

# Synthesis and Modification of Aromatic Polyesters with Chloroacetyl 3,5-Dibromo-*p*-hydroxybenzoic Acid

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**ABSTRACT:** Aromatic copolyesters based on diphenylolpropane and 3,5-dibromo-*p*-hydroxybenzoic acid (*p*-HBA) were synthesized by an acceptor-catalyzed polycondensation method. During the synthesis, equimolar mixtures of chloranhydrides of isophthalic and terephthalic acids were used. The effects of *p*-HBA on the tensile and thermal properties of the polyesters were investigated. The breaking stress and modulus of elasticity increased with the amount of *p*-HBA up to 10% in molar mass. A further increase in *p*-HBA caused deterioration of the tensile prop-

erties. The elongation at break decreased at low *p*-HBA contents (<5%). The addition of *p*-HBA increased the molecular packing and the limiting oxygen index and improved the thermal behavior of the synthesized polyesters. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 1755–1762, 2009

**Key words:** mechanical properties; polyesters; structure–property relations; thermal properties; thermogravimetric analysis (TGA)

## INTRODUCTION

The chemical and physical properties of polymers are often modified by different agents to increase their inherent properties. Benzoic acids have a large area of application in the polymer industry.

Lin and Hendrianto<sup>1</sup> synthesized and characterized hydrogen-bonded side-chain and crosslinked liquid polymers containing donor benzoic acids. They showed that benzoic acid caused more homogeneous phase behavior and that the *d*-spacing values of the copolymers in the smectic A phase increased with a higher hydrogen-bonded crosslinking density between benzoic acids, and this occurred because of the formation of hydrogen bonds between benzoic acids from different backbones.

Kihara and Miura<sup>2</sup> obtained hydrogen-bonded liquid-crystal polymers by the photopolymerization of 4-(6-acryloyloxyhexyloxy) benzoic acid and 4-hexyloxy-4'-cyanobiphenyl.

Blencowe et al.<sup>3</sup> synthesized and characterized hyperbranched polyesters incorporating benzoic acid. The use of carbodiimide coupling reagents enabled the production of soluble polyesters possessing molar masses and degrees of branching ranging from 2500 to 11,000 and from 0.22 to 0.33, respectively.

Rao and Sathyanarayana<sup>4</sup> synthesized toluidine amino benzoic acid copolymers by an inverse emulsion pathway with benzoyl peroxide as a novel oxidant. The solubility and crystallinity of the copolymers increased with amino benzoic acid.

Nasar et al.<sup>5</sup> prepared amine-terminated, AB<sub>2</sub>-type hyperbranched polyamides of different molar masses from 3,5-bis(4-aminophenoxy)benzoic acid by a fractional precipitation technique. They showed that the tensile strength of the resultant polymer decreased with an increase in functional groups.

Ahmed and Basfar<sup>6</sup> investigated the influence of benzoic acid on thermal, crystallization, and mechanical properties of isotactic polypropylene under irradiation. Benzoic acid prevented the detrimental influence of irradiation on the tensile strength of polypropylene, and polypropylene/benzoic acid blends demonstrated improved tensile strength.

Rao and Sathyanarayana<sup>7</sup> synthesized copolymers of aniline and *ortho/meta*-[amino benzoic acid] by chemical polymerization with an inverse emulsion pathway. The copolymers were soluble in organic solvents, and the solubility increased with the amino benzoic acid content. The amino benzoic acid groups restricted conjugation along the polymer chain.

Singh and Sekhon<sup>8</sup> studied the electrical conductivity of gel electrolytes containing different hydroxyl-substituted benzoic acids and poly(vinylidene fluoride)-hexafluoropropylene. They reported that the conductivity depended on the benzoic acid concentration. The conductivity of the polymer gel electrolytes was found to be higher than that of the

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liquid electrolytes. The increase in the conductivity with polymer addition was found to depend on the concentration of the acid present.

Yokoyama et al.<sup>9</sup> investigated the condensation of (octylamino)benzoic acid dimer phenyl esters with various substituent orientations and found narrow molar mass distributions, which indicated that the polycondensation involved a chain growth polymerization mechanism.

Tyburczy et al.<sup>10</sup> synthesized and modified fillers with derivatives of benzoic acids in elastomers. They concluded that benzoic acid increased the crosslink density and tensile strength of the elastomers.

Kricheldorf et al.<sup>11</sup> prepared copolyesters of 4-hydroxybenzoic acid, 3-(4'-hydroxyphenoxy)benzoic acid, 4-acetoxybenzoic acid, and 4-(3'-acetoxyphenoxy)benzoic acid by polycondensation. All the synthesized copolyesters in solution were highly crystalline materials that were neither meltable nor soluble, whereas some of the copolyesters prepared by polycondensation in bulk were semicrystalline, meltable, and soluble.

Castillo et al.<sup>12</sup> prepared a series of polymeric salts of *p*-substituted benzoic acids in poly(methyl methacrylate-*co*-*N,N*-dimethylaminopropylacrylamide), and alternating-current impedance studies of film-attached electrodes were carried out. The ionic conductivity was found to be highly dependent on the chemical structure produced by the substituted benzoic group, and high conductivity was obtained when Benzoic acid (BA) was strong.

Hsiao et al.<sup>13</sup> synthesized polyhydrazides and poly(amide hydrazide)s from bis(ether benzoic acid)s or their diacyl chlorides with terephthalic dihydrazide, isophthalic dihydrazide, or *p*-aminobenzoyl hydrazide by means of a phosphorylation reaction or low-temperature solution polycondensation. They reported good thermal properties. Hashimoto et al.<sup>14</sup> examined the feasibility of obtaining living polymers with low polydispersity via weakly acidic benzoic acids. They obtained living polymers with narrow molecular mass distributions (weight-average molecular weight/number-average molecular weight < 1.2).

Burillo et al.<sup>15</sup> grafted poly(*N,N*-dimethylaminoethyl methacrylate) onto a commercial polyethylene film by means of  $\gamma$  irradiation, and the grafted films were reacted with various liquid-crystal-forming benzoic acids. They obtained a variety of morphologies depending on the type of benzoic acid. When the amount of benzoic acid was less than 50%, the resultant materials were amorphous. At higher benzoic acid ratios, free-acid microcrystals dispersed in the amorphous polymer were obtained. When the acid ratio was over 80%, the resultant material became partly crystalline.

Mallakpour and Rafiemanzelat<sup>16</sup> synthesized a new class of optically active poly(amide imide)s via

the direct polycondensation reaction of bis(*p*-amido benzoic acid)-*N*-trimellitylimido-*L*-leucine and 4,4'-methylene bis(4-phenylisocyanate). The resulting polymers had inherent viscosities in the range of 0.09–1.10 dL/g. These polymers were optically active, thermally stable, and soluble in amide-type solvents.

Shinn and Lin<sup>17</sup> copolymerized poly(ethylene terephthalate) with *p*-acetoxy-benzoic acid *p*-acetoxy-benzoic acid. They found that the crystallinity of a copolyester with 80% benzoic acid increased generally with 4 h of solid-state polymerization. Higashi et al.<sup>18</sup> studied the mechanistic features of the reaction with thionyl chloride in pyridine in benzoic acid with *p*-chlorophenol or aniline. They obtained aromatic polyesters of high molecular weights (MWs) by direct polycondensation.

Although stabilizers are frequently used, their effects on the mechanical and thermal properties of polymers need further investigation. It is believed that this new field of investigation will lead to a new understanding of the applications of these stabilizers. In our previous works,<sup>19–21</sup> similar syntheses of industrial polymers and their modification were carried out, and we investigated the effects of *p*-butoxyphenyl cyclohexyl phosphinic acid and different phosphinic metallic acids on the mechanical and thermal properties of polymers based on bisphenol A and phenolphthalein.

In a recent work,<sup>22</sup> we obtained polyesters based on diphenylolpropane and phenolphthalein with a novel monomer, and their properties were reported. The research conducted in our laboratories involves the synthesis and modification of polyesters. The introduction of a halogen into a molecule of 3,5-dibromo-*p*-hydroxybenzoic acid (*p*-HBA) raises its fire resistance. Therefore, it is of interest to use a brominated derivative of *p*-hydroxybenzoic acid.

In this work, the effects of *p*-hydroxybenzoic acid on the tensile properties, thermal stability, and limiting oxygen index (LOI) of aromatic polyesters were investigated.

## EXPERIMENTAL

### Materials and processing

Chloroacetyl *p*-HBA was employed in the synthesis of new aromatic copolyesters. Initially, liquid bromine was added to the *p*-hydroxybenzoic acid. The bromination procedure of *p*-HBA and its characteristics are given in the literature.<sup>23</sup> The benzoic acid was heated in a thionyl chloride (SOCl<sub>2</sub>) environment, with dimethylformamide used as a catalyst. This chlorination increased the reactivity of *p*-HBA during the polymerization process. The structure of

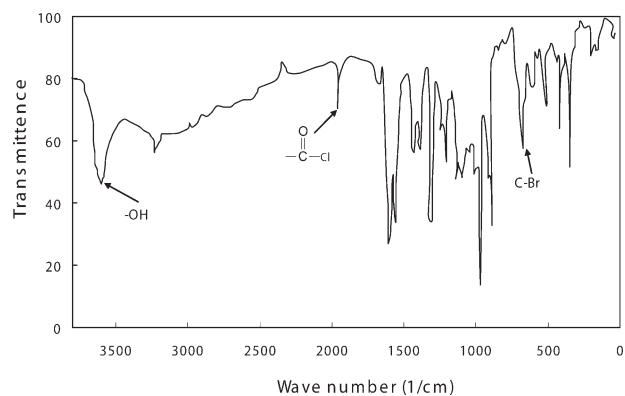


Figure 1 IR spectrum of *p*-HBA.

chloroacetyl *p*-HBA was confirmed by IR spectroscopy and elemental analysis.

The IR spectrum in Figure 1 exhibits characteristic absorptions at  $1980\text{ cm}^{-1}$  due to  $-\text{CO}-\text{Cl}$  bonds, at  $680\text{--}690\text{ cm}^{-1}$  due to the  $\text{C}-\text{Br}$  bond, and at  $3300\text{--}3600\text{ cm}^{-1}$  due to hydroxyl groups. These results confirm the structure of benzoic acid.

Elemental analysis was performed in a special laboratory of the Mendeleev University of Chemical Technology in Moscow. A quantitative elemental analysis experiment was carried out. The specimens were burnt, and the products were separately analyzed. Elemental analysis results for chloroacetyl *p*-HBA are given in Table I.

The reactivity of chloroacetyl *p*-HBA was controlled by electronic acceptor assistants located in the ortho position with respect to the hydroxyl group. The presence of bromine atoms lowered the reactivity of the hydroxyl groups by their steric influence and by the possible formation of weak hydrogen bonds between bromine atoms and hydroxyl groups.<sup>24</sup>

Diphenylpropane, chloroacetyl 3,5-dibromo-*p*-hydroxybenzoic, and equimolar quantities of chloranhydrides of isophthalic and terephthalic acids were synthesized by means of acceptor-catalyzed polycondensation at  $20^\circ\text{C}$  in a solution of dichloroethane with a concentration of  $0.5\text{ mol/L}$ . Triethylamine was employed as the proton acceptor catalyst. The molar quantity of triethylamine was equivalent to the number of available hydroxyl groups. In this work, chloroacetyl *p*-HBA was used to improve the tensile and thermal properties of the copolyesters, and it was added in molar mass percentages.

The reaction was composed of two stages, each stage lasting 1 h. Initially,  $0.022\text{ mol}$  of diphenylpropane ( $0.005\text{ kg}$ ) and  $0.0022\text{ mol}$  of chloride benzoic acid were reacted in  $10^{-5}\text{ m}^3$  of dichloroethane with  $3.35 \times 10^{-9}\text{ m}^3$  ( $0.0242\text{ mol}$ ) of triethylamine. This reaction lasted for 1 h. In the second stage,  $0.022\text{ mol}$  ( $3.12 \times 10^{-9}\text{ m}^3$ ) of triethylamine and  $0.022\text{ mol}$  of dichloroanhydrides of isoterephthalic acids were added, and this reaction also lasted for 1

h. The yield was calculated from the reactions presented in Scheme 1.

The structure of the new copolyesters was confirmed by IR spectroscopy, as shown in Figure 2. The presence of the absorption bands, which corresponded to the ester bond ( $1735\text{--}1740\text{ cm}^{-1}$ ) and  $\text{C}-\text{Br}$  bond ( $680\text{--}690\text{ cm}^{-1}$ ), and the absence of the absorption bands of corresponding hydroxyl groups ( $3300\text{--}3600\text{ cm}^{-1}$ ) point to the fact that the polycondensation of the copolymers and chloranhydrides of isophthalic and terephthalic acids was completed.

The new copolyesters were synthesized with different amounts of *p*-HBA (from 0 to 90%). Each synthesis resulted in a different yield and viscosity, as shown in Table II. The material properties deteriorated at *p*-HBA contents higher than 20%. Therefore, it was decided not to use more than 20% *p*-HBA in the experiments.

## Test methods

### IR measurements

The molecular structures of benzoic acid and the new copolyester were identified with a PerkinElmer (Norwalk, CT) 283 IR spectrometer. The copolymer was dissolved in dichloroethane, and the solution was poured into a 100-mm-diameter plate. After the solvent was evaporated, the copolymer was heated *in vacuo* to  $100^\circ\text{C}$  for 2 h, and then the IR measurements were performed.

### Viscosity measurements

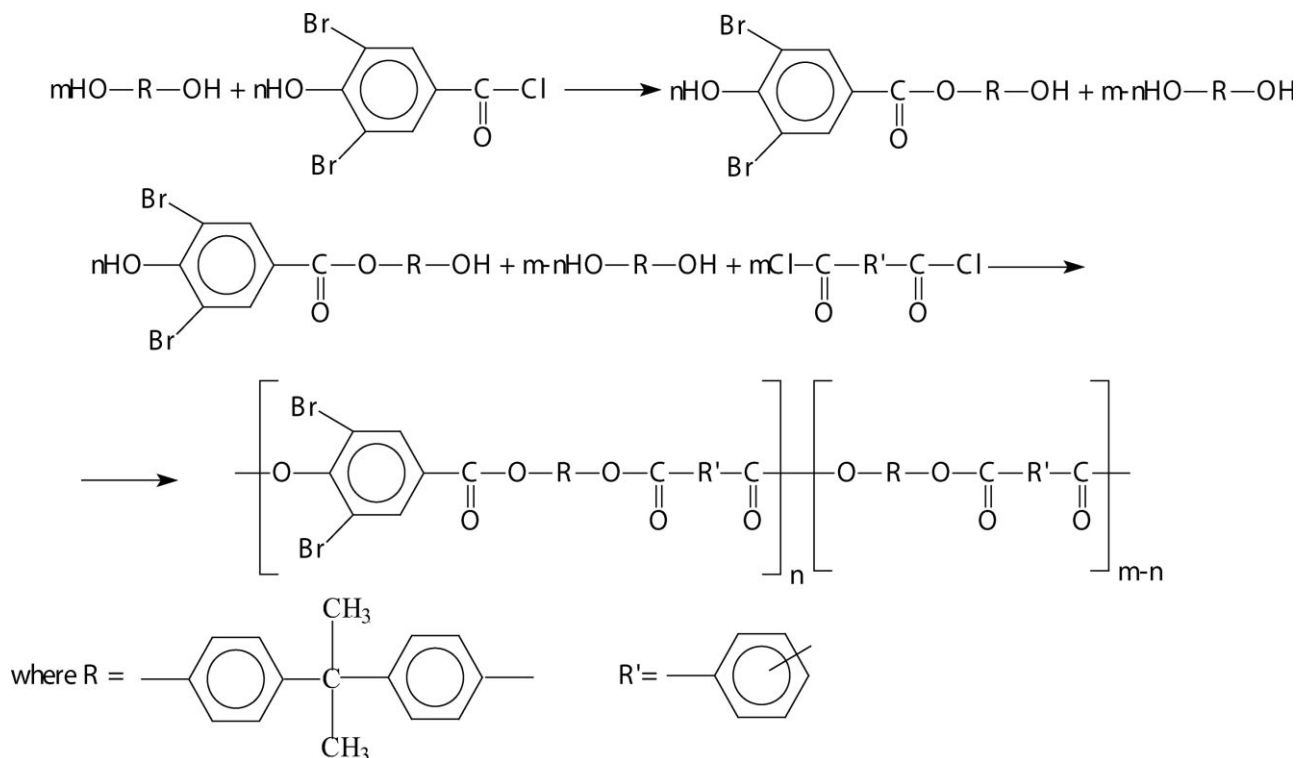
The reduced viscosity measurements were performed according to GOST 10028-81 (Russian State Standards) with an Ubbelohde viscometer with a diameter of 0.56 mm. The experiments were conducted at room temperature ( $20^\circ\text{C}$ ), and the concentration of the polymer in the solution was  $0.5\text{ g/dL}$ . Dichloroethane was used as a solvent.

### Scanning electron microscopy (SEM) and X-ray measurements

SEM measurements were carried out on an ISM-35 scanning electronic microscope (JEOL, Tokyo, Japan) at a working voltage of 15 kV with a resolution of 8 nm. To increase the topographical contrast, the object was inclined aside the deflector, which reflected electrons by  $60\text{--}75^\circ$ .

TABLE I  
Elemental Analysis Results of Chloroacetyl *p*-HBA

Element	Calcd (%)	Found (%)
C	26.79	26.74
H	0.96	0.96
Br, Cl	62.04	62.12



Scheme 1

The X-ray structural analyses were carried on a DRON-3 instrument (Burevestnik, Saint Petersburg, Russia). The diffraction graphs were obtained with a cuprum analyzer using  $\text{Cu K}\alpha_1$  radiation with a wavelength of 1.5405 Å.

#### Tensile tests

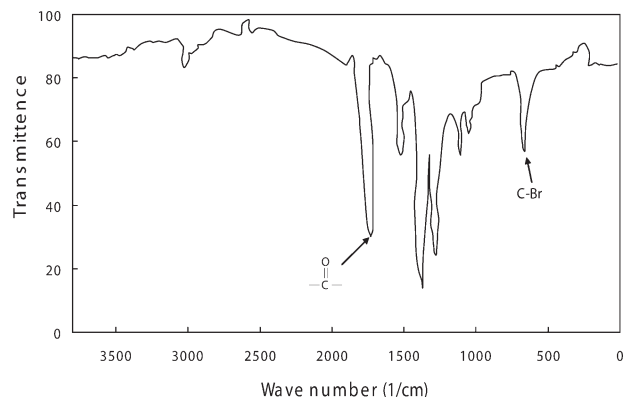
Then, the measurement of the tensile properties of the block copolyetherethers was carried out according to GOST 17-316-71 (Russian State Standards) with film specimens ( $100 \times 10 \times 0.1 \text{ mm}^3$ ) on an MRS-500 tensile test machine (Saint Petersburg, Rus-

sia) with a constant deformation rate of 40 mm/min at 20°C.

The film tensile test specimens were obtained as follows: a polymeric solution, dissolved in dichloroethane, was poured onto the flat surface of a 100-mm-diameter plate, and the dichloroethane was allowed to evaporate. The resultant polymeric sheets were put into an SPT-200 oven (Horyzont, Krakow, Poland) *in vacuo* at 100°C and dried for 2 h.

#### Thermomechanical and thermogravimetric analyses

Thermogravimetric analyses of polyesters were performed with a derivatograph (MOM, Budapest,



**Figure 2** IR spectrum of the synthesized copolyester with 5% *p*-HBA.

**TABLE II**  
Influence of *p*-HBA on the Yield and Reduced Viscosity of the Resultant Copolymers

No.	Initial substance		Yield (%)	Reduced viscosity (dL/g)
	Diphenylolpropane content (mass %)	<i>p</i> -HBA content (mass %)		
1	100	—	98.7	1
2	99	1	98.3	1
3	97	3	98.0	1.1
4	95	5	98.4	1.2
5	90	10	98.5	1.4
6	80	20	97.5	0.9
7	50	50	96.0	0.6
8	30	70	95.2	0.5
9	10	90	94.3	0.4

Hungary) at a heating rate of 5 K/min under atmospheric conditions.

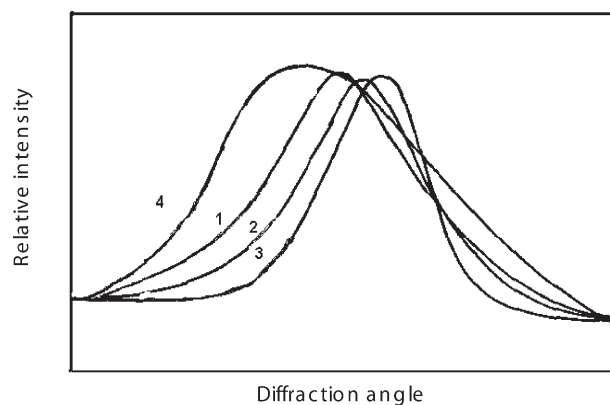
Amorphous polymers can exist in three physical conditions: glassy, rubbery (highly elastic), and viscous flow regions. In thermomechanical tests, polymer test specimens are subjected to a constant stress, and the temperature is slowly increased. The deformation of the polymer is measured as a function of temperature. In the displacement temperature diagram, the phase changes are clearly marked. The glass-transition temperature is taken as the temperature at which the polymer changes from a glassy state to a rubbery state, and the softening temperature is the temperature at which the material becomes viscous.

Thermomechanical analyses of the polymers were conducted under room (atmospheric) conditions. The tests were carried out on a Zhurkoba Pribor (Russia, Moscow) thermomechanical analyzer. The temperature was increased at the rate of 4 K/min, and the load was maintained to produce a constant tensile stress of 0.05 MPa. The thickness and width of the test specimens were 0.1 and 8 mm, whereas the distance between the clamps was 80 mm. A thermal chamber with a diameter of 30 mm and a length of 150 mm was employed. The temperature gradient of the thermal camera was 2°C along the length and 0.1°C along the diameter. The deformation of the specimen was measured by a strain gauge. The temperature and deformation were recorded on an x-y recorder.

The fire resistivity of the polymers was evaluated by the LOI test method. The test was carried out on film strips fixed vertically in the cylindrical chamber, through which passed a laminar stream of a mixture of nitrogen with oxygen. Tests were conducted at various ratios of the gas mixture until the optimum burning of the sample was reached. The sample was set on fire from the top end with the help of a gas torch, which was then withdrawn.

## RESULTS AND DISCUSSION

The influence of *p*-HBA on the yield and reduced viscosity of the resultant copolymers is shown in Table II. The table shows that the yield slightly decreased at higher *p*-HBA ratios. The reduced viscosity of the copolymer increased with *p*-HBA (until 10%) from 1 to 1.4 dL/g, and then it started to decrease with the further addition of *p*-HBA. The presence of highly polar bromine atoms in *p*-HBA must have increased the length of the polymer chains, and this resulted in increased viscosity. The further addition of *p*-HBA decreased the molecular chains, and as a result, the viscosity was dramatically decreased. The reason for this could be the lower solubility of *p*-HBA and the steric effects



**Figure 3** Diffractograms of the polyesters with (1) 1% *p*-HBA, (2) 5% *p*-HBA, (3) 10% *p*-HBA, and (4) no *p*-HBA.

caused by the presence of bromine atoms. Although the reactivity of *p*-HBA was slightly lower than that of the initiating reagents, its reactivity was sufficient for the reception of the high-molecular-weight polymers in the environment of acceptor-catalyzed polymerization.

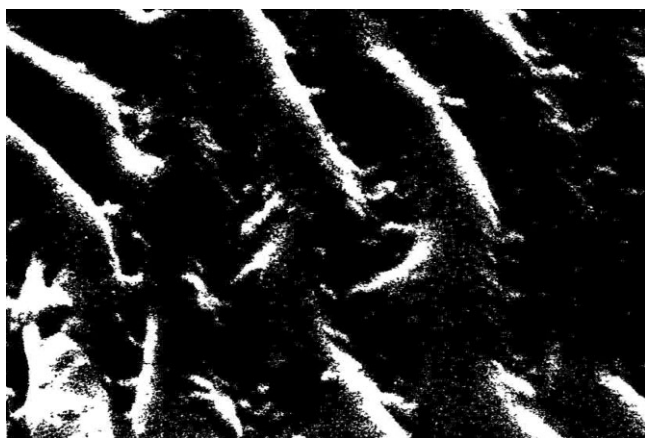
Because polymers based on *p*-hydroxybenzoic acids are known to be high crystalloids,<sup>25</sup> the crystallinity of the modified polyesters was investigated. The results of an X-ray structural analysis of film samples of the synthesized polyesters are given in Figure 3. The figure shows that at higher amounts of *p*-HBA, the diffraction curve became narrower, and the diffractograms were displaced to the right, indicating higher values of the dispersion angle ( $2\theta$ ). This increase in the dispersion angle means reduced intermolecular distance between the molecular chains. It is probable that the bromine atoms placed along the main molecular chains pulled the atoms of the other chains and thus reduced the distance between the molecular chains and at the same time increased the molecular chain length (causing an increase in the viscosity).

The SEM pictures show the formation of fibrillate structures with inclusions of crystal formations between the fibers. The sizes of the molecular formations changed from 200 to 300 Å (see Figs. 4 and 5). It can be concluded that *p*-HBA on the polyesters increased the tendency to crystallize. The X-ray measurements did not reveal a crystal structure, but they showed that the size of the crystallites increased with *p*-HBA. The enhancement of the tensile and thermal properties of the polyesters for *p*-HBA contents up to 10% could be attributed to this fact.<sup>26</sup> In the literature, it has been reported that high amounts of benzoic acid (50–80%) increased the crystallinity of the copolymers,<sup>4,15,17</sup> whereas when the acid ratio was less than 50%, only microcrystals dispersed inside the amorphous region were observed.

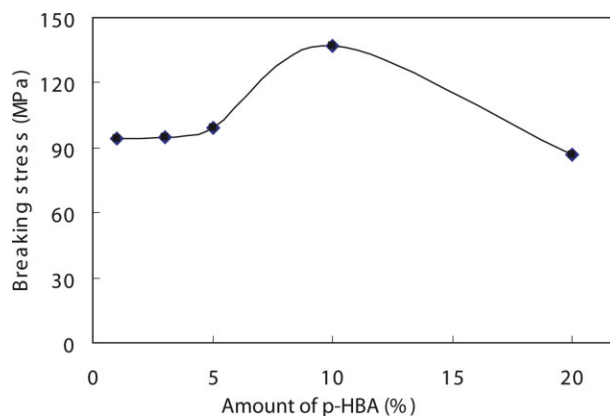


**Figure 4** Electron microscopic pictures of the polyester containing 10% *p*-HBA.

The breaking stress of the synthesized polyesters significantly increased with *p*-HBA. Figure 6 shows that the addition of 10% *p*-HBA increased the breaking stress by 46%. The stress did not change with further increases of *p*-HBA. This improvement in strength was probably attained as a result of better ordering of the macromolecular chains caused by the increased intermolecular polar forces. The polarity depended also on the distance between the molecular chains.<sup>25,27</sup> It can be argued that the presence of highly polar bromine atoms increased the polar forces between the molecular chains, reduced the distance between the chains (as confirmed by X-ray measurements), and, as a result, improved the tensile strength. The bulky nature of the C<sub>6</sub>H<sub>6</sub> units of *p*-HBA was also expected to increase the backbone strength of the molecular chains and so enhance the tensile properties. As a third effect, it may be argued that the addition of *p*-HBA increased the tendency to crystallize and so improved the tensile properties.



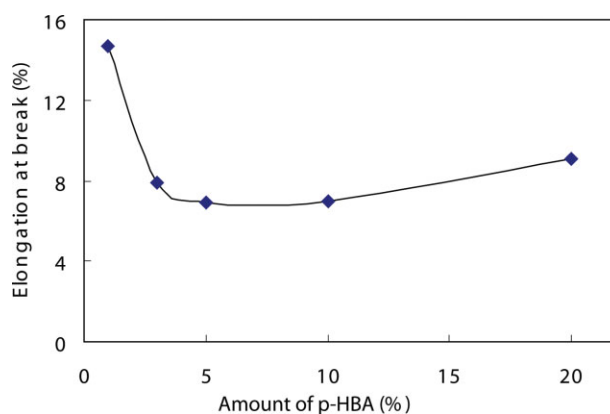
**Figure 5** Electron microscopic pictures of the polyester containing 50% *p*-HBA.



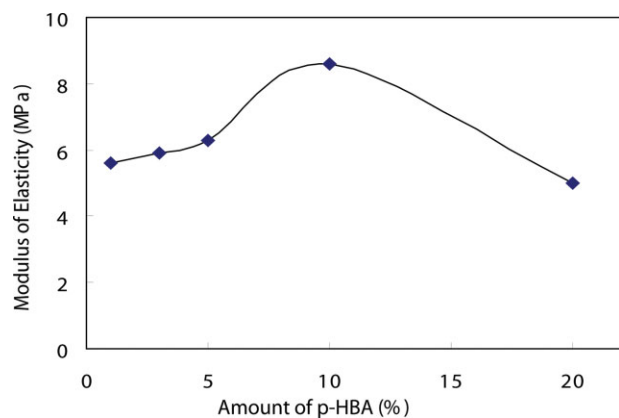
**Figure 6** Breaking stress versus the *p*-HBA concentration as a molar mass percentage. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

Figure 7 shows that small amounts of *p*-HBA (<5%) reduced the elongation at break ( $\epsilon$ ) by 53%. Further additions of *p*-HBA did not significantly change  $\epsilon$ . This reduction in  $\epsilon$  was caused by the increased rigidity of the macromolecules. It is probable that, as the length of the chains outside of crystal formations was reduced, the polymers were further stiffened and became less ductile.

Crystalline polymers are known to have a higher modulus of elasticity ( $E$ ).<sup>28</sup>  $E$  of the modified polyesters increased with the addition of *p*-HBA (see Fig. 8).  $E$  reached a maximum value (increasing by 54%) at 10% *p*-HBA and then slowly decreased with the further addition of *p*-HBA. Although a crystalline structure was not observed in our measurements, the fibrous crystallites dispersed through the amorphous range caused better packaging of the molecular chains and increased  $E$ . The viscosity results show (Table II) that bromine atoms were responsible for the increase in MW. This increase in MW may



**Figure 7**  $\epsilon$  versus the *p*-HBA concentration as a molar mass percentage. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

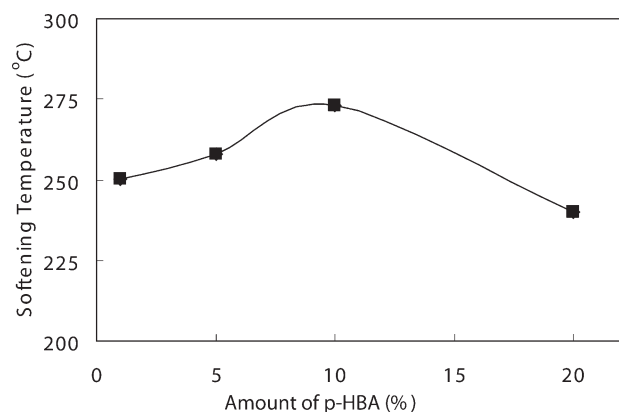


**Figure 8**  $E$  versus the  $p$ -HBA concentration as a molar mass percentage. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

also have contributed to the improvement of the tensile strength.

It is interesting to remember that the values of  $E$  and the breaking stress increased, whereas  $\epsilon$  decreased, with up to 10%  $p$ -HBA. This result agrees with the literature,<sup>29</sup> where it is reported that as the tensile strength of a material increases, its  $\epsilon$  value decreases. There is an accepted relationship between the tensile strength of polymers and the hardness.<sup>30,31</sup> The increase in the tensile strength may also correspond to an increase in hardness. Therefore, it can be concluded that the addition of small amounts of  $p$ -HBA to the resultant copolymer strengthened and hardened it and made it brittle. On the other hand, with higher quantities of  $p$ -HBA, the bulky nature of the polymer increased, the polarity of the bromine atoms was not strong enough to maintain the cohesive nature of the copolymer, and the properties deteriorated.

The thermomechanical test results for the newly synthesized polyesters showed that the softening temperature increased from 250 up to 273°C with the addition of  $p$ -HBA from 0 up to 10% (see Fig. 9



**Figure 9** Softening temperature versus the  $p$ -HBA concentration as a molar mass percentage.

**TABLE III**  
Thermal Properties of the Modified Polyesters

Modifier content (mass %)	Thermal stability (°C)			LOI (%)
	2% mass loss	10% mass loss	50% mass loss	
0	380	430	515	29
1	380	425	505	29.7
3	395	440	510	32.0
5	415	450	525	37.0
10	420	460	570	43.0
20	415	420	530	47.4

and Table III). A further increase in the amount of  $p$ -HBA resulted in a sharp reduction of the softening temperature. This may be the result of the significantly reduced molar mass.

Table III shows that the addition of chloroacetyl  $p$ -HBA significantly increased the heat stability of the polyesters. The highest heat stability was obtained with the addition of 10%  $p$ -HBA. The temperature for the mass losses of 2, 10, and 50% increased by 11, 8, and 13%, respectively, for 10%  $p$ -HBA. Such an increase in the thermal stability of the resultant polyesters can be possibly explained by the better ordering of the molecular structures attained by the introduction of an additional aromatic ring containing hydroxyl groups into the main polymeric chain. This structure promoted the formation of main polymeric chains with greater lengths. Additionally, the polar atoms of bromine also increased the thermal stability. This occurred because the bromine atoms inhibited the decomposition of chains by destroying the formed peroxides and deactivated the free radicals, which could be sources of new polymerization centers.

Higher amounts of  $p$ -HBA degraded the heat stability. This is probably connected to several factors: the increase in the polydispersity of the polymer and reduction of its molar mass, the frailty of the main molecular structures, and the increase in the number of end groups that are capable of reactions and are therefore initiators of thermal destruction by chain scission.

The modified polyesters at burning did not drop in forms of ignition; that is, they did not act as secondary sources of ignition. The analysis of the results of the fire resistance of the synthesized polyesters showed that the values of LOI increased with the  $p$ -HBA content (see Table III). The bromine atoms were believed to react with oxygen atoms and to be responsible for the increase in the oxygen index. This increase in LOI of the synthesized polyesters continued up to 20%  $p$ -HBA. Although the results are not presented here, all the synthesized polyesters were stable in diluted solutions of acids and alkalis.

## CONCLUSIONS

Polyesters were synthesized from diphenylolpropane, dichloranhydrides of isophthalic and terephthalic acids, and *p*-HBA. The structure and tensile and thermal properties of the newly synthesized polyesters were investigated. The X-ray structural analysis showed that the presence of *p*-HBA increased the crystallites and decreased the distance between the polymeric chains. The presence of bromine atoms increased the molecular forces between the polymeric chains. The viscosity of the copolymer increased with *p*-HBA (up to 10%), and this indicated a lengthening of the polymer chains. With larger amounts of *p*-HBA (>10%), the molecular chains started to shorten, and the viscosity decreased.

The addition of small amounts of *p*-HBA (up 10% in molar mass) improved the tensile and thermal behavior of the polyesters through an increased molecular chain length, an increased number of crystallites, and better packaging with shorter distances between the chains.

The softening temperature increased with *p*-HBA until 10% and then deteriorated with the further addition of *p*-HBA. The best thermal stability was observed at 10% *p*-HBA. Similarly, the introduction of *p*-HBA significantly increased the LOI.

All the test results showed that the introduction of 10% *p*-HBA favored the improvement of the following properties: the breaking stress, *E*, thermal stability, softening temperature, and LOI. Further increases in *p*-HBA degraded the tensile and thermal properties of the synthesized polyesters.

The new polyesters are suggested for consideration in various industrial applications as nonflammable and constructional polymeric materials.

## References

- Lin, H. C.; Hendrianto, J. *Polymer* 2005, 46, 12146.
- Kihara, H.; Miura, T. *Polymer* 2005, 46, 10378.
- Blencowe, A.; Davidson, L.; Hayes, W. *Eur Polym J* 2003, 39, 1955.
- Rao, P. S.; Sathyanarayana, D. N. *Synth Met* 2003, 138, 519.
- Nasar, S.; Jikei, M.; Kakimoto, M. *Eur Polym J* 2003, 39, 1201.
- Ahmed, S.; Basfar, A. A. *Nucl Instrum Methods Phys Res Sect B* 1999, 151, 169.
- Rao, P. S.; Sathyanarayana, D. N. *Polymer* 2002, 43, 5051.
- Singh, H. P.; Srekhon, S. S. *Eur Polym J* 2003, 39, 93.
- Yokoyama, A.; Saito, S.; Shimizu, Y.; Yokozawa, T. *Macromol Rapid Commun* 2005, 26, 1931.
- Tyburczy, M.; Zaborski, M.; Baryn, W. *Macromol Symp* 2003, 194, 329.
- Kricheldorf, H. R.; Döring, V.; Schwarz, G. *J Polym Sci Part A: Polym Chem* 2003, 31, 3021.
- Castillo, L. F. D.; Hernández, C.; Huanosta, A.; Ogawa, T. *Polym Int* 1999, 40, 87.
- Hsiao, S. H.; Dai, L. R.; He, M. H. *J Polym Sci Part A: Polym Chem* 2000, 37, 1169.
- Hashimoto, T.; Takahashi, T.; Kodaira, T. *J Polym Sci Part A: Polym Chem* 2000, 38, 781.
- Burillo, G.; Bucio, E.; Cervera, E.; Ogawa, T. *J Appl Polym Sci* 2000, 78, 972.
- Mallakpour, S.; Rafiemanzelat, F. *J Appl Polym Sci* 2004, 93, 1647.
- Shinn, T. H.; Lin, C. C. *J Appl Polym Sci* 2003, 47, 1105.
- Higashi, F.; Mashimo, T.; Takahashi, I. *J Polym Sci Part A: Polym Chem* 2003, 24, 97.
- Ozden, S.; Shaov, A. H.; Charayev, A. M.; Bidanikov, A. Y. *Polym Polym Compos* 1998, 6, 103.
- Ozden, S.; Shaov, A. H.; Charayev, A.; Mikitaev, A. K.; Bidanikov, A. Y. *Polym Polym Compos* 2001, 9, 213.
- Ozden, S.; Shaov, A. H.; Charayev, A. M.; Gurdaliyev, X. X. *J Appl Polym Sci* 2001, 80, 2113.
- Ozden, S.; Shaov, A. H.; Charayev, A. M. *J Mater Sci* 2001, 36, 4479.
- Jasnitskij, B. G.; Korobejnikova, I. E.; Bogun, T. A. U.S.S.R. Pat. 810666 (1984); *Bull Invent* 1984, 9.
- Kolesnikov, G. S.; Smirnova, O. V.; Mikitaev, A. K. *Vysokomol Soedin* 1967, 9, 684.
- Tagir, A. A. *Physical Chemistry of Polymers*; Chemistry Publishing House: Moscow, 1978.
- Buller, K. W. *Heat- and Temperature-Resistant Polymers*; Vygodskii, Y. S., Ed.; Chemistry Publishing House: Moscow, 1984.
- Lipatov, Y. S. *Physical Chemistry of Filled Polymers*; Chemistry Publishing House: Moscow, 1977.
- Askadsky, A. A. *Fiziko-Chemistry Polyarylates*; Chemistry Publishing House: Moscow, 1968.
- Bargel, H.-J.; Schulze, G. *Materials Science*; VDI-Verlag GmbH: Werkstoffkunde, Germany, 1980.
- Ashby, M. F.; Jones, D. R. H. *Engineering Materials*; Pergamon: Oxford, 1984.
- Fried, J. R. *Polymer Science and Technology*; Prentice Hall: Upper Saddle River, NJ, 1998.