

# Syntheses and Characterization of Poly(butylene terephthalate) Copolyesters Modified with *p*-Acetoxybenzoic Acid

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**ABSTRACT:** Poly(butylene terephthalate) (PBT) copolyesters modified with seven compositions of *p*-acetoxybenzoic acid (PABA) ranging from 10 to 70 mol % were prepared. The X-ray diffraction patterns, the polarizing microscopy behaviors, and thermal analysis showed that the modified PBT contained more PABA homopolymer units (PABA–PABA) than PBT–PABA units in the copolyesters. On increasing PABA mole percentage, PBT crystallinity decreased and thermal stability increased. It was found that although the PBT copolyesters did not exhibit a clear liquid crystalline texture like the copolyester of poly(ethylene terephthalate) modified with PABA did, the PBT copolyester containing 70 mol % of PABA exhibited the typical shear thinning behavior of a liquid crystalline polymer. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1085–1095, 2001

**Key words:** poly(butylene terephthalate); *p*-acetoxybenzoic acid; modified copolyesters; blends; characterization

## INTRODUCTION

Thermotropic liquid crystalline polyesters (LCPs), which have a low melting temperature, are reputed to be second-generation engineering plastics, and many kinds of LCPs have been reported.<sup>1–3</sup> LCP molecules are easily oriented by shear stress and elongational flow during processing and form multilayer structures whose layers have various orientation states. 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

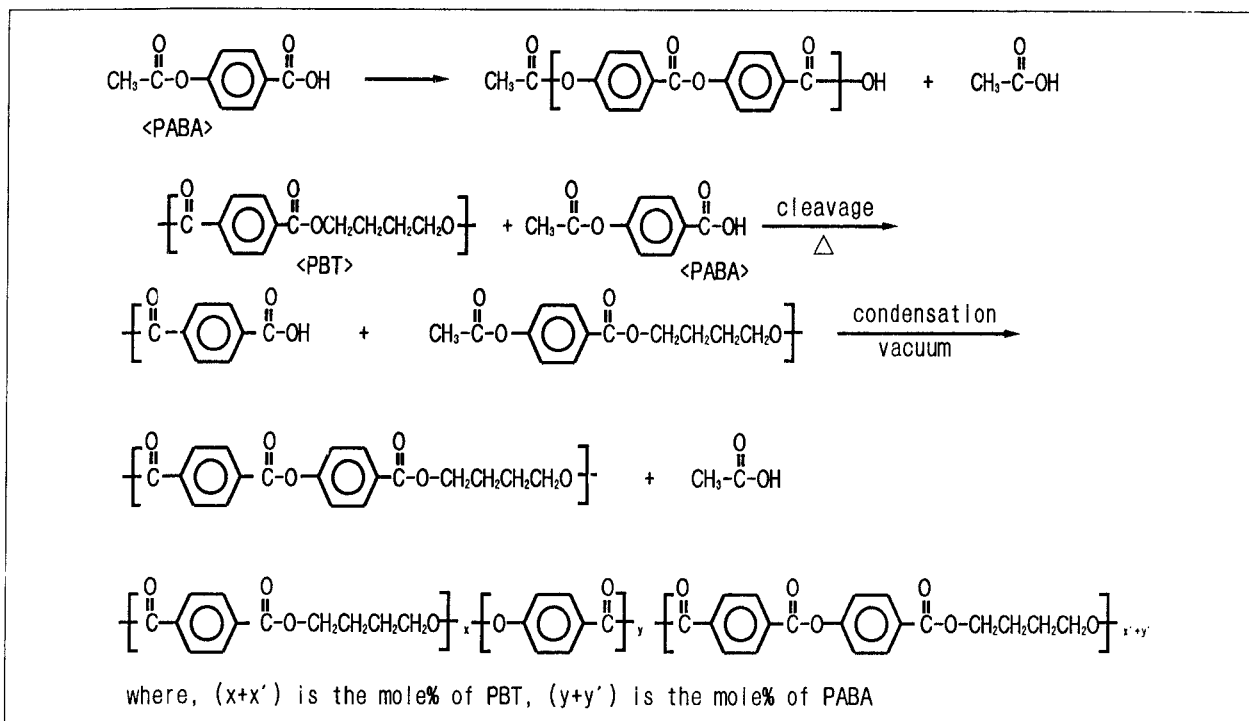
excellent properties, the blending of LCP with conventional polymers could result in materials that can be used as an alternative for short-fiber reinforced thermoplastic composites; these *in situ* composites have many potential advantages over short-fiber reinforced polymers.

These LCPs can be prepared by conventional techniques, that is, through solution condensation, interfacial condensation, or melt condensation processes. Poly(ethylene terephthalate) (PET) in particular, when reacted with another reactant such as *p*-hydroxybenzoic acid (PHB)<sup>1–10</sup> or *p*-acetoxybenzoic acid (PABA)<sup>9–14</sup> as a source of a mesogenic unit, has been used as a moiety to prepare an LCP.<sup>4–5</sup> In a sense, PABA can be considered as part of the same category as PHB because the former is prepared by acetylation of PHB with acetic anhydride. The first indication of

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The reaction mechanism of PBT with *p*-acetoxybenzoic acid



**Figure 1** The possible reaction mechanism of PBTA-*x*.

a liquid crystalline characteristic in polyesters came from Tennessee Eastman's Jackson and Kuhfuss, who synthesized copolyesters from PET and PHB.<sup>6-10</sup> Evidence of the liquid crystalline character of copolyesters was also published by other researchers.<sup>15-19</sup> Most LCPs, obtained by the melt reaction of PET and PABA or PHB, contain 60 mol % 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 nuclear magnetic resonance (NMR) spectrophotometry and X-ray diffraction studies. The structure and properties of PET-60PABA or PET-60PHB and their blends have been well documented.<sup>1-3,15-19</sup> Recently we also synthesized and characterized PET copolymers modified with a broad range of PABA compositions. It was found that PET copolyesters with a composition of more than 40 mol % PABA form thermotropic nematic liquid crystals.<sup>20</sup>

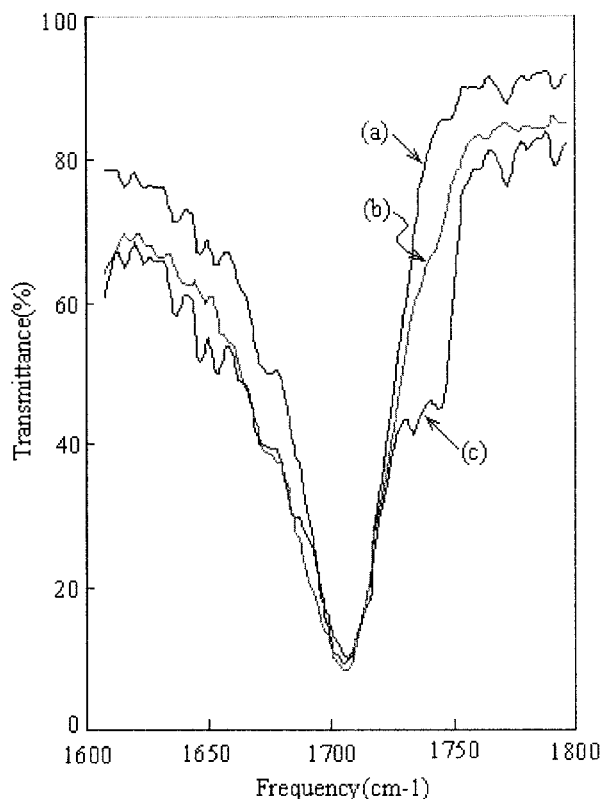
Preparing copolyesters from poly(butylene terephthalate) (PBT) and PABA in order to investigate whether such PBT copolyesters exhibit the same kind of liquid crystalline character as do PET-60PABA or PET-60PHB should be of great

interest because PBT possesses a chemical structure similar to PET, except PBT has 4 *n* in the repeating unit of the aromatic polyesters  $[-(\text{CH}_2)_n\text{O}-]$  instead of the 2 *n* in PET. To the best of our knowledge, no work has yet been published on the preparation of PBT copolyesters by reaction with PABA. Therefore, the objective of the present research was to synthesize several PBT-based copolyesters containing PABA compositions ranging from 10 to 70 mol % and to characterize the thermal and rheological behaviors of these copolyesters.

## EXPERIMENTAL

### Materials

Modified polyesters were prepared by reacting *p*-acetoxybenzoic acid (PABA) with PBT [poly(butylene terephthalate)], a method similar to that described by Jackson and Kuhfuss for using solid-state polymerization to synthesize a modified PET.<sup>1-5</sup> PABA was prepared by conventional acetylation of *p*-hydroxybenzoic acid with acetic anhydride in acetic acid. Commercial-grade PBT



**Figure 2** IR spectra of (a) PBT, (b) PBTA-20, and (c) PBTA-60.

( $M_n$ : 31,400;  $M_w$ : 68,300) was supplied by Sunk-yung Industry Company, Suwon, Korea.

#### Preparation of Modified Copolyesters from PBT and PABA

Modified copolyesters from PBT and PABA were prepared by procedure similar to that used for PET copolyesters modified with PABA as reported in our previous work.<sup>20</sup> A mixture of *p*-acetoxybenzoic acid (10–70 mol %) and PBT particles (30–90 mol %) was placed in a flask equipped with a stainless-steel stirrer and a short head with an inlet and an outlet for nitrogen. After the reaction flask was evacuated and purged with nitrogen to remove all the air, it was heated under reduced pressure (0.1 mmHg) in a metal bath at 110°C to dry the reactants. The flask was removed from the bath, and the bath was heated to 245°C. The flask was then placed back in the bath; while the contents were stirred in a nitrogen atmosphere, acetic acid was slowly distilled out. After that, a vacuum of 0.1 mmHg was applied while stirring. The polymeric products thus obtained were designated as PBTA-*x*,

where *x* represents mole percent of PABA. For example, the designation PBTA-60 means the copolyester possesses 60 mol % PABA and 40 mol % PBT. Figure 1 illustrates the possible reaction mechanism of PBTA-*x*.

#### Characterization

##### X-ray Diffraction

X-ray diffraction (XRD) patterns were obtained by the reflection method with a Rigaku Denki X-ray diffractometer using Nickel-filtered  $\text{CuK}\alpha$  radiation (30 KV, 20 mA). The modified copolyesters were ground to make a powder sample. The crystallinities of the samples were calculated by the same method as reported in the literature.<sup>21</sup>

##### Optical Microscope

Optical observation was made with a Leitz-Ortholux polarizing microscope equipped with a heating stage (Mettler FP-2) in the temperature range of 20–300°C. The sample was prepared by heating a 18 mm  $\times$  18 mm piece of glass plate at 245°C and then pressing the melts with another piece of hot glass plate, so that it formed a sandwich with the thin film inside. This sandwich was then quenched under atmospheric conditions. 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

Thermal analysis with a heating rate of 10°C/min was performed under nitrogen using a PerkinElmer differential scanning calorimeter (DSC 7) and a PerkinElmer thermal analyzer. To measure thermal stability, thermogravimetric analysis (TGA) was performed using the same instrument as for DSC. In the TGA measurement the weight change of a material was measured at a heating rate of 10°C/min.

##### Dynamic Mechanical Measurement

Viscoelastic properties were measured with rheometrics mechanical spectrometer (RMS) using a parallel plate, which had a test gap of 2 mm and a plate diameter of 25 mm. Before measuring the modified copolyester powders and PBT were dried in a vacuum oven at 105°C for 24 h. The powder samples were directly poured on the disc in the

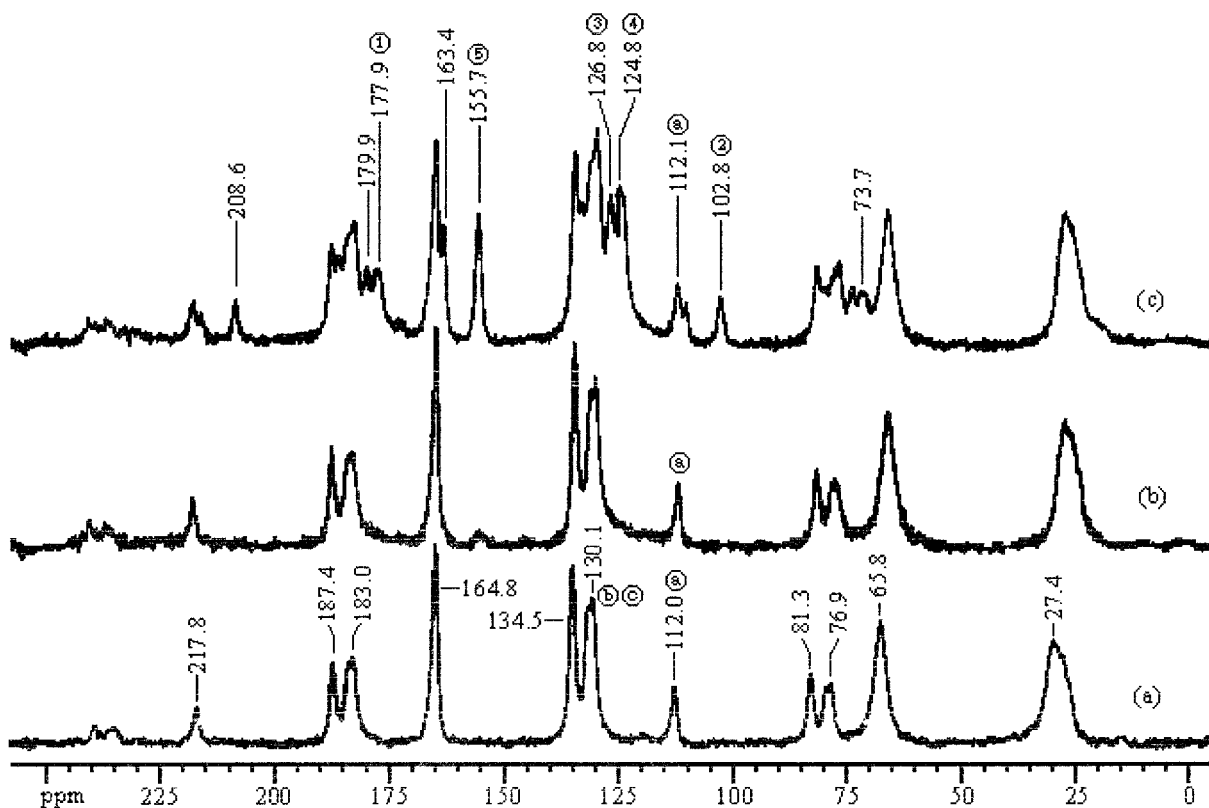
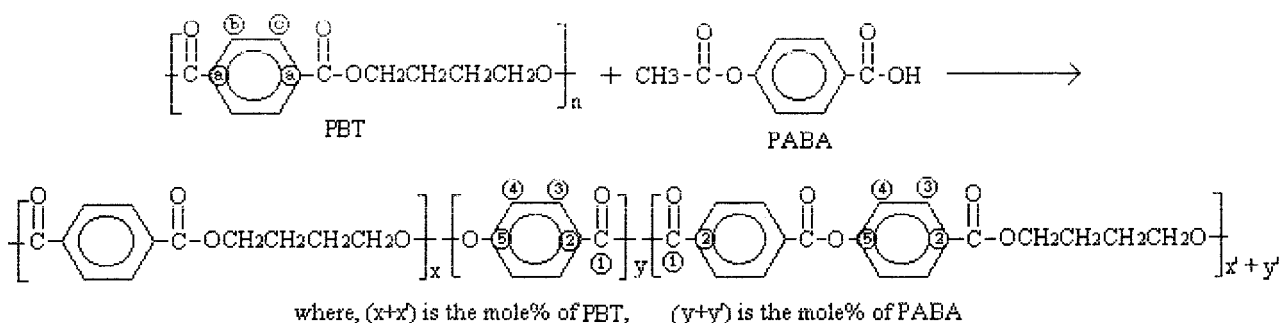


Figure 3  $^{13}\text{C}$ -NMR spectra of (a) PBT, (b) PBTA-20, and (c) PBTA-60.

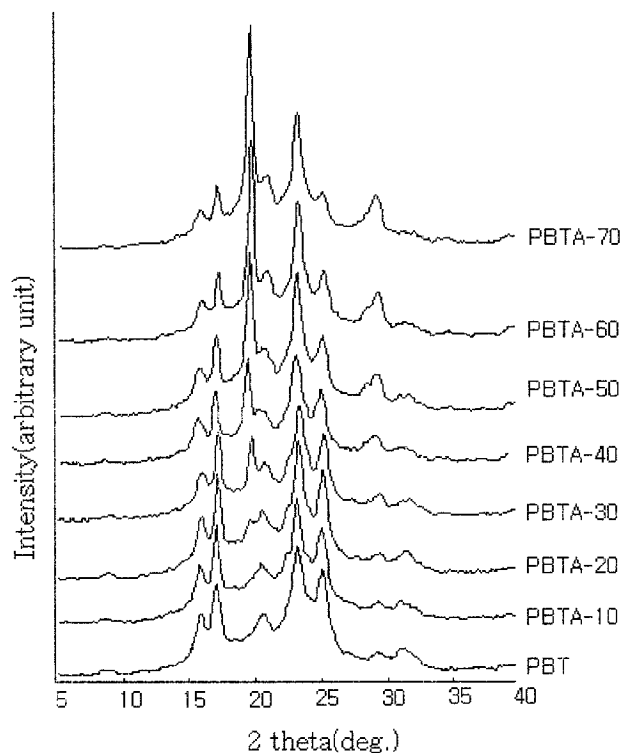
RMS test chamber. During measurement a flow of nitrogen was used to reduce sample oxidation.

## RESULTS AND DISCUSSION

### Structure of PBT Modified with PABA

It has been reported that for the sequence distribution of the PET-60PHB copolyester by  $^1\text{H}$ -NMR spectrophotometry,<sup>9</sup> the PHB unit has a random distribution in the copolymer.<sup>14,18</sup> Nicely et al.<sup>22</sup> also studied the sequence distribution of the PET-60PABA copolyester by NMR spectrophotometry. According to their analysis, the spectra of this co-

polyester provide direct measures of the probability of a PABA unit being bonded to another PABA or to a PET unit. In comparison to PET-PHB or PET-PABA copolyesters, however, PBTA- $x$  modified with PABA whose PABA content are higher than 30 mol % was not readily dissolved in common organic solvents such as trifluoroacetic acid, phenol-tetrachloroethane (60:40), sulfuric acid, cresol, and chloroform. For this reason, definitive molecular weights were difficult to determine. The structures of PBTA- $x$  were roughly characterized by solid-state NMR and IR spectrophotometry. Figure 2(a-c) shows the IR spectra of PBTA, PBTA-20, and PBTA-60, respectively, near  $1750\text{ cm}^{-1}$ . It can be



**Figure 4** XRD patterns of PBTA-*x* and PBT.

seen that the intensity of the characteristic peak of around  $1750\text{ cm}^{-1}$  resulting from the  $\text{C}=\text{O}-\text{O}$  being next to the phenylene oxide group increases with increasing PABA content. Solid-state  $^{13}\text{C}$ -NMR spectra of PBT, PBTA-20, and PBTA-60 are shown, respectively, in Figure 3(a–c). Characteristic peaks due to the phenylene ring in PBT can also be observed in Figure 3 around 112.0, 130.1, and 134.5 ppm for all three polymers. The formation of PBT–PABA or PAPA–PABA units in the copolyesters can be proven by the appearance of new peaks from the PABA moiety around 102.8, 124.8, 126.8, 155.7, and 177.9 ppm for (b) PBTA-20 and (c) PBTA-60 and from the increase in intensity of the new peaks in tandem with increasing PABA content. More detailed assignment of peaks are also shown in Figure 3. According to the  $^{13}\text{C}$ -NMR and IR spectra results, the structures are supposed to contain two kinds of polymers composed of PABA–PBT copolymer and of PABA–PABA homopolymer (PPABA). The expected structure can be also identified indirectly by polarizing microscopy and X-ray diffractometry.

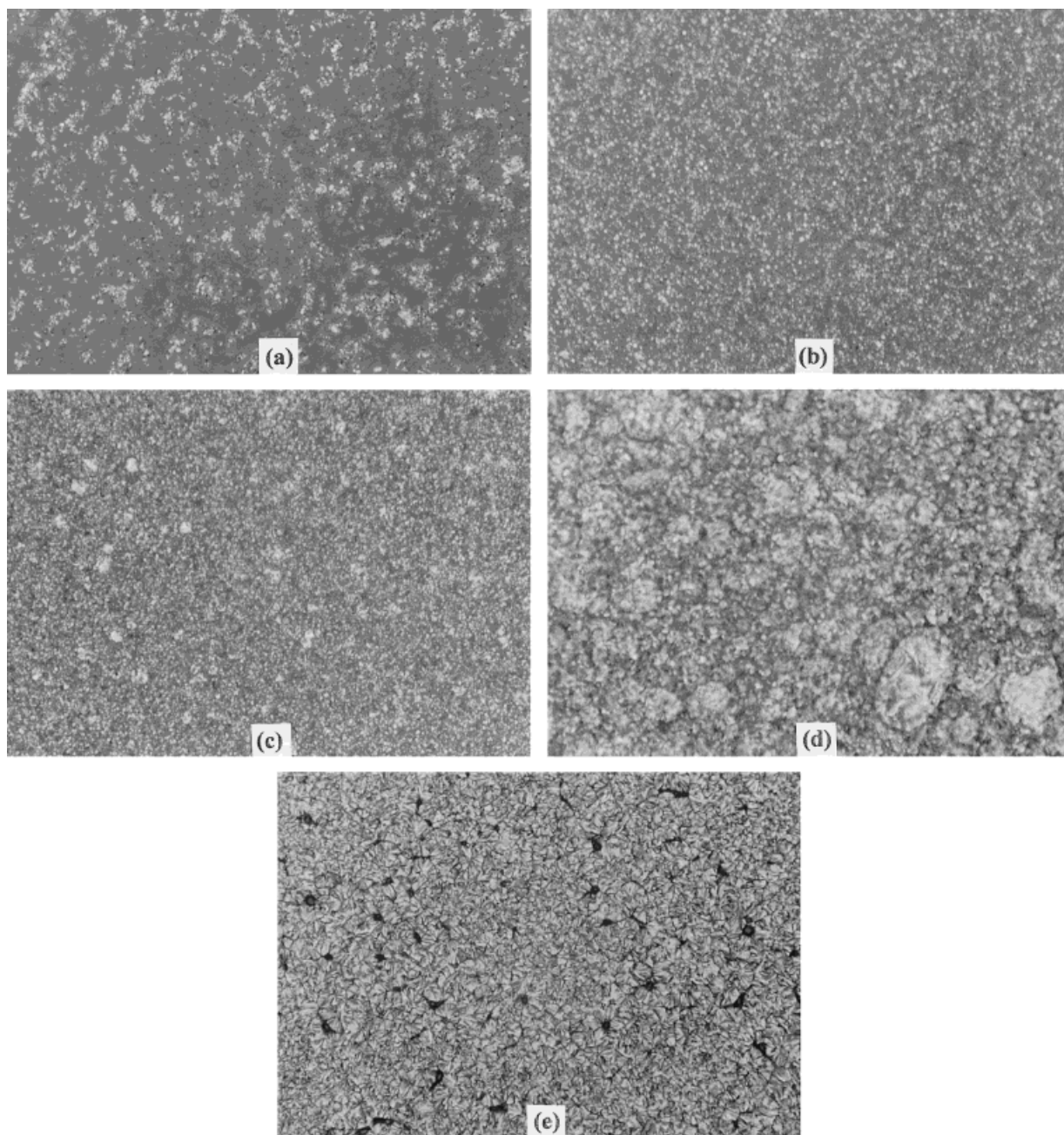
#### XRD Patterns of PBTA-*x*

The XRD patterns for the PBTA-*x* copolyesters can provide more detailed information on their

structure—how the copolyesters consist of both PBT–PABA copolymer and PABA–PABA homopolymer—even though the method is indirect. Figure 4 shows the XRD patterns of PBT and PBTA-*x* copolyesters. PBT shows sharp peaks at  $2\theta = 17.4^\circ$ ,  $20.7^\circ$ ,  $23^\circ$ , and  $25.3^\circ$ , indicating the PBT used in this work has an  $\alpha$ -form crystalline structure.<sup>30</sup> The XRD patterns of PBTA-*x* ( $x = 10$  or  $20$ ) are similar to that of virgin PBT, meaning the crystalline structure of PBTA-*x* with a low PABA content is not as greatly affected by the reaction between PBT and PABA. However, a small but new distinct peak appears at  $2\theta = 20^\circ$  for PBTA-20, and the peak becomes sharper and larger when the PABA content in PBTA-*x* increases. This result suggests that the reaction between PABA and PABA is more dominant than that between PABA and PBT because the peak at  $2\theta = 20^\circ$  comes from the crystalline structure of PPABA [poly(*p*-acetoxybenzoic acid)]. It may be assumed that the crystallization pattern of PBT is affected mainly by the PPABA homopolymer rather than the PABA–PBT copolymer, although the  $\alpha$ -form crystalline structure of PBT is preserved for all types of PBT-*x*. On the other hand, in comparing the XRD patterns of PBT and PBTA-*x*, the characteristic peaks of PBT that appear at  $2\theta = 25^\circ$  and  $2\theta = 31^\circ$  decreased remarkably, while the characteristic peak of PPABA, at  $2\theta = 29^\circ$ , increased relatively as the mole percent of PABA increased. This means that reactions between PBT and PABA and/or between PABA and PABA take place simultaneously and competitively, since such peaks at the characteristic  $2\theta$  angles (ca.  $25^\circ$ ,  $29^\circ$ , and  $31^\circ$ ) were not observed in the XRD pattern of its corresponding monomer, PABA. For any PBTA-*x*, however, the inherent peaks of PBT still remain in the XRD patterns, as shown even in the case of PBTA-70, meaning some part of the PBT has not completely participated in the reaction with PABA (the PBT–PABA reaction). These facts were subsequently also shown by the results of polarizing microscopy observation.

#### Polarizing Optical Micrographs of PBTA-*x*

Figure 5 shows the polarized optical micrographs of PBTA-*x* at about  $280^\circ\text{C}$ . In a PBTA-*x* with increasing PABA content, the two phases were either very sluggishly mobile or not mobile at all, even such a high temperature. Contributing to the driving force of this phenomenon is the low degree of chain mobility of the PABA–PABA ho-

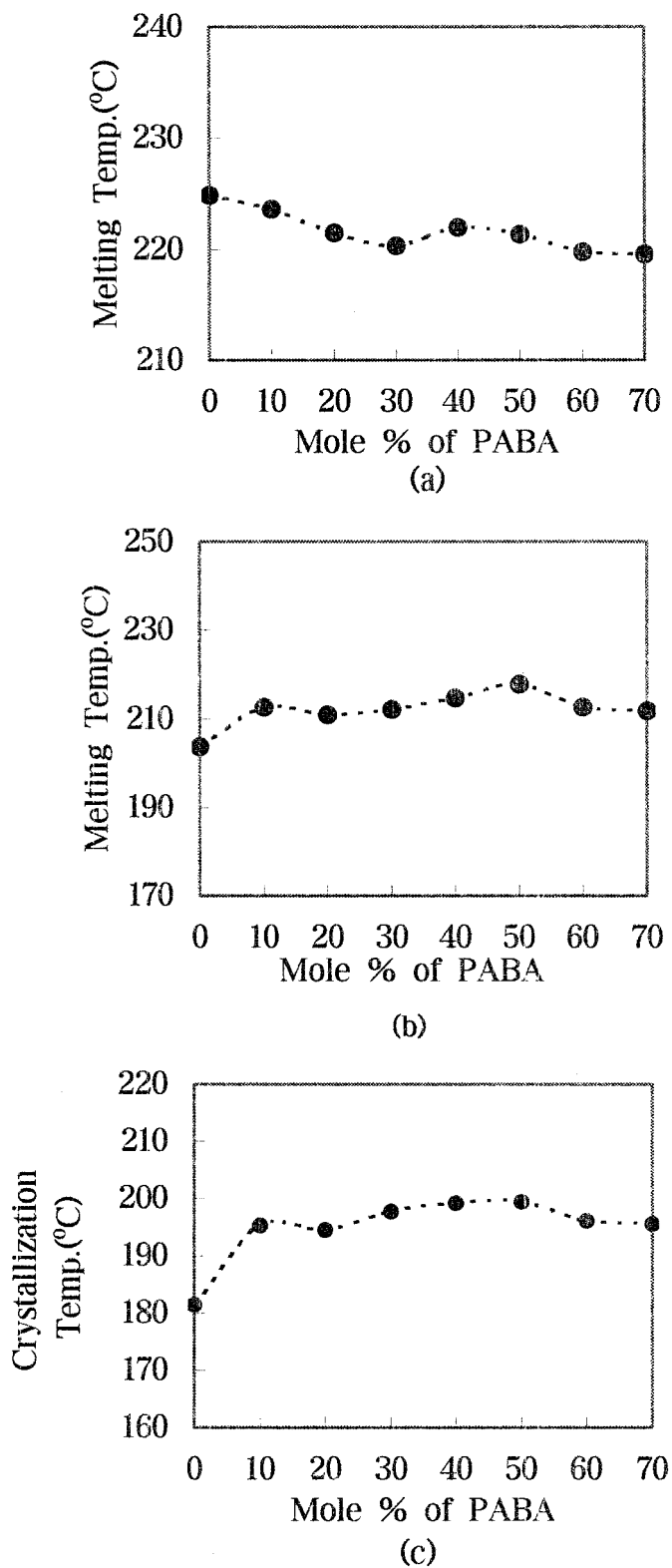


**Figure 5** Polarized optical micrographs of PBTA-*x*: (a) PBTA-20 at 280°C; (b) PBTA-30 at 280°C; (c) PBTA-40 at 280°C; (d) PBTA-60 at 290°C; and (e) PBTA-70 at 295°C. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

mopolymer, which is classified as a wholly aromatic liquid crystalline polymer.

It is believed that the morphologies of those polymers, as shown by polarizing optical micrographs, are closely related to the reaction mechanism, which can be deduced by such experimental techniques as XRD, solubility, and thermal analysis. It was conjectured that the reaction be-

tween PABAs would predominate over that between PABA and PBT, meaning the reaction could produce a copolymer, which was predicted to be a PABA–PABA homopolymer having a melting temperature about 600°C.<sup>3</sup> The polarizing optical micrograph of PBTA-20 [Fig. 5(a)] shows particles unmelted at 280°C. As the content of PABA increases in PBT, it can be seen that more



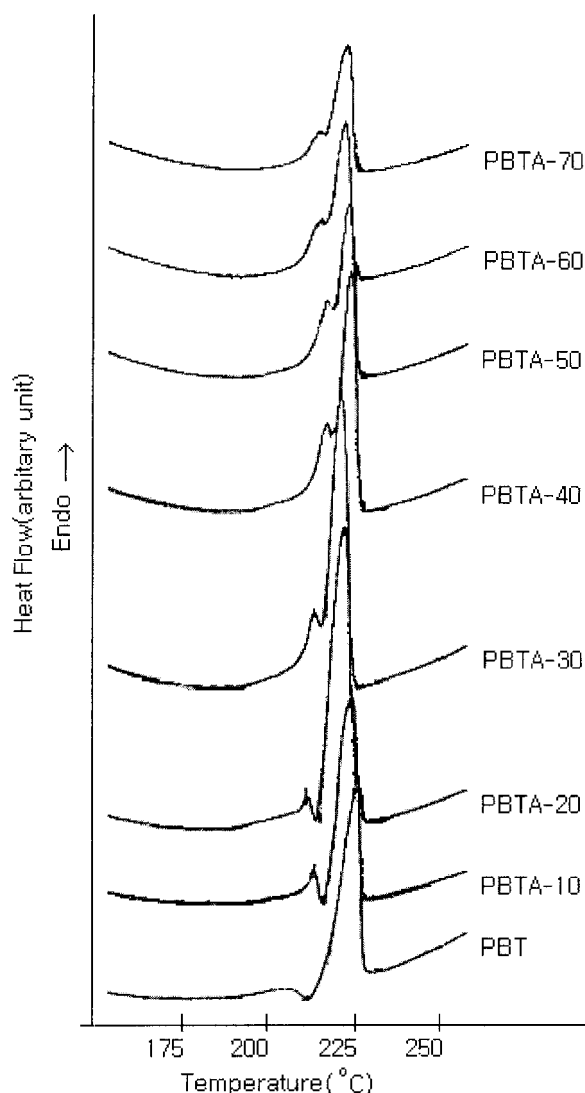
**Figure 6** Thermal behavior of PABA-x: (a) higher melting temperature on the second heating scan of DSC thermograms; (b) lower melting temperature on the second heating scan of DSC thermograms; (c) crystallization temperature of PBTA-x copolyesters as a function of PABA mole percent.

of the crystalline phase becomes dominant in the matrix, and the crystalline phase becomes discrete. However, more detailed data are needed to draw a conclusion on the structure of the polymers. At any rate, it has been determined that a PBTA-*x* possessing a high mole percent of PABA will also have crystalline phases at high temperature and will maintain isotropic and anisotropic biphases, except that the crystalline phases will not be continuous. Liquid crystalline polyesters have streak textures of a typical color that are consistent with the anisotropic mesomorphic phases in the polarizing microscope. But the PBT copolyesters prepared in this work did not show such a clear liquid crystalline texture on the polarizing micrographs as well as XRD patterns. It should be noted that, on the contrary, PET copolyesters having more than 40 mol % exhibit the thermotropic liquid crystalline behavior that we saw in our previous work.<sup>20</sup>

### Thermal Properties

Figure 6 shows the melting temperatures [Fig. 6(a,b)] and crystallization temperatures [Fig. 6(c)] of PBTA-*x* copolyesters. Two melting peaks were observed in the DSC thermograms at the second heating scan, as shown in Figure 7. The main  $T_m$  at higher temperatures decreases with increasing PABA concentration up to 30 mol % of PABA and then levels off, and the second small peak below the main peak increases slightly with increasing PABA content. The additional melting peak at a lower temperature is thought to arise from PBT crystals that form from the amorphous phase during annealing and that form from recrystallization of crystals that have lower melting points.<sup>23-26</sup>

Figure 8 shows the heat of fusion [Fig. 8(a)] and heat of crystallization [Fig. 8(b)] of PBTA-*x* as a function of PABA mole percent. As the concentration of PABA is increased, especially above a 30 mol % content of PABA, decreases of  $\Delta H_m$  remarkably are observed in PBTA-*x*. It is supposed this may be because of the reduced crystallinity in the modified PBT copolymerized with PABA. The cold crystallization temperatures,  $T_c$ , of PBTA-*x* increase as the PABA concentration increases. In other words, we could say that the gap between  $T_m$  and  $T_c$  becomes smaller as the PABA content increases. This means the rate of crystallization is relatively high in PBTA-*x*. The  $\Delta H_m$  of PBTA-*x* is then changed by two patterns; in one pattern,  $\Delta H_c$

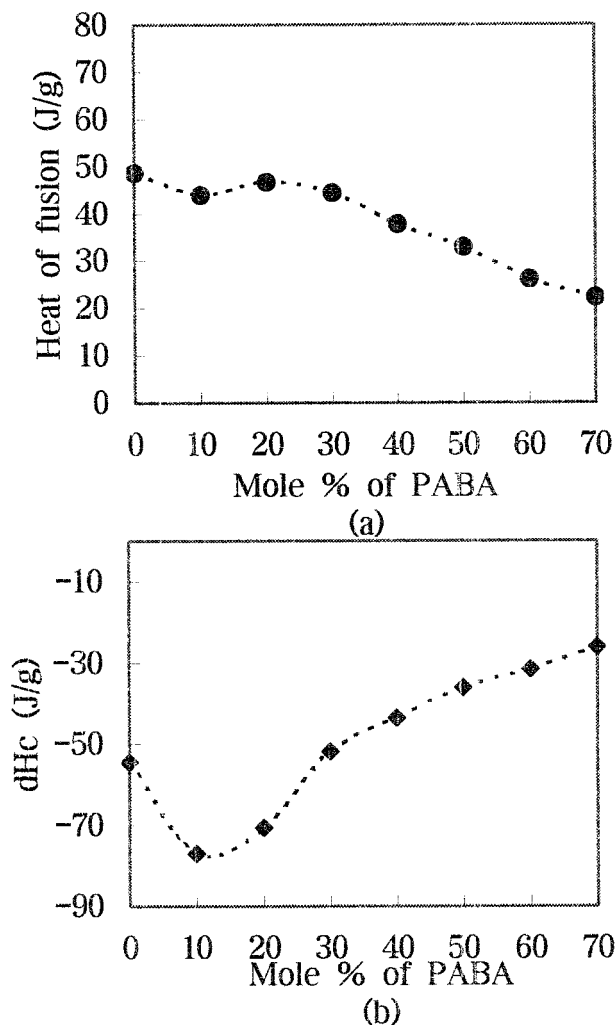


**Figure 7** DSC thermograms of PBTA-*x* at the second heating scan.

increases with PABA content up to 20 mol %; in the other,  $\Delta H_c$  drastically decreases with PABA content above 30 mol % of PABA. It is supposed that the first pattern may result from PABA enhancing crystallization of PBT, even though PABA usually restricts it, because the small concentration of the PABA-PBT copolyester may act as a nucleating agent in the matrix of PBT. The second pattern may be due to restricted crystallization in modified copolyesters from gradually increasing PABA content, just as was the case for the decrease of  $\Delta H_m$ .

Thermal stability of some polymeric material is characterized primarily by the decomposition temperature in the thermogravimetric analysis





**Figure 8** (a) Heat of fusion of PBTA- $x$  as a function of PABA composition; (b)  $\Delta H_c$  of PBTA- $x$  as a function of PABA composition.

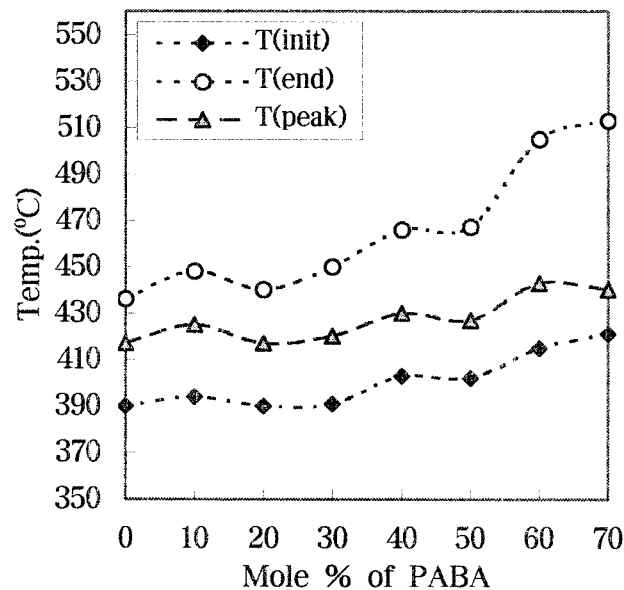
(TGA). The category of a thermogravimetric curve in TGA is determined by the peak decomposition temperature ( $T_{peak}$ ) as well as the initial decomposition temperature ( $T_i$ ) and the end decomposition temperature ( $T_e$ ). Figure 9 shows the  $T_i$ ,  $T_e$ , and  $T_{peak}$  of PBTA- $x$ . As can be seen, the initial and peak temperatures ( $T_i$  and  $T_{peak}$ ) were not changed as much by the PABA compositions. However, the end temperature increased to above 500°C, that is, the temperature difference ( $T_{i-e}$ ) between the initial and the end temperatures increased with increasing PABA content, meaning thermal stability improved as PABA was added to PBT.

#### Rheological Properties

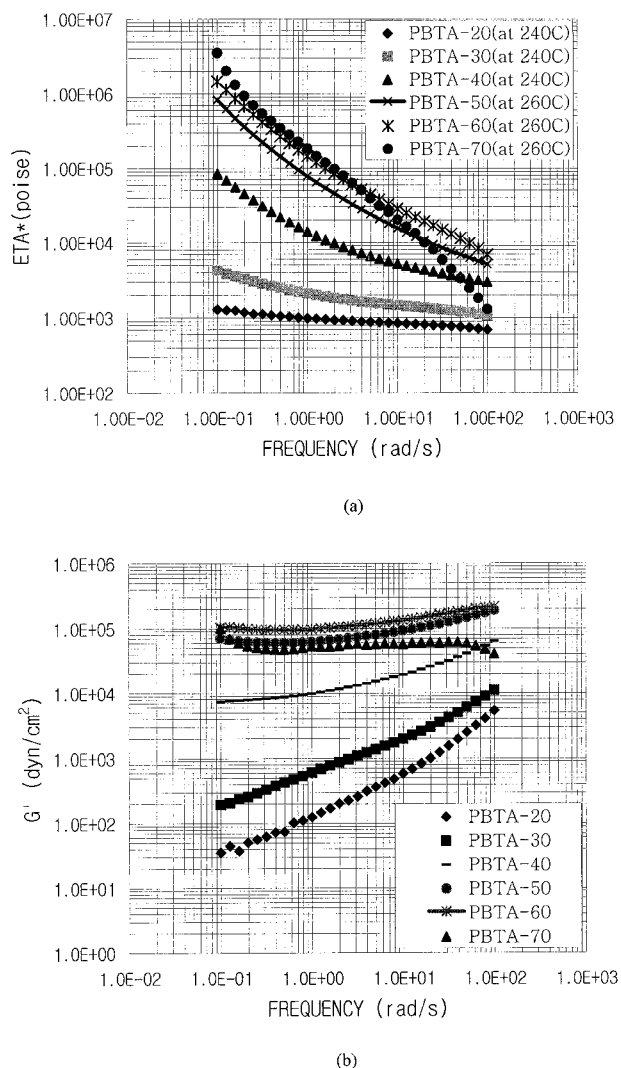
When polymers are in the isotropic phase, the shear-rate dependence of the viscosity follows a

well-known pattern: at shear rates that are sufficiently small, the viscosity is constant (Newtonian plateau); at larger shear-rate values, the polymeric liquid becomes shear thinning. The behavior of LCPs differs from that of ordinary polymers in at least one important aspect—there is no indication that viscosity trends toward a Newtonian plateau when the shear rate is decreased. The tendency of the molecules to be aligned along the flow direction is the most prominent feature of LCP, and in processing thermotropic LCPs, strong coupling between flow and orientation can be observed. Therefore, the properties of thermotropic LCPs are influenced by the processing parameters to a greater extent than are traditional thermoplastic polymers. Viscosity–shear rate data have been reported for PET–60PABA and other aromatic copolyesters and for cellulose ethers.<sup>27–29</sup>

The rheological behaviors of PBTA- $x$  are shown in Figure 10. In the case of PBTA- $x$ , shear-thinning behavior appeared in  $x = 40 \sim 70$ . But this does not mean that all the modified polymers exhibiting shear-thinning behavior are always liquid crystalline polymers. From polarizing microscopy analysis it was learned that the crystal phases that did not melt at 290°C increased as PABA content was increased in PBT. It had been believed that the existence of the crystal phase is the driving force of shear-thinning behavior at low shear



**Figure 9**  $T_{init}$ ,  $T_{end}$ , and  $T_{peak}$  of PBTA- $x$  as a function of PABA composition.



**Figure 10** (a) Complex viscosity and (b)  $G'$  behavior of PBTA- $x$  at different temperatures ( $x = 20\sim 40:240^\circ\text{C}$ ,  $x = 50\sim 70:260^\circ\text{C}$ ).

rate in PBTA- $x$ . However, the plots of shear rate against complex viscosity for the modified PBT [Fig. 10(a)] indicate that the PBTA- $x$  of  $x = 60$  and 70 exhibits the typical curve (just like an  $S$  shape) of the thermotropic liquid crystalline polymers.

It is commonly observed that as the content of PABA mol percent in PBTA- $x$ , except PBTA-70, is increased, the storage moduli ( $G'$ ) increase. This means that as PABA concentration is increased, chain mobility decreases. The lower moduli in PBTA-70 compared to PBTA-50 and PBTA-60 are noteworthy. This result may be related to the liquid crystalline properties of the copolyester, although there is no definitive evidence that those

modified PBT are thermotropic liquid crystalline polymers.

## CONCLUSIONS

A representative procedure for designing modified polyesters is to synthesize copolyesters containing an acid functional group using a melt polymerization method that controls the reaction by temperature and pressure only. In this study PBT was selected as a reactant polymer, and *p*-acetoxybenzoic acid was used as a reactant monomer for the mesogenic unit. Several copolyesters of PBT with a PABA content varying between 10 and 70 mol % were prepared by the melt reaction of PABA and PBT without a catalyst. The modified PBTs obtained by this copolymerization were characterized by  $^{13}\text{C}$ -NMR and IR spectroscopy, X-ray diffraction (XRD) patterns, polarizing microscopy, thermal analysis, and rheometrics. From XRD patterns, behaviors shown with polarizing microscopy, and thermal analysis, it was determined that seven types of PABA-modified PBT contained more of the homopolymerization products of PABA-PABA than of PBT-PABA units. This led to the conclusion that PBTA- $x$  has structures consisting of poly(PABA), known as a wholly aromatic liquid crystalline polymer, and PBT, which had been used as the reactant polymer. When PABA mole percent increases, the crystallinity of PBT decreased, but thermal stability increased. It was found that PBT copolyesters do not exhibit a clear liquid crystalline texture as do copolyesters of poly(ethylene terephthalate) modified with PABA. It should be noted, however, that the PBT copolyester containing 70 mol % of PABA exhibited the typical shear-thinning behavior of a liquid crystalline polymer.

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