Rheometrics Mechanical Spectrometer (RMS), using cone & plate between 240 and 260°C. Strain was fixed at 30%. A cone of radius 1.24 cm and cone angle of 0.1 radian were used. The cone & plate measurements are commonly used for the low melt viscosity, while the parallel plate geometry is used to measure viscoelastic properties of high melt viscosity samples. Before measurements, the modified copolyester powders were dried in a vacuum oven at 105°C for 24 h. The powder samples were directly poured on the disc in the RMS test chamber. During the measurement, nitrogen flow was used to reduce sample oxidation.

RESULTS AND DISCUSSION

Polymer Structure by NMR Spectrophotometry

It was reported that for the sequence distribution of the PET/60PHB copolyester by ¹H-NMR spectrophotometry,⁹ the PHB unit has a random distribution in the copolymer.^{28,29} Nicely et al. also



Figure 3 Characteristic peak change with the mole % of PABA in the PETA-*x* copolyester.

PABA mole %	Degree of Crystallinity (%)	$T_g^{}_{(^{\circ}\mathrm{C})^{\mathrm{a}}}$
0	50 5	00.0
0	53.7	83.0
10	44.4	83.2
20	_	84.1
30	30.4	54.6
40	21.0	43.0
50	_	48.3
60	_	49.8
70	23.0	52.8
	PABA mole % 0 10 20 30 40 50 60 70	PABA mole % Degree of Crystallinity (%) 0 53.7 10 44.4 20 30 30.4 40 21.0 50 60 70 23.0

Table IV Degree of Crystallinity and Glass Transition Temperature (T_g) of PETA-x Copolyesters

^a Data are obtained by TSC.

studied the sequence distribution of the PET/ 60PABA copolyester by NMR spectrophotometry.³⁰ According to their analysis, the spectra of these types provide direct measures of the probability of a PABA unit being bonded to another PABA or to a PET unit.³⁰ Figure 2 shows the proton NMR spectra at 300 MHz with the assignments of the absorptions for PETA-60. In Figure 2, 7.535 and 7.448 ppm indicate the unit of PABA-PABA and PABA-PET, respectively. The ratio of the peak lengths of the PABA-PET bond to the PABA-PABA bond is 1.72 in Figure 2. This means that PABA-PET units have more seguence than PABA-PABA units due to the transesterification reactions by the vacuum stage in the reaction processes. And it can be seen in Figure 3 that the intensities of PABA-PET bond tend to be stronger than PABA-PABA as the mole % of PABA in PET increase. From the results above, it can be predicted that the reaction between PET and PABA follows the mechanism in Figure 1.

X-ray Diffraction Patterns

The physical and mechanical properties of polymers are profoundly dependent on the degree of crystallinity. It is well known that the degree of crystallinity can be determined by a variety of experimental techniques such as X-ray diffraction (XRD), DSC, density measurements, IR spectroscopy, and NMR spectroscopy.^{32–35} In this work, XRD was applied to determine the degree of crystallinity. To calculate the degree of crystallinity of the polymers, it is very important to divide the patterns of XRD by crystalline phase and amorphous phase since imperfections in crystals are not easily distinguished from the amorphous phases. The diffraction patterns were obtained for PETA-*x* copolyesters at the Bragg angles between $2\theta = 10^{\circ}$ and $2\theta = 30^{\circ}$, as a measure of the degree of crystallinity of samples using wide-angle X-ray spectrometry. The degree of crystallinity of PETA-*x* copolyesters are listed in Table IV. By the addition of PABA into PET, the degree of crystallinity is decreased because of the disrupting order of the PET-PABA copolymer by the presence of PABA. As shown in Figure 4, the X-ray diffraction patterns of PETA-*x* copolyesters are quite different in the relative intensities and the position of 2θ from that of the PET base polymer.

When 10 mole % of PABA was incorporated into PET, the patterns and the relative intensities of that are almost the same as PET base polymer. As the mole % of PABA is increased above 20 mole %, it is seen that a new peak around $2\theta = 20^{\circ}$ appears more clearly. This peak at around 2θ $= 20^{\circ}$ is the characteristic peak of poly(p-acetoxybenzoic acid) [PPABA]. In addition, new sharp peaks are observed at around 23° and 29° along with the characteristic peaks of PPABA at 2θ $= 19.8^{\circ}$. From those facts it can be said that the patterns shown in the PET-rich composition are mainly due to PET, which possesses an isotropic property. However, in the PABA-rich composition that has an anisotropic property, the patterns of the copolyesters of PETA-40 through PETA-70 are mainly ascribed to the PABA. Those results



Figure 4 XRD patterns of PETA-x copolyesters.





(b)

Figure 5 Polarizing micrographs of (a) PETA-30 and (b) PETA-40.

are consistent with the following polarizing micrograph data in the points that these polymers exhibit the thermotropic liquid crystalline behavior at the compositions above 40 mole % of PABA in PET-*x* copolyesters.

Polarizing Optical Micrographs

Liquid crystalline polyesters have typically colored streak textures that are consistent with the anisotropic mesomorphic phases in the polarizing microscope. The PETA-10 and PETA-20, reacted with a small amount of PABA, did not show any symptom to liquid crystal behavior above the melting temperature (T_m) . That is, the spherulite of PET at room temperature is completely disappeared when the temperature is elevated above T_m . PETA-30 shows peculiar morphology of some crystals not melted above T_m [Fig. 5(a)].Then, the crystals existing at that temperature began to disappear at 275°C, and completely disappeared at 280°C. It can be explained by the fact that the

crystals are composed of a PET–PABA unit that melted at high temperature about 280°C and have so low molecular weight. The PETA-40 shows more distinct crystal shapes than PETA-30 [Fig. 5(b)]. In comparison with PETA-30, the crystals made at high temperature above 290°C were not melt. This means that the liquid crystalline behavior begins to be observed when about 40 mole % of PABA is incorporated into PET. These phenomena are also proved by ¹H-NMR analysis, the viscosity behavior by RMS, as well as X-ray diffraction patterns.

The PETA-50 shows distinct liquid crystalline phase at 201°C [Fig. 6(a)]. The crystalline phases are much more agglomerative than PETA-40 at higher temperature, 283°C [compare Figure 6(b) with Figure 5(b)]. Figure 7a is the morphology of PETA-60 at room temperature (20°C), showing spherulites. When the temperature is increased above its T_m , PETA-60 shows the liquid crystalline phases [Figure 7(b)]. As the temperature is higher, the texture of the crystalline phase disappears slowly [Figure 7(c)-7(f)] but is not melted.





Figure 6 Polarizing micrographs of PETA-50 at (a) 201 and (b) 283°C.



Figure 7 Polarizing micrographs of PETA-60 at (a) 20, (b) 237, (c) 247, (d) 262, (e) 272, and (f) 282°C.

To confirm the recrystallization of the liquid phase, the specimens were cooled down to low temperature. Then, in the PET-rich components, a liquid crystalline behavior was not observed. Figure 8(a) shows the shape of PETA-70 at 270°C. The PETA-70 has not mobility even at very high temperature, 295°C [Fig. 8(b)]. This is consistent with the viscosity behavior by RMS, which will be discussed later. From the results, one could see that there are many more limitations to flow when the mole % of PABA is above 70%, since the polymer possess more rigid moiety than flexible spacer one.

Thermal Properties

We tried several measurements to detect the nematic \rightarrow isotropic transition, but the phase transition was not detected by the DSC method. Krigbaum and Salaris³⁶ concluded on the basis of







(b)

Figure 8 Polarizing micrographs of PETA-70 at (a) 270 and (b) 295°C.

the polarizing microscope and DSC experiments that the copolyester containing 30 mole % PABA exhibits the crystal \rightarrow nematic transition temperature (T_m) at 207°C and the nematic \rightarrow isotropic transition temperature (T_i) at 244°C. Once a virgin sample is heated above T_i , then cooling and reheating produces a different thermogram, showing T_i endotherm disappeared. They explained that the loss of the T_i transition might be due to the molecular weight reduction, sequence randomization, or erroneous identification of the transition. We, however, believe that the reasons for disappearing It endotherm are not solely due to the above phenomena. In fact, Lader and Krigbaum suggested that the copolyester containing 30 mole % PABA does not exhibit a nematic phase as in our experiment results.³⁷ On the other hand, Meesiri et al.³⁸ reexamined the copolyester containing 32 mole % PABA. They concluded that the highest endotherm was due to a perfect crystal,

produced by the particular thermal history of this sample. They found that none of the other samples showed comparable melting peak separation, but all showed the mesophase melt. Birefringence of the 32 mole % of PABA samples also did not disappear at 243°C. The optical microscopy results indicated that the transition to the isotropic phase is completed only above the decomposition temperature, so that no thermal analysis for the nematic \rightarrow isotropic transition is possible.³⁸ In our studies, the phase transition of the nematic \rightarrow isotropic temperatures was not detected by the DSC method. The thermal properties of the PETA-*x* copolyesters were continuously changed, depending on the compositions, giving isotropic melts to anisotropic melts. The melting temperature and the heat of fusion also seem to change continuously with composition. The melting temperature of PET before modified by PABA is about 250°C. As the PABA mole % increases, the melting temperatures of the modified copolyesters are lowered, and also the heat of fusion (ΔH_m) is dramatically decreased. These phenomena were observed regardless of the thermal history. As the PABA concentration increased, the melting temperature of PET was decreased by 60°C and the overall crystallinity was also decreased [Figure 9(a),(b)], respectively. In these figures, subscripts 1 and 2 denote the data for virgin samples on the first scanning and for reheated samples on the second scanning, respectively. Similar results were obtained for the glass transition temperature $(T_{\sigma};$ Table IV). The results are indicative of an eutectic phase separation or isodimorphism. That is, the PABA in the PET-*x* copolyesters plays the role to decrease the crystallinity of the modified copolyester by their randomness in some sense. The disruption in the sequencing of the monomer units along the backbone chain reduces the crystallinity. But, it is observed that the critical mole % of PABA giving rise to the decreasing T_m is about 20 \sim 30 mole % from the thermal behavior as a function of PABA composition. The PABA of 60 mole % composition does not exhibit melting temperature, probably due to its wholly random structure. The melting temperature difference between the virgin sample and the reheated one is about 2–7°C. The cold crystallization temperatures T_c was also decreased similarly as for the melting temperatures [Fig. 10(a)].However, T_c was decreased linearly up to 20 mole % of PABA and afterward T_c was not decreased largely with the change of PABA mole %. These are probably attributed to the same



Figure 9 (a) Melting temperature and (b) heat of fusion of the PETA-*x* copolyester as a function of PABA composition.

reason in the case of the decrease of T_m . Compared to the small change of T_c for the varying concentration of PABA, ΔH_c is decreased dramatically, as in the drastic decrease of the heat of fusion with the increase of PABA concentration [Fig. 10(b). see also Fig. 9(b)].

The category of a thermogravimetric curve in TGA is determined by the average decomposition temperature (T_{aver}) as well as the lower decomposition temperature (T_i) and the upper decomposition temperature (T_e) . Figure 11 show T(i), T(e), and T(peak) of the PETA-x copolyesters. As one can see, the initial decomposition temperature (T_i) was not changed with the compositions. However, the peak temperature is increased up to 465°C and the end decomposition temperature is largely increased to 538°C-that is, the temperature differences between the initial and the end (ΔT_{i-e}) decomposition temperature (Fig. 12) and



Figure 10 (a) Crystallization temperature and (b) heat of crystallization (dH_c) of PETA-*x* copolyester as a function of PABA composition.

the average degradation temperatures (T_{aver}) (Figure 13) are increased upward by 113 and 482°C, respectively.

Rheological Properties

When polymers exist in the isotropic phase, the shear rate dependence of the viscosity follows a



Figure 11 T(i), T(e), and T(peak) of the PETA-*x* as a function of PABA mole %.



Figure 12 The differences between initial and end temperature (dT_{i-e}) for PETA-x copolyesters.

well-known pattern: at shear rates sufficiently small, the viscosity is constant (Newtonian plateau); at larger values of the shear rate, the polymeric liquid becomes shear thinning. The behavior of LCPs differs from that of ordinary polymers in at least one important aspect, i.e., there is no indication that the viscosity trends to reach a Newtonian plateau when the shear rate is decreased. The tendency of the molecules to be aligned along the flow direction is most prominent feature of the LCP, and in processing thermotropic LCPs, the strong coupling between flow and orientation is observed. The properties of thermotropic LCPs are, therefore, influenced by the processing parameters to a greater extent



Figure 13 The average degradation temperature (Taver) for PETA-*x* copolyesters.



Figure 14 Complex viscosity behavior of PETA-50, PETA-60 at 240°C, and PETA-70 at 260°C.

than traditional thermoplastic polymers are. The viscosity-shear rate data have been reported for PET/60PABA and other aromatic copolyesters and for the cellulose ethers.^{39–44} In this work, the rheological properties of the PET-x copolyesters having full range of PABA composition from 10 to 70 mole % were investigated. The complex viscosity (η^*) of PET-*x* copolyesters were measured at constant temperature 240°C except for PETA-70 at 260°C. The reason for the difference measuring temperature between PETA-70 and the other PETA-*x* is that PETA-70's melt viscosity at 240°C is too high to detect the value at normal instrument condition. The outstanding difference between isotropic and thermotropic polymers is the onset of the nonlinear viscoelastic behavior; for instance, the shear thinning occurs at a much lower shear rate for thermotropic polymers than for isotropic polymers of comparable viscosity. At low shear rates, the thermotropic polyesters could not move smoothly because of the crystallinities, while at high shear rates the structure was disrupted to allow stable flow. In this study, the shear thinning behaviors at low shear rate were found in PETA-50, PETA-60, and PETA-70 copolyester series, which show liquid crystalline behaviors as proved by polarizing microscope (Fig. 14). The copolyesters that did not exhibit liquid crystalline properties did not show the shear thinning behavior at low shear rate, as shown in Figure 15.

CONCLUSIONS

One of the presentative methods to design the thermotropic liquid crystalline polymers is to syn-



Figure 15 Complex viscosity behavior of PETA-20, PETA-30, and PETA-40 at 240°C.

thesize the polyesters containing the rigid-bar. There are two ways to synthesize the LCP; one is a solution polymerization using solvents, the other is a melt polymerization controlled by temperature and pressure. Melt polymerization is a kind of modification reaction that generally uses the known polymers as reactants in that polymerization. The common types of modification reaction are mainly the graft reaction by radicals produced by peroxide. However, in this study the copolymerization reaction was applied as a modification reaction type. PET was selected as reactant polymer that is the representative polyester polymer. To enhance the liquid crystal behavior, the polyesters should contain the rigid-bar, which is mesogenic unit. p-Acetoxybenzoic acid is used as reactant monomer for mesogenic unit. In this study, several PET-x copolyesters having various PABA compositions from 10 to 70 mole % were prepared by the melt reaction PABA and PET without a catalyst, where the *x* denotes the mole % of PABA. The modified polyesters obtained by this copolymerization were characterized by ¹H-NMR spectrometry, XRD pattern, polarizing microscopy, thermal analysis, and rheometry. For the PET modified with PABA containing the PET-PABA unit, the characteristic peak around 7.5 ppm in the ¹H-NMR spectrum was higher as the PABA content was increased. Those phenomena were also proved by XRD pattern. And the changes of morphology on increasing temperature from room temperature to 300°C were observed by polarizing microscope. The anisotropic phases appeared for the PETA-x copolyesters of 50 mole % of PABA composition, and for the copolyesters

of 60 and 70 mole % of PABA compositions the nematic liquid crystalline texture appeared clearly on the wholly matrix. As the mole % of PABA increased, melting temperature, heat of fusion, crystalline temperature, the degree of crystallinity, and the glass transition temperature of the modified PET decreased. The thermal stabilities of those copolyesters, however, were increased as the mole of PABA increased. The dependence of the melt viscosity on the shear rate followed that of the typical liquid crystalline polymers for the PETA-50 \sim 70 copolyesters. From the results, it was concluded that the PETA-xhaving PABA compositions equal to or higher than 50 mole % exhibits typical thermotropic liquid crystalline behavior.

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