

Synthesis, Characterization, and Hydrolytic Degradation of Copolyesters of 3-(4-Hydroxyphenyl) propionic Acid and *p*-Hydroxybenzoic Acid, Vanilic Acid, or Syringic Acid

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ABSTRACT: A series of copolyesters were prepared by a direct polycondensation of 3-(4-hydroxyphenyl) propionic acid and *p*-hydroxybenzoic acid (HBA), vanilic acid (VA), or syringic acid (SGA) of different composition in pyridine using diphenyl chlorophosphate and lithium bromide as condensing agents. The effects of methoxy substitution in the benzene ring and copolymer composition on the synthesis and thermal properties as well as hydrolytic degradation were examined. The methoxy substitution increased a glass transition temperature and a solubility, while it decreased a crystallinity and a thermal stability. The HBA series copolyesters showed a homogenous nematic phase, while the VA and SGA series copolyesters neither revealed an anisotropic melt nor formed a mobile melt below around 350°C. The hydrolytic degradation of melt-pressed films was performed in a 5% sodium hydroxide aqueous solution at 40°C to test a biodegradability of the copolyesters. HBA-50 and HBA-30 exhibited the much higher degradation rate than HBA-70, showing that the aliphatic ester linkage was more degradable than aromatic one. The degradation rates of VA-50 and SGA-50 were remarkably slower than that of HBA-50 due to the steric hindrance of the methoxy group in the *ortho* position. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 2474–2481, 2000

Key words: copolycondensation; aromatic hydroxy acids; characterization; biodegradable; thermotropic liquid crystallinity; hydrolytic degradation

INTRODUCTION

In recent years there has been a great need for biodegradable polymeric materials, since waste polymers cause serious destruction of the environment. A number of biodegradable polyesters have been developed and some of them are now commercially available, e.g., poly(L-lactic acid), poly(ϵ -caprolactone), poly(1,4-butanediol succinate), and poly(3-hydroxybutyric acid). Although these aliphatic polyesters show a good biodegradability, their thermal and mechanical properties

are often inferior to those of commodity synthetic polymers. A variety of chemical and physical modifications including copolymerization or polymer blends have been tried in order to enhance these poor physical properties.^{1–7} It is well known that thermotropic liquid crystalline (LC) polyesters have excellent mechanical properties due to the high oriented molecular chain. Thus it would be of considerable interest to develop biodegradable polyesters exhibiting liquid crystalline property. From this point of view, Kricheldorf et al. have prepared some biodegradable LC copolyesters using natural nontoxic aromatic hydroxy acids such as 3-(4-hydroxyphenyl) propionic acid (HPPA), *p*-hydroxybenzoic acid (HBA), *p*-hydroxycinnamic acid (HCA), and vanilic acid (VA).⁸ However, no

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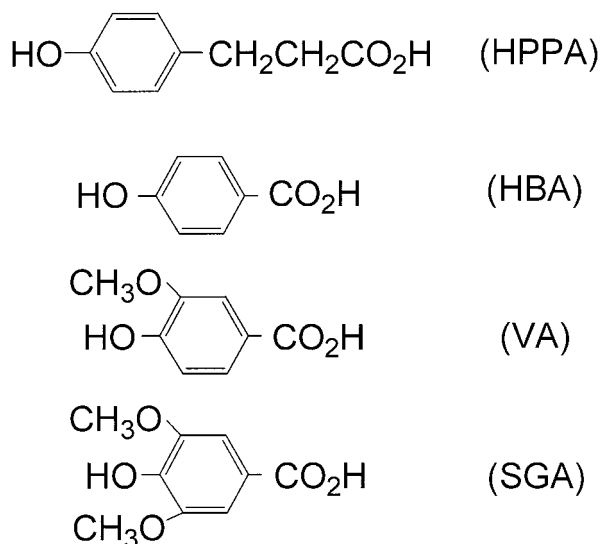


Figure 1 Structural formula and codes of monomers used in this study.

biodegradability of these LC copolyesters has been reported. Jin et al. have prepared biodegradable LC ternary copolyesters containing HBA, HCA, and glycolic acid as the reactive aliphatic component.⁹

In this study, a series of copolyesters of HPPA and HBA, VA, or syringic acid (SGA) were prepared by a direct polycondensation using diphenyl chlorophosphate and lithium bromide as condensing agents. The effects of methoxy group in the benzene ring and copolymer composition on the synthesis, thermal properties, optical microscopy, and hydrolytic degradation are examined.

EXPERIMENTAL

Materials

Structural formulas and codes of monomers used in this study are shown in Figure 1. HPPA, HBA, VA, and SGA were commercially available and used without further purification. Pyridine was distilled over calcium hydride. Anhydrous lithium bromide was dried at 170°C for 4 h. Other reagents were used as received.

Polycondensation

Copolyesters were prepared by direct polycondensation in pyridine by using diphenyl chlorophosphate (DPCP) and lithium bromide as condensing agents.¹⁰ Lithium bromide (10 mmol) dissolved in

pyridine (20 mL) was treated with DPCP (13 mmol) at room temperature and the solution was added dropwise for 30 min to a hot solution of the mixture of HPPA (5 mmol) and HBA (5 mmol) in pyridine (10 mL) preheated at 117°C for 5 min. The whole solution was heated at 117–118°C for 3 h. After the reaction, the resultant mixture was cooled to room temperature and poured into methanol. Then the precipitated polymer was filtered and washed thoroughly with methanol and dried at 80°C under vacuum for 24 h. The yield of the polymer was 1.34 g (96%) and inherent viscosity was 1.22 dL/g, measured at 0.5 g/dL in phenol/1,1,2,2-tetrachloroethane (60/40 by weight) at 30°C. The other copolymers were prepared by the analogous procedures.

Characterization

The inherent viscosity was measured at 30°C in 0.5% phenol/1,1,2,2-tetrachloroethane (60/40 by weight) solution using Ubbelohde viscometer. ¹H-NMR and ¹³C-NMR spectra were obtained at 25°C in CDCl₃ using a JEOL JNM-EX90A FT-NMR spectrometer with tetramethylsilane as the internal standard. Infrared spectra (IR) was made on a Shimadzu model IR-408 spectrophotometer using a thin film. Gel permeation chromatography (GPC) was carried out on a Shimadzu LC-9A system at 40°C using chloroform as the eluent at a flow rate of 1 mL/min. Polystyrene standards with low polydispersities were used for calibration. Differential scanning calorimetry (DSC), thermomechanical analysis (TMA), and thermogravimetry (TG) were performed in a nitrogen atmosphere with DSC-50, TMA-50, and TG-30 Shimadzu thermal analyzers, respectively. The heating rate was 20°C/min for the DSC and TG measurements and 10°C/min for the TMA measurement, respectively. The optical texture observation was carried out on a Nikon AL-PHAPOL polarizing microscope equipped with a Leica 350 hot stage.

Hydrolytic Degradation

The hydrolytic degradation of copolyesters was carried out in 5% sodium hydroxide solution at 40°C on melt-pressed films. The film specimens (10 × 10 mm in size and ca. 0.15 mm thick) were immersed in a small bottle containing 10 mL of above alkaline solution that was placed in a controlled incubator for various periods of time. After the hydrolysis, the film was washed with water

Table I Synthesis of Copolyesters

| Polymer Code | Molar Ratio in Monomer Feed | Molar Ratio in ^a Copolyester | Yield (%) | η_{inh}^b (dl/g) | M_w^c | M_w/M_n^c |
|--------------|-----------------------------|---|-----------|-----------------------|---------|-------------|
| HBA-30 | HBA/HPPA (30/70) | — ^d | 87 | 0.54 | — | — |
| HBA-50 | HBA/HPPA (50/50) | — | 83 | 1.22 | — | — |
| HBA-70 | HBA/HPPA (70/30) | — | 85 | — | — | — |
| VA-30 | VA/HPPA (30/70) | VA/HPPA (29/71) | 90 | 0.46 | 21800 | 3.86 |
| VA-50 | VA/HPPA (50/50) | — | 88 | 0.58 | — | — |
| VA-70 | VA/HPPA (70/30) | — | 90 | 0.57 | — | — |
| SGA-30 | SGA/HPPA (30/70) | SGA/HPPA (33/67) | 90 | 0.60 | 32100 | 4.01 |
| SGA-50 | SGA/HPPA (50/50) | SGA/HPPA (48/52) | 93 | 0.72 | 34400 | 3.96 |
| SGA-70 | SGA/HPPA (70/30) | — | 96 | 0.83 | — | — |

^a Measured by ¹H-NMR.

^b Measured in 0.5% phenol/1,1,2,2-tetrachloroethane (60/40 by weight) at 30°C.

^c Determined via GPC in chloroform using polystyrene standards.

^d Could not be measured.

thoroughly and dried overnight at 80°C *in vacuo*. The degree of degradation was estimated from the weight loss expressed as g/m², which was calculated by dividing the weight loss by the surface area of the film. The weight loss averaged for two specimens was employed.

RESULTS AND DISCUSSION

Synthesis of Copolyesters

A series of copolyesters were prepared by a direct polycondensation of HPPA with HBA, VA, or SGA

in pyridine using diphenyl chlorophosphate and lithium bromide as condensing agents.¹⁰ Polycondensation results are listed in Table I. The copolyesters with moderate to high inherent viscosities were obtained in excellent yield. The inherent viscosities of VA-50 and SGA-50 are lower than that of HBA-50 probably due to the steric hindrance of the methoxy groups in the *ortho* position. The inherent viscosity for HBA-70 could not be determined since it was not entirely dissolved in phenol/1,1,2,2-tetrachloroethane (60/40 by weight). The GPC curves indicated that VA-30, SGA-30, and SGA-50 had M_w values of 21,800,

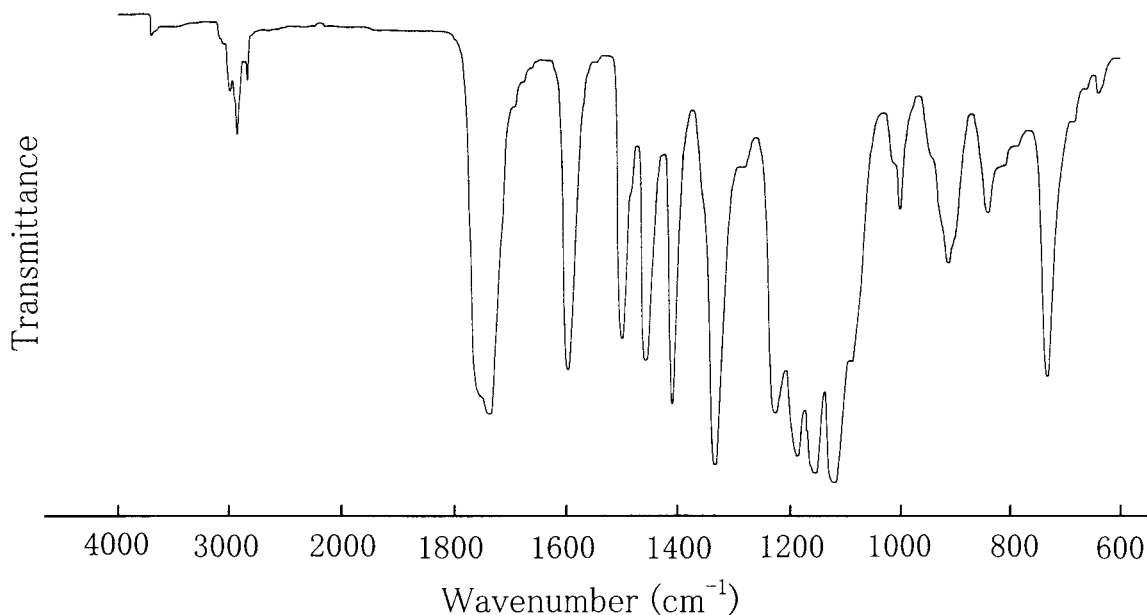


Figure 2 IR spectrum of SGA-50 thin film.

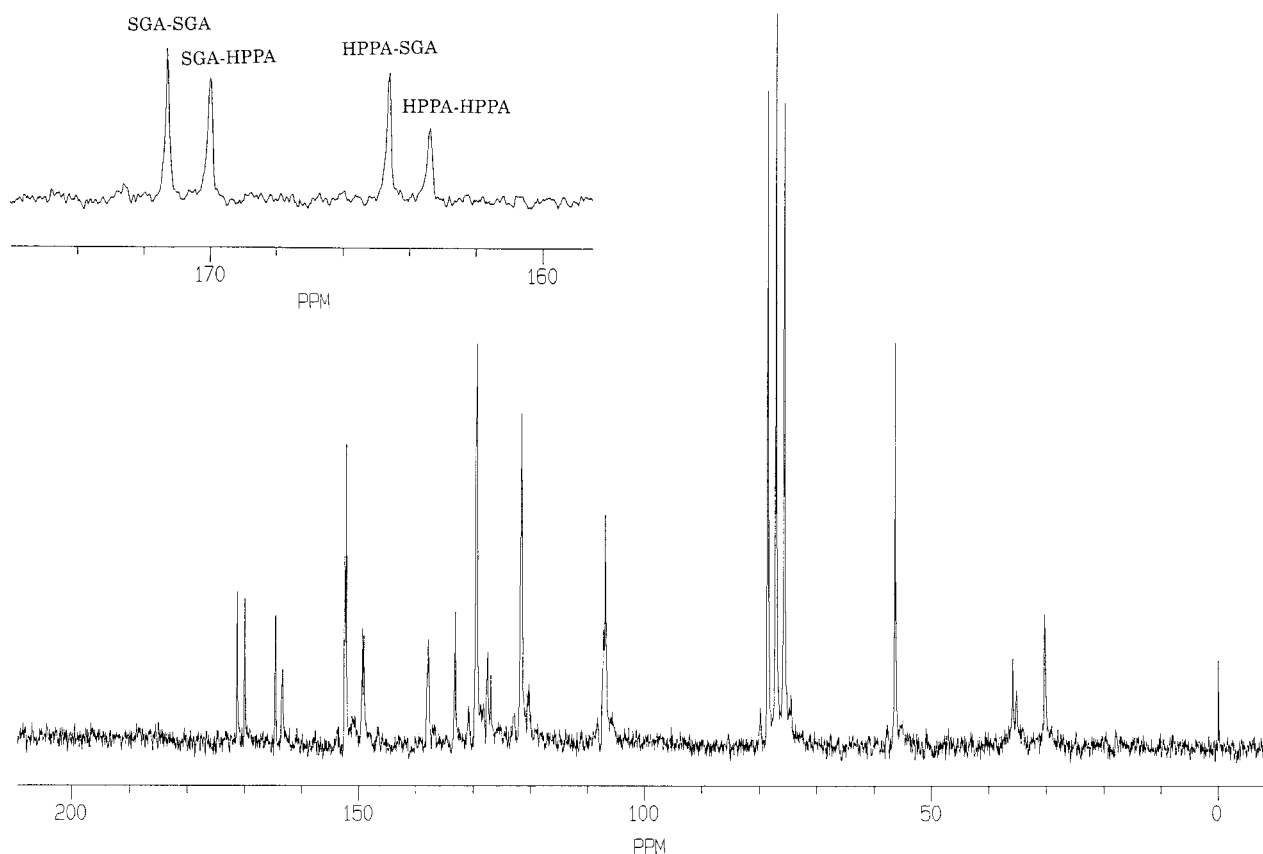


Figure 3 ^{13}C -NMR spectra of SGA-50 in CDCl_3 at 25°C .

32,100, and 34,400, respectively, for standard polystyrene.

The formation of copolyesters was confirmed by IR and ^1H - and ^{13}C -NMR spectroscopy. The IR spectra of copolyesters showed characteristic absorption bands of ester group at 1740 cm^{-1} and phenyl group at 1600 and 1500 cm^{-1} , respectively. In addition, absorption band of methoxy group was appeared at 1240 cm^{-1} for the copolyesters containing VA or SGA (Fig. 2). Because SGA-30, -50, and VA-30 are soluble in chloroform, their ^1H - and ^{13}C -NMR spectra were recorded. In the ^1H -NMR spectra of these copolyesters, signals for the aromatic ring at 6.8–7.6 ppm, the ethylene group at 3.0 ppm, and the methoxy group at 3.9 ppm were observed, respectively. The molar compositions of the copolyesters were calculated from relative intensities of the methoxy group in VA or SGA and the ethylene group in HPPA, which is listed in Table I. The composition of the copolyesters is a good agreement with those expected from the feed composition. Figure 3 shows the typical ^{13}C -NMR spectra of SGA-50. The signals of the α -methylene (adjacent to carbonyl group), the

β -methylene (adjacent to aromatic ring), and the methoxy group are appeared at 30.3, 35.9, and 56.4 ppm, respectively, and those between 121.6 and 152.2 ppm are responsible for aromatic carbons. Special attention was paid to carbonyl region between 162 and 172 ppm. The four carbonyl signals of roughly equal intensities appear, which are assigned to the four possible diads (HPPA–HPPA at 163.4 ppm, HPPA–SGA at 164.6 ppm, SGA–HPPA at 170.0 ppm, SGA–SGA at 171.3 ppm), suggesting the existence of random sequence for copolyesters.^{8,11}

Thermal Properties of Copolyesters

DSC heating and cooling curves are shown for as-prepared copolyesters in Figure 4 and Figure 5, respectively. Measured glass transition temperatures (T_g), melting temperatures (T_m) (on heating run) and crystallization temperatures (T_{mc}) (on cooling run) are summarized in Table II. TMA was also performed for melt-quenched films to obtain a T_g since it could not be detectable for some copolyesters. T_g 's obtained from two

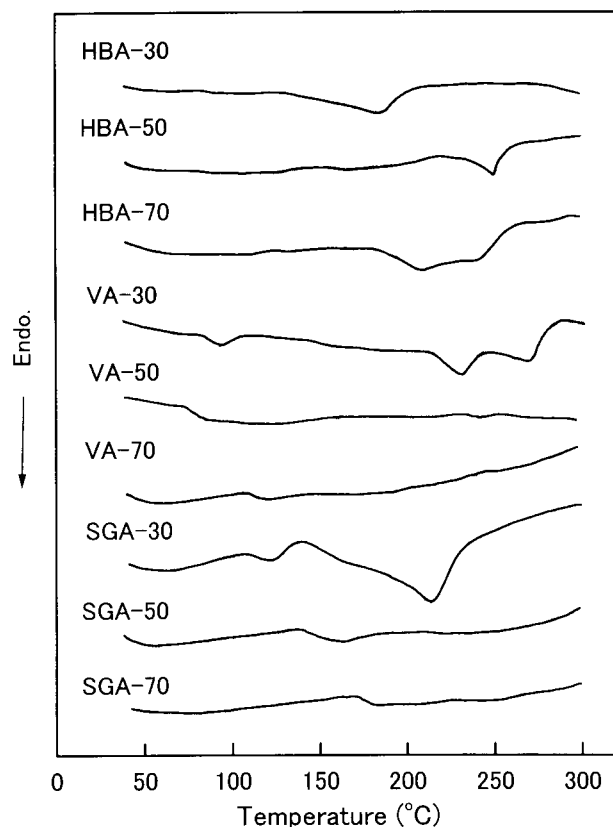


Figure 4 DSC heating curves of copolyesters.

thermoanalytical techniques (DSC and TMA) are in a good agreement. T_g increases in the following order—HBA < VA < SGA series copolyesters—which would be ascribed to the chain stiffening effect due to an increase in the rotational energy barrier caused by the bulky methoxy groups in the *ortho* position to the phenolic oxygen in the benzoate unit. It also increases with decreasing HPPA content, suggesting the chain stiffening effect caused by the more rigid HBA, VA, or SGA component. The melting endotherms (T_m) on heating run are appeared for HBA-30, -50, -70 (broad peak), VA-30 (double peaks), and SGA-30. The corresponding crystallization exotherms on cooling run (T_{mc}) are also appeared (Fig. 5). In contrast, no T_m is detected for VA-50, -70 and SGA-50, -70, suggesting that the packing of the polymer chains is disturbed with increasing the content of the bulky methoxy groups in the benzene ring, subsequently causing a decrease in the crystallinity of polymer. The transition from anisotropic to isotropic was not detected by the DSC method.

Thermotropic LC properties were examined by a polarized microscope. The homogenous nematic

phase was observed for HBA series copolyesters above T_m and it was stable up to around 350°C. Figure 6 represents the optical texture taken under a polarized-light microscopy from the nematic state (260°C) of HBA-50. Kricheldorf et al. also have demonstrated that HBA-50 prepared by polycondensation of the trimethylsilylester of acetylated HPPA with acetylated HBA forms a homogenous nematic melt.⁸ However, VA-30, -50 and SGA-30, -50 revealed an isotropic melt containing dispersed solid particles in the melt and a homogeneous isotropic melt (a dark field under polarized-light microscopy), respectively, indicating that the methoxy groups in the benzene ring disturb the formation of thermotropic liquid crystal in the copolyesters. This is probably because the methoxy groups in VA and SGA series copolyesters render the polymer chain more irregular and/or decrease the intermolecular force between the polymer chains in comparison with HBA series copolyesters. VA-70 and SGA-70 did not form mobile melt up to around 350°C.

The thermal stability of the copolyesters were evaluated by TG in N_2 . The TG data of copolyesters are summarized in Table III and representative TG curves are shown in Figure 7. HBA-50 exhibits the highest T_d , 410°C, the temperature where 1% weight loss was observed, among the copolyesters. T_d decreases in the following order—HBA > VA > SGA series copolyesters—in-

Table II Phase Transition Temperatures of Copolyesters

| Polymer Code | T_g^a (°C) | T_g^b (°C) | T_m^a (°C) | T_{mc}^a (°C) | LC Phase ^c (°C) |
|--------------|--------------|--------------|-----------------------|-----------------|----------------------------|
| HBA-30 | — | 63 | 187 | 192 | Nematic |
| HBA-50 | — | 72 | 238 | 225 | Nematic |
| HBA-70 | — | 102 | 180–241 ^d | 238 | Nematic |
| VA-30 | 83 | 80 | 232, 268 ^e | 264 | — ^f |
| VA-50 | 91 | 86 | — | — | — ^f |
| VA-70 | 108 | — | — | — | — ^g |
| SGA-30 | 115 | 108 | 215 | 200 | — ^h |
| SGA-50 | 144 | 136 | — | — | — ^h |
| SGA-70 | 168 | — | — | — | — ^g |

^a Determined by DSC.

^b Determined by TMA.

^c Measured by polarized microscopy.

^d Broad peak was observed.

^e Double peaks were observed.

^f Isotropic melt + crystallites.

^g Infusible up to around 350°C.

^h Homogenous isotropic melt.

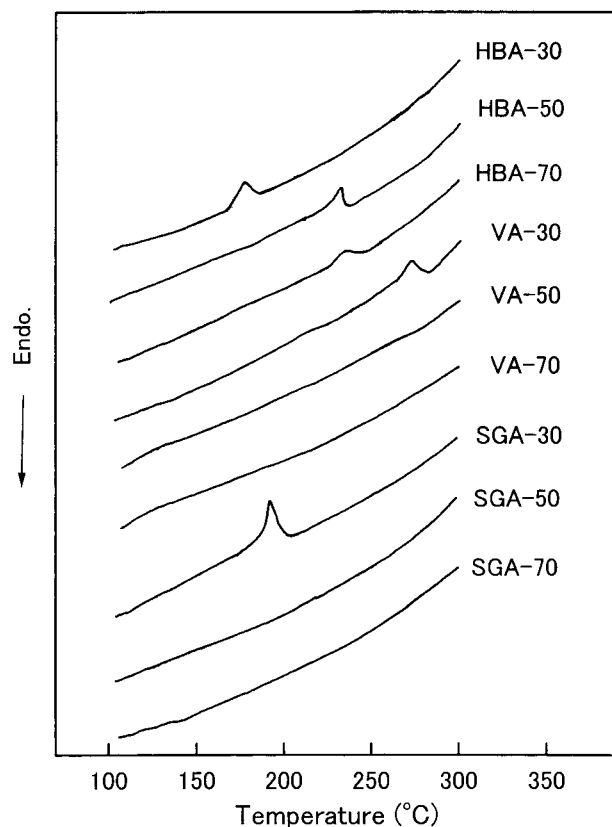


Figure 5 DSC cooling curves of copolyesters.

dicating that methoxy groups in the benzene ring reduce the thermal stability of polymers. It also decreases remarkably as the content of HPPA decreases to 30 mol %. The weight of residues at 600°C (R_{600}) are about the same for all of the copolyesters.

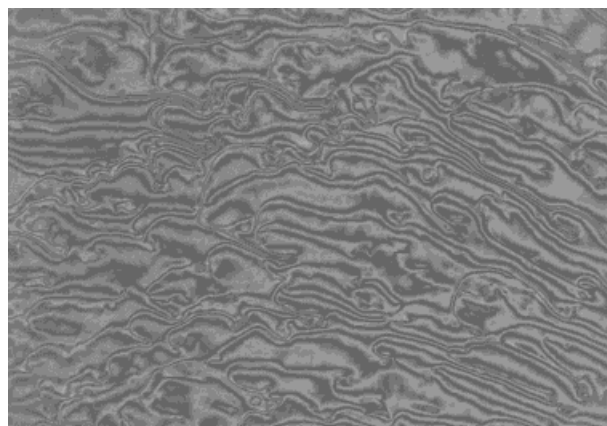


Figure 6 Polarized-light microphotograph of a melt of HBA-50 at 260°C (magnification 350×).

Table III Thermogravimetry of Copolyesters^a

| Polymer Code | T_d (°C) | T_{10} (°C) | T_{50} (°C) | R_{600} (wt %) |
|--------------|------------|---------------|---------------|------------------|
| HBA-30 | 408 | 438 | 506 | 41 |
| HBA-50 | 418 | 462 | 520 | 43 |
| HBA-70 | 363 | 435 | 536 | 42 |
| VA-30 | 403 | 434 | 485 | 37 |
| VA-50 | 398 | 440 | 485 | 39 |
| VA-70 | 356 | 410 | 472 | 35 |
| SGA-30 | 395 | 435 | 475 | 34 |
| SGA-50 | 390 | 434 | 470 | 38 |
| SGA-70 | 360 | 431 | 465 | 36 |

^a T_d (1% weight loss temperature), T_{10} (10% weight loss temperature), T_{50} (50% weight loss temperature), and R_{600} (char yield at 600°C) determined by TG in nitrogen at a heating rate of 20°C/min.

Solubilities of Copolyesters

The solubilities of copolyesters are given in Table IV. Homopolymers from HPPA, HBA, VA, or SGA are insoluble in organic solvents listed in Table IV,^{11,12} while the solubility is increased dramatically for the copolyesters. This enhanced solubility behavior indicates that the copolyesters are random copolymers—neither a block copolymer nor a blend of two homopolymers as suggested by ¹³C-NMR spectra shown in Figure 3. The solubil-

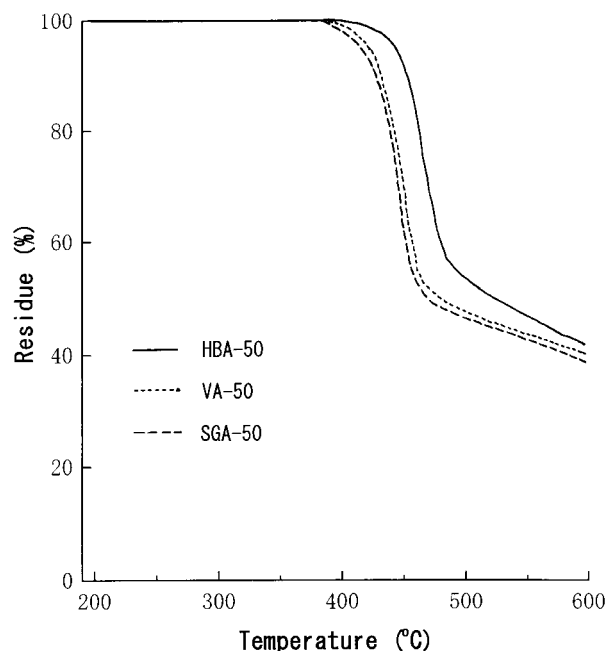


Figure 7 TG curves in N_2 for HBA-50, VA-50, and SGA-50.

Table IV Solubility of Copolyesters^a

| Polymer Code | Solvents | | | |
|--------------|-------------------|-----|------|----------|
| | CHCl ₃ | DMF | DMSO | Pyridine |
| HBA-30 | - | - | + | ± |
| HBA-50 | - | - | - | ± |
| HBA-70 | - | - | - | - |
| VA-30 | ++ | + | + | + |
| VA-50 | - | - | ± | ± |
| VA-70 | - | - | - | - |
| SGA-30 | ++ | ++ | ++ | + |
| SGA-50 | ++ | + | ++ | + |
| SGA-70 | - | ± | ± | + |

^a Solubility: soluble at room temperature, ++; soluble on heating, +; partially soluble on heating, ±; insoluble, -. DMF: *N,N*-dimethylformide; DMSO: dimethyl sulfoxide.

ity of copolyesters increases in the following order—HBA < VA < SGA series copolyesters—probably due to the depression of crystallinity caused by the presence of the methoxy group in the benzene ring as described above. It is interesting to note that VA-30, SGA-30, and SGA-50 are soluble in common organic solvents such as chloroform and dimethyl sulfoxide.

Hydrolytic Degradation of Copolyesters

The hydrolytic degradation of copolyesters have been investigated on the melt pressed films immersed in 5% sodium hydroxide aqueous solution at 40°C. It has been demonstrated that copolyesters derived from HPPA and lactic acid or mandelic acid have been very sensitive to hydrolytic degradation *in vitro*.^{13,14} However, copolyesters derived from HPPA and aromatic hydroxy acids in this work would take a considerably longer period of time to be biodegraded sufficiently by microorganism or enzymes at ambient temperature. For a quick estimation of comparative hydrolytic degradability and good reproducible data, alkali hydrolysis was employed in order to test a biodegradability of copolyesters.^{15–18} Figure 8 shows weight loss of melt-pressed films exposed to 5% sodium hydroxide aqueous solution at 40°C against degradation time. Weight losses for HBA-30 and HBA-50 films increase abruptly with degradation time and these films disappeared completely in 5% sodium hydroxide aqueous solution after 24 h incubation. In contrast, the weight loss for HBA-70 was only 2% after the same period of incubation. In addition, the weight losses

for VA-50 and SGA-50 are much smaller than copolyesters containing HBA after 72 h incubation. The weight loss would be caused by the hydrolysis of ester linkages of copolyesters. There are two types of ester linkages in the copolyesters: the ester linkage between the aromatic carboxylic group and the aromatic hydroxyl group (aromatic ester linkage), and that between the aliphatic carboxylic group and the aromatic hydroxyl group (aliphatic ester linkage). The hydrolysis of ester linkages begins with a nucleophilic attack of hydroxide ion on the carbonyl group. The electrophilicity of the aliphatic carbonyl group is significantly higher (by a factor 10²–10⁴) than that of aromatic the carbonyl group,⁸ implying that the aliphatic ester group is cleaved much faster than the aromatic one. Hence, the much faster degradation rate for HBA-30 and -50 would be ascribed to the presence of a more degradable aliphatic ester linkage in copolyesters, while the much slower rate of HBA-70 is responsible for the longer blocks of the HBA units forming the aromatic ester linkage. The content of aliphatic ester linkage is larger for HBA-30 than for HBA-50, but the latter degrades faster than the former, showing that the HPPA–HPPA aliphatic ester linkage is more resistant to nucleophilic attack than the HPPA–HBA one. VA-50 and SGA-50 exhibit much a slower degradation rate than HBA-50, although these copolyesters have the almost similar number of aliphatic ester linkages, which would be attributed to the steric hindrance of methoxy group in *ortho* positions to degradable aliphatic ester linkage. This would be supported by the slower degradation rate of SGA-50, which is more sterically hindered in terms of the pres-

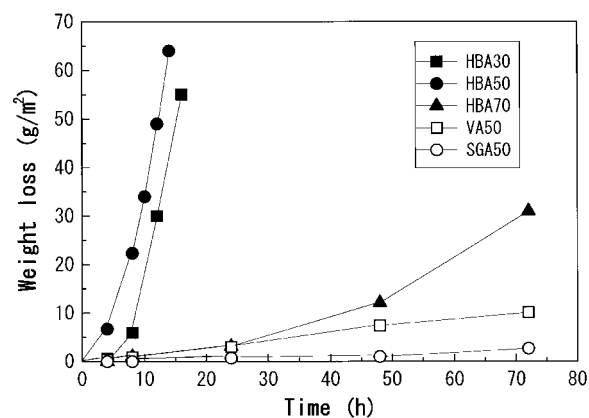


Figure 8 Weight loss of copolyester films against degradation time degraded in 5% sodium hydroxide aqueous solution at 40°C.

ence of two methoxy groups in the *ortho* positions. The alkaline hydrolysis products for copolyesters were identified using GPC. HBA-50 film was degraded at 40°C for 24 h in a 5% sodium hydroxide aqueous solution. After degradation, the solution was acidified with hydrochloric acid to pH 2 and freeze dried. It was dissolved in tetrahydrofuran and filtered, then the filtrate was subjected to GPC analysis. Approximate equal amounts of HPPA and HBA monomers appeared along with a trace amount of some oligomers, demonstrating that HBA-50 is degraded completely into monomer units.

A biodegradation of the copolyesters including an enzymatic degradation and a degradation in activated sludge is now in progress and will be published in the future.

CONCLUSION

Moderate to high molecular weight copolyesters of HPPA with HBA, VA, or SGA were successfully prepared by a direct polycondensation method in pyridine using diphenyl chlorophosphate and lithium bromide as condensing agents. The methoxy groups in the benzene ring increased a T_g and a solubility, while they decreased crystallinity and thermal stability. HBA series copolyesters showed a homogenous nematic phase, while VA and SGA series copolyesters neither revealed an anisotropic melt nor a formed mobile melt below around 350°C. The degradation rate in a 5% sodium hydroxide aqueous solution at 40°C decreased in the following order—HBA-50 > HBA-30 ≫ HBA-70 > VA-50 > SGA-50—which could be explained by the decrease of the degradable aliphatic ester linkage and by the steric hindrance of the methoxy groups in the *ortho* position. It was found that the degradation rate de-

pended greatly on the chemical structure and composition of copolymers.

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