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Synthesis, Characterization, and *in Vitro* Degradation of a Novel Thermotropic Ternary Copolyester Based on *p*-Hydroxybenzoic Acid, Glycolic Acid, and *p*-Hydroxycinnamic Acid

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ABSTRACT: The direct copolycondensation of aromatic hydroxy acid with aliphatic α-hydroxy acid was achieved by using certain amounts of a third comonomer with or without a catalyst. High molecular weight main-chain thermotropic liquid crystalline terpolyesters with a potentially biodegradable property based on *p*-hydroxybenzoic acid (PHBA), glycolic acid (GA), and the bridge comonomer *trans-p*-hydroxycinnamic acid (PHCA) were synthesized via a one-step melt copolycondensation process. Solution viscosity, Fourier transform infrared spectrometer (FTIR), and nuclear magnetic resonance (^{1}H NMR, ^{13}C NMR) measurements were used to identify the formation and structure of this terpolymer; a random sequence distribution of the comonomeric units along the polymeric chains was concluded. A single glass transition temperature at about 82 °C and a broad endothermic transition with a maximum at 150 °C were discerned in the DSC profiles of the as-prepared polymers. Wide-angle X-ray diffraction (WAXD) analysis indicated the occurrence of a nematic structure in the as-injected fiber of the terpolymer. This nematic liquid crystallinity was further confirmed from the characteristic textures under optical polarizing microscopy (POM): a Schlieren-type texture for low molecular weight copolymers or banded textures for high molecular weight ones over a wide temperature range. The anisotropic–isotropic transition was not clearly detectable until the polymer decomposition. The *in vitro* degradation of the thermotropic liquid crystalline ternary copolyester was evaluated by water absorption, inherent viscosity, morphology, and thermal properties after treatment in buffer media in the absence of enzyme. It is clearly shown that the hydrophilicity was greatly improved due to the incorporation of GA segments. The copolymer degraded via a simple hydrolysis of the ester bonds of GA-rich segments, and the aromatic counterpart could also be involved in the hydrolysis. These degradations occurred predominantly in the amorphous or less aligned regions.

Introduction

Research on polymers has been mainly addressed to the synthesis of new materials with specific performance in the last 30 years. Liquid crystalline (LC) polymer was developed to combine high mechanical and thermal properties with excellent processability. Several kinds of polymers like KEVLAR or VECTRA represent clear examples in this direction. Recently, on the other hand, the scientific community have paid increasing attention to the degradability of polymer materials. Hydrolytic and enzymatic degradation of the polymeric backbone was investigated to reduce the ecological problems related to plastic recycling. In addition, such an investigation was also directed toward to biomedical application of polymeric materials because there is a significant potentiality of polymers as drug-releasing implants, as bioabsorbable surgical sutures, or as the absorbable component in selectively biodegradable vascular grafts.[1-3] Various synthetic biodegradable and biocompatible polymers have been developed to meet certain specific requirements for such kinds of biomaterials.[4] There are numerous studies to understand the relationships between the structure, morphology, mechanical property, degradability, and processability to meet various requirements in other aspects of reconstructive surgery.[5-7]

Except for the critical influence from the chemical constitution, any alternation in crystallinity and mor-

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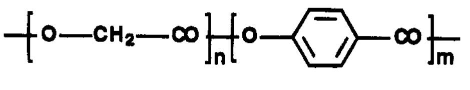
phology would result in a big change of degradation behaviors of polymers since the general degradation mechanism is of hydrolytic nature and proceeds through the two phases in those semicrystalline polymers. However, most of conventional biodegradable polymers based on aliphatic polyesters, such as poly(glycolic acid) (PGA), usually have a lower T_g and a higher T_m, so their performance and processability could not sometimes match the requirements even although they have quite good biodegradability. A wide variety of chemical or physical strategies, including the copolymerization, polymer blend, and composite or cross-linking networks, have been explored to match individual requirements.[8-11]

For liquid crystalline polymers (most of them also belong to the polyester family), it is well-known that they usually possessed an excellent processability and self-reinforced mechanical strength due to the unique morphology or the highly oriented macromolecules.[12] However, from our knowledge, there is no synthetic biodegradable polymer could exhibit thermotropic behavior, although some synthetic polypeptides like poly(γ-benzyl L-glutamate) and cellulose derivatives are lyotropic.

Therefore, our current research is aimed at exploring the possibility of developing an easily-processable, biodegradable, and/or biocompatible polymer with enhanced mechanical properties. The efforts for such a high-performance biodegradable polymer mainly involve molecule design and synthesis strategy. The basic considerations are based on (1) the excellent biodegradability and biocompatibility of linear aliphatic polyesters derived from hydroxy acids;[1-3] (2) the effectiveness of flexible spacer blocks in depressing the transition temperatures and in improving the solubility of liquid crystalline polymers,[12] and (3) the most important role played by the simplest aromatic hydroxy acid as *p*-hydroxybenzoic acid (PHBA) in developing mesogenic polymers.[12] Accordingly, the expected biodegradable thermotropic liquid crystalline polymers should be composed by some aromatic polyester as mesogenic segments and some aliphatic polyester units as both flexible spacer and biodegradable sites. Since copolymerization of various monomers with different rigidity is one of the most effective methods of modifying the LC polymers, in our previous studies,[13,14] either the one-step copolymerization method or the two-step transesterification method was employed to synthesize the two series of potentially biodegradable thermotropic liquid crystalline copolyesters as follows:



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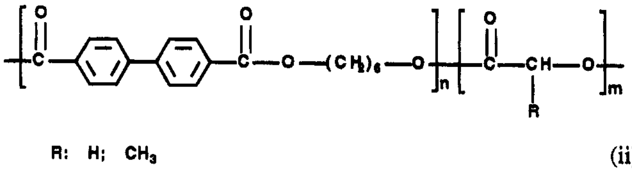
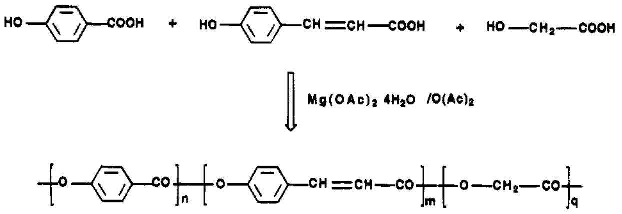


(ii)

The incorporation of the aliphatic hydroxy acid into the main chains of rigid aromatic polyesters did decrease the melting temperature of the copolyesters and also made them thermotropic.[13] However, owing to the poor copolycondensability of aliphatic α-hydroxy acid with the aromatic ones, its degree of polymerization is usually quite limited.[14,15] The alternative approach of polymerizing diethyl biphenyldicarboxylate and aliphatic diol with glycolic acid or polylactide like in ii failed to produce a very high molecular weight copolymer with a satisfactory mechanical property.[14] In both cases, a higher polymerization temperature had been employed to increase the molecular weight of the growing chains. However, severe thermal decomposition could not be avoided.

Scheme 1. Synthesis of the Terpolymers Based on PHBA, PHCA, and GA



Kricheldorf et al.[16] investigated the copolymerization of 4-hydroxycinnamic acid (PHBA)/3-(4-hydroxybenzyl)-propionic acid (PHPA) in various compositions, which showed a good copolycondensability. More recently, Pillai and his co-workers[17] reported a preliminary result on the novel thermotropic liquid crystalline copolyesters derived from 8-(3-hydroxyphenyl)octanoic acid (8-MHOA) and PHBA, in which fair copolycondensability was demonstrated. Its capability of forming a liquid crystal phase at a relatively low temperature due to the incorporation of the 8-MHOA was evident as well. Their thermal stability, however, was lower if compared to those of all-aromatic polyesters. This means that these extra monomers not only control the melting temperatures as the flexible spacers do but also affect the degradation behaviors. Therefore, in our present study, a third comonomer, PHCA, is selected as the comonomer with PHBA and GA to balance the liquid crystallinity and biodegradability for development of a biodegradable liquid crystalline copolyester. Another consideration for the use of PHCA is that the double bond in the cinnamyl group would be used as the potential reactive site[18-20] for a second-stage cross-linking reaction to produce an LC network.

This paper gives the results of studies on the synthesis, characterization, and *in vitro* degradation behavior of such a thermotropic biodegradable copolyester.

Experimental Section

Materials. Glycolic acid (99%) was purchased from Aldrich Chemical Co, Gillingham, U.K.; 4-hydroxybenzoic acid (99%) and acetic anhydride (99%) were from Aldrich Chemical Co., Milwaukee, WI. Magnesium acetate tetrahydrate (99%) and *trans*-4-hydroxycinnamic acid (98%) were from Aldrich-Chemie, Steinheim, Germany. All these monomers and solvents were from commercial sources and were used without further purification.

Polymer Synthesis (Scheme 1). Typically, the polymers were synthesized in a 250-mL, two-necked, round-bottomed flask equipped with a mechanical stirrer with a nitrogen inlet valve and a vacuum distillation outlet, which was fitted with a vacuum takeoff. To the flask were introduced 6.08 g (80 mmol) of glycolic acid, 16.58 g (120 mmol) of *p*-hydroxybenzoic acid, and 13.12 g (80 mmol) of *trans*-*p*-hydroxycinnamic acid, and 50 mg of $Mg(OAc)_2{\cdot}4H_2O$ (as a transesterification catalyst) and 30 mL of acetic anhydride (as a condensation reagent) were introduced into the flask. It was immersed into an electrostatically preheated silicone oil bath at 170 °C after the flask was previously evacuated and purged with nitrogen alternatively three times at room temperature to remove the moisture and residual air. It should be indicated that a great nitrogen flow was necessary to purge into the flask in order to avoid the thermal oxidation of the less stable PHCA monomer. The reaction mixture became a clear colorless liquid accompanied by the distillation of acetic anhydride. The temperature was then raised to 200 °C and maintained until almost all of the solvent was distilled off, and the reaction mixture became turbid upon increased viscosity. During this process, sublimation was found near the flask neck, which could be remelted into the system when the temperature was further increased. After the temperature reached 215 °C a vacuum of 15 Torr was applied and maintained during the whole polycondensation process of 20 h. A characteristic melt turbidity with bright, light yellow color under stirring could be observed during the final stage of the polycondensation, and it exhibited a strong tendency toward forming fibers. The resulting polymer was removed from the flask while it was in its molten state, and then the as-prepared polymer was mechanically powdered and washed with acetone and methyl alcohol several times to remove the residual monomers or solvent. Finally it was dried *in vacuo* at 80 °C for 24 h; 25.5 g of polymer was obtained in a yield of 83%. The inherent viscosity (η_{inh}) was measured in mixtures of trifluoroacetic acid (TFA)/chloroform ($CHCl_3$) (20/80 by volume) at a concentration of about 4 g in 100 mL at 25.0 °C with a Cannon−Ubbelohde-type viscometer.

Measurements. Differential scanning calorimetry (DSC) measurements were performed on a DuPont DSC-2910 thermal analyzer at a heating or cooling rate of 10 °C/min under nitrogen circulation; an aluminum pan was used as a reference. Thermogravimetric analyses (TGA) were also obtained on a DuPont TGA-951 at a heating rate of 10 °C/min in nitrogen or in air.

Fourier transform infrared spectra (FTIR) were made on a Nicolet 5PC FTIR spectrometer with a resolution of 2 cm^{-1}; the thin film used for FTIR analysis was directly prepared by shear-pressing the molten polymer on the hot NaCl plate.

Carbon-13 nuclear magnetic resonance measurements were made at a Varian 270-MHz NMR spectrometer in a 1/1 mixture of deuterated chloroform and trifluoroacetic acid ($CDCl_3$/TFA-*d*).

The wide-angle X-ray diffraction (WAXD) photograph was obtained from the as-injected fiber using a transmission flat-film camera with Cu Kα radiation. In addition, $\theta/2\theta$ diffractometer scans were also recorded from large bundles of parallel fiber along the direction corresponding to the meridian of the fiber diagram, using a Rigaku Geigerflex diffractometer (Cu Kα radiation with a Ni filter) using 40 kV and 30 mA. The scans were made in the angular range of 5−45° (2θ) at a goniometer speed of 5°/min.

Optical micrographs were obtained on a Polyvar (Reichert-Jung) polarized microscope in conjunction with a LINKAM TH600 hot stage at an arbitrary heating rate of 10 °C/min.

The water content of the polymer was determined by soaking the film samples in a buffer solution either of pH 10.0 or of pH 7 at 37.0 or 60.0 °C, respectively. At every fixed period of time, the specimens were taken out for weighing. Samples were gently blotted prior to the weighing to remove the excess surface water. The water content is expressed here as the percentage of the initial dry polymer. Reported water contents were the average of 5−10 specimen determinations. The degree of the *in vitro* degradation and the water absorption of the polymer were evaluated according to equations (1) and (2)

$$\text{degree of } \textit{in vitro} \text{ degradation } (\%) = 100(W_0 - W_D)/W_0 \quad (1)$$

$$\text{water absorption } (\%) = 100(W_W - W_0)/W_0 \quad (2)$$

where W_0 is the initial weight of the copolymer sample, W_w is the wet weight of the copolymer after hydrolyzing a desired period in a buffer solution, and W_D is the weight of the dried copolymer sample after hydrolyzing for a desired period in a buffer solution.

Results and Discussion

Polycondensation. It has been shown that a 40/60 mol % GA/PHCA copolymer is amorphous, whereas a 60/40 mol % GA/PHBA copolymer could exhibit nematic liquid crystallinity.[13] Furthermore, if more than 50 mol % PHBA was used in GA/PHBA copolycondensation at 180−235 °C, no high molecular weight copolyester could be obtained due to the poor copolycondensability of GA with PHBA and due to the high melting temperature of the resulting GA/PHBA copolymer. Here in the present study, a third comonomer was employed to modify the copolymerization and try to make a balance between molecular weight and liquid crystallinity.

Table 1. Synthesis Conditions and Properties of PGHCAs

polymer	composition[a] PHBA/PHCA/GA	reaction condition[b] temp (°C)	time (h)	yield (%)	η_{inh} (dL/g)
PGHCA-09	43.0/28.5/28.5	200	1		
		210	20	88	0.43
PGHCA-15	43.0/28.5/28.5	200	17	93	0.55
PGHCA-11	43.0/28.5/28.5	218	5	90	0.55
PGHCA-13	43.0/28.5/28.5	200	14		
		216	2	95	0.75
PGHCA-06	43.0/28.5/28.5	210	4		
		215	16	83	0.82

[a] In mole percentage. [b] Under vacuum.

It was obvious that in this tricomponent system (Table 1), GA/PHBA/PHCA, there was no solidification during the whole reaction process at a temperature of around 200 °C, and a high molecular weight copolymer could be readily obtained even in the absence of catalyst. This means that the incorporation of PHCA could not only greatly decrease the melting points but also promoted the copolycondensability of GA and PHBA. As a comparison, the melting transition of the 60 mol % PHBA-containing binary copolymer[13] occurred at 267 °C; the PGHCA terpolymer with the same PHBA content, however, melted at 150 °C, that is, more than 115 °C lower! That the polycondensation was carried out in a homogeneous state unlike the obvious heterogeneous state in most GA/PHBA systems was attributable to the compatible reactivity of PHCA with PHBA or PHCA with GA, leading to the formation of PHBA/PHCA/GA randomly linked sequences. Regarding the catalysts, it was found that magnesium acetate is the most effective catalyst for this system. Acetic anhydride was used as the solvent in order to have a rapid homogeneous mixture and to reduce the risk of the sublimation of the reactants.

It should be pointed out that the condensation polymerization of GA/PHBA/PHCA is quite sensitive to the reaction temperature. Only within a narrow temperature window from 190 to 230 °C could a linear, high molecular weight copolyester (inherent viscosity up to 1.12 dL/g) be obtained. If the polymerization was carried out at high temperature over 220 °C, highly cross-linked products with a T_g of 115 °C but no melting transition would be produced. Besides, if the reaction time was extended at a lower temperature like 180 °C, insoluble product would be developed as well. FTIR analysis on these unusual products suggested that the two kinds of side reactions would occur: one is Fries rearrangement of the aromatic cinnamyl ester at lower reaction temperature, and the other is a thermal cross-linking reaction of the double bond in the cinnamyl group at higher reaction temperature.

Chain Structure. The compositions of the copolyester were established by FTIR and NMR. The products were identified as polyesters by their FTIR spectrum as shown in Figure 1: the characteristic carbonyl

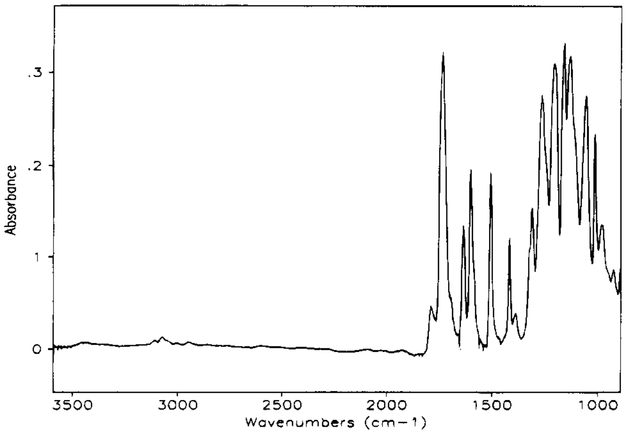


Figure 1. FTIR spectrum of PHBA/PHCA/GA terpolyester (the film was formed by directly shearing the molten sample on a hot NaCl plate).

stretching frequencies of the ester groups (C=O) appear at 1733.3 and 1787.3 cm^{-1}, which correspond to the aromatic ester groups and the glycolic ester group, respectively. The −CH stretching vibration of the aliphatic CH_2 segment was observed at 2949.4 and 3010.7 cm^{-1}. The two sharp absorption peaks at 1600.2 and 1505.6 cm^{-1} were assigned to the C=C stretching vibrations on the para-disubstituted aromatic ring. The stretching vibrations at 1263.5 and 1205.7 cm^{-1} were assigned to C_{arom}−COO− and C_{ali}−COO−, respectively.[17] The vibrations at 1634.9 and 980.9 cm^{-1} could be referred to as C=C and *trans*−CH=CH- in the cinnamyl unit.[21]

In order to have a further understanding into the sequence structure and the sequence distribution of the terpolyester, a high-resolution NMR analysis on the as-prepared sample was made. The carbon-13 NMR spectrum of the terpolyester is shown in Figure 2. Detailed assignment of the individual chemical shifts is based on the previous analysis results on a GA/PHBA binary copolyester.[13] Similarly, there are several multiple peaks of the aromatic and aliphatic carboxylic esters in the range of 167.60−170.30 ppm and of the quaternary aromatic carbons adjacent to the phenolic oxygen in both benzoate and cinnamyl units of 148.86−156.17 ppm. The appearance of these new peaks originated from the heterolinked ester segments as illustrated in Chart 1. On the basis of the NMR analysis, it could be concluded that there are no unreacted monomers in the terpolyester; a random ternary copolymer of PHBA/PHCA/GA with various sequence constitution and distribution has been formed; the resulting terpolyester is not a blend of the three homopolymers.

Thermal Property. Figure 3 shows the DSC traces of the as-prepared PGHCA terpolyester with a feed composition of PHBA/PHCA/GA = 43.0/28.5/28.5 mol %. Unlike the PGHB series copolyesters, there is a small step in the baseline at 60−82 °C associated with the glass transitions of the terpolyester, whose position is a function of the molecular weights as shown in Table 2. Similar glass transitions have been reported for the copolyester of PHBA with PHPA[16] or the copolyester of PHBA with 8-MHOA.[17] In the first heating run the T_g is followed by a broad melting process with a final peak at 150 °C with a transition enthalpy of 3.7 J/g, which corresponds to the crystal to nematic transition. This low heat of transition is typical of the totally aromatic thermotropic liquid crystalline copolyester, which is believed to be directly associated to the random distribution of the comonomeric units along the molecular chain and the rotational disorder of the chains in the crystal. Considerable reduction of the melting temperature of the terpolyester in comparison with that of the PHBA/GA binary copolymer is attributed to the incorporation of the cinnamyl unit, which could lead to the disruption of the crystalline structure in a PHBA homopolymer; similar effects have been observed in copolyesters of PHBA with a variety of other monomers.[12,22] Increasing the temperature, another broad but small endothermic peak appears from 168 to 194 °C. On cooling from the nematic state, only a single sharp exotherm appeared at 110−120 °C with an enthalpy of 1.0−2.5 J/g, whose value was depending on the temperature at which the cooling started and, of course, on the cooling rate as well. This transition is assigned to the nematic to crystal transition. Moreover, it should be indicated that the resulting sample possessed a smaller heat of transition than that of the as-prepared ones. The isotropization could not be detected, due to the severe decomposition. It could be concluded that only short benzoate blocks were present in the terpolyester because the copolyester containing longer benzoate units would behave like a homopolymer of PHBA[24] with a first-order transition at about 275−285 °C.

It is interesting, but still not be well understood, that no melting points could be discerned from the DSC traces for the relatively low molecular weight as-prepared PGHCA, although it, sometimes, could be measured on the second heatup. The wide-angle X-ray diffraction measurement of the hand-drawn PGHCA fiber from the injected granular showed a high degree of molecular orientation. A characteristic WAXD photograph of the oriented nematic structures is given in Figure 4.

Nevertheless, both DSC and WAXD results indicated the terpolyester possesses low crystallinity, which suggests that the as-prepared polymer has an irregular connection of monomers with a wide sequence distribution other than completely random ones; therefore, more or less, it was just a macrorandom terpolymer. This point of view was supported by DSC evaluations of different PGHCA samples, such as the as-pressed film and the as-injected fiber. Thus, in the as-injected fiber case, the endothermic enthalpy is almost double that of the as-prepared sample, although its location seems to remain unchanged. This behavior was explained as a result of oriented domains developed by the reorganization of those locally-ordered segments during the injection process.

From the dynamic thermogravimetric analysis (Table 2), it was shown that the terpolyester is stable at least for a short time at 340−350 °C (also as shown in Figure 5) similar to the PHBA/PHPA copolyesters[16] but far higher than the homopolyester of GA even though it is incomparable with the aromatic polyesters. Furthermore, the thermal stability has shown its dependence on the molecular weights of the terpolyesters as indicated in Table 2.

Liquid Crystal Texture. The most intriguing property of the terpolyester under investigation is its capability of forming a mesogenic phase upon heating. As reported earlier,[13] the binary copolyesters of PHBA/GA in the cases of 60−70 mol % PHBA contents could display a nematic liquid crystal character above 260−280 °C. For the present ternary copolyesters, however,

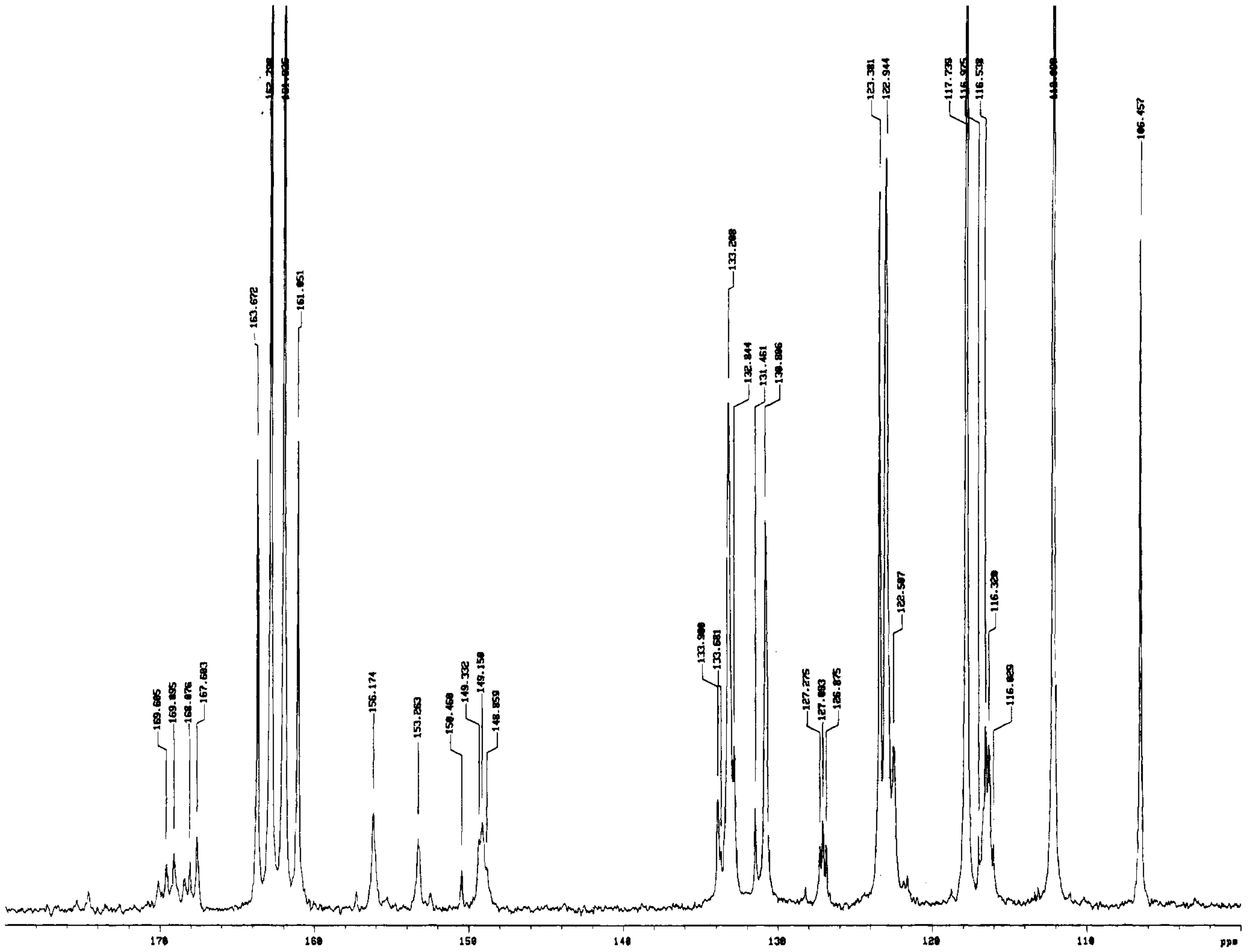
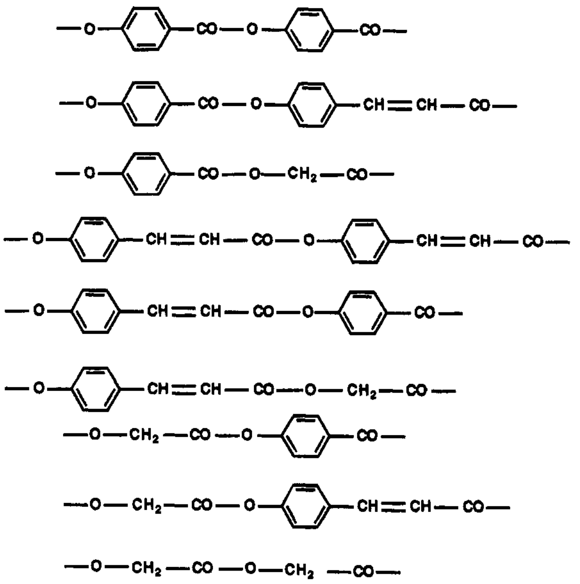


Figure 2. 270-MHz ^{13}C NMR spectrum of PGHCA-6 in $CDCl_3$/TFA-*d*.

Chart 1. Different Chemical Linkages in the PGHCA Terpolyester



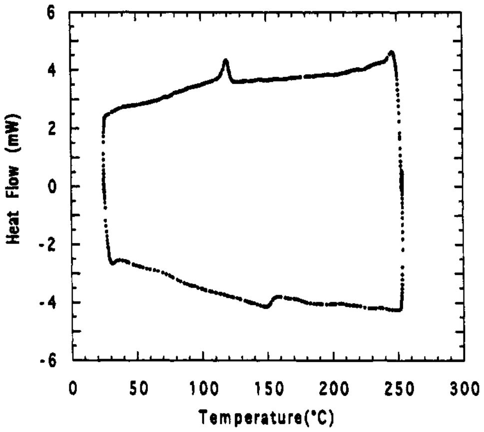


Figure 3. DSC thermograms of as-prepared PGHCA-6 under nitrogen at 10 °C/min.

a typical nematic texture could be formed as shown in Figure 6a. The variation with molecular weight on the preferred textures of PGHCAs on glass covers is illustrated in Figure 6 by photomicrographs taken under crossed polars. For the comparatively low molecular weight polymers like PGHCA-1, -2, -3, or -5, the observed threadlike or schlieren textures could clearly indicate that the nematic phase was formed above their glass transition temperatures; meanwhile, for the medium and high molecular weight ones, as PGHCA-4 and -6, a banded texture could be developed from 150 to 350 °C by shearing the sample in the molten state (Figure 6b). The so-called banded texture is believed to be a characteristic texture of a high molecular weight nematic liquid crystalline polymer since those commercially available LCPs such as X7G, VECTRA, or XYDAR usually exhibited this kind of texture.[23,24] Therefore, it is reasonable to conclude that the resulting PGHCA is a nematic liquid crystalline polymer.

Table 2. Thermal Properties and Phase Behaviors of PGHCA Terpolyesters

polymer no.[a]	T_g (°C)	T_m (°C)	T_f[b] (°C)	T_h[b] (°C)	loss of wt at different temp (°C) 1%	5%	10%	50%
PGHCA-02	60		180	250	301	339	367	576
PGHCA-03	65		180	210	303	347	381	569
PGHCA-04	71		180	210	323	368	401	575
PGHCA-09	80				321	359	375	527
PGHCA-15	79	126			334	365	370	526
PGHCA-11	72	135			333	373	394	565
PGHCA-13	81	145			340	370	386	547
PGHCA-06	82	150	190	190	342	373	393	556
PGHCA-06	82	150	190	190	339[c]	362[c]	383[c]	518[c]

[a] PHBA/PHCA/GA = 43.0/28.5/28.5 (mol ratio) except PGHCA-02 (PHBA/PHCA/GA = 28.5/43.0/28.5). [b] From the observation under POM: T_f, flow temperature; T_h, homogeneous temperature. [c] Measured under air; all others were obtained under nitrogen at 10 °C/min.

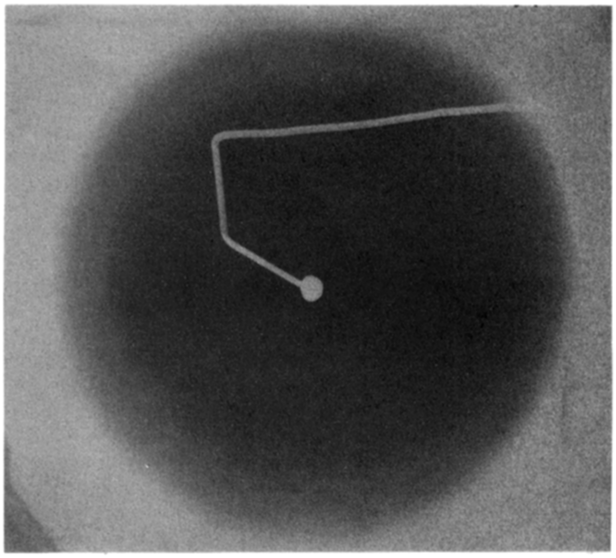


Figure 4. Room-temperature-recorded wide-angle X-ray diffraction pattern for an as-injected strand from the nematic melt.

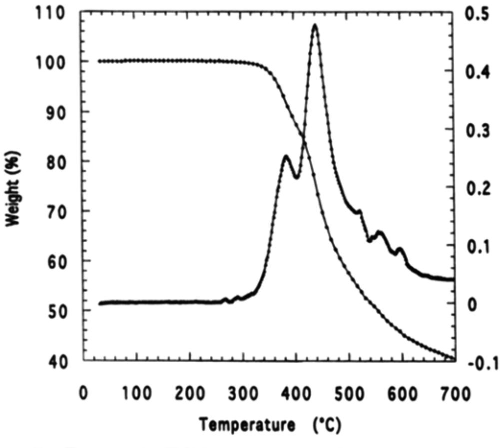


Figure 5. Dynamic TGA spectrum of as-prepared PGHCA-6 under nitrogen at 10 °C/min.

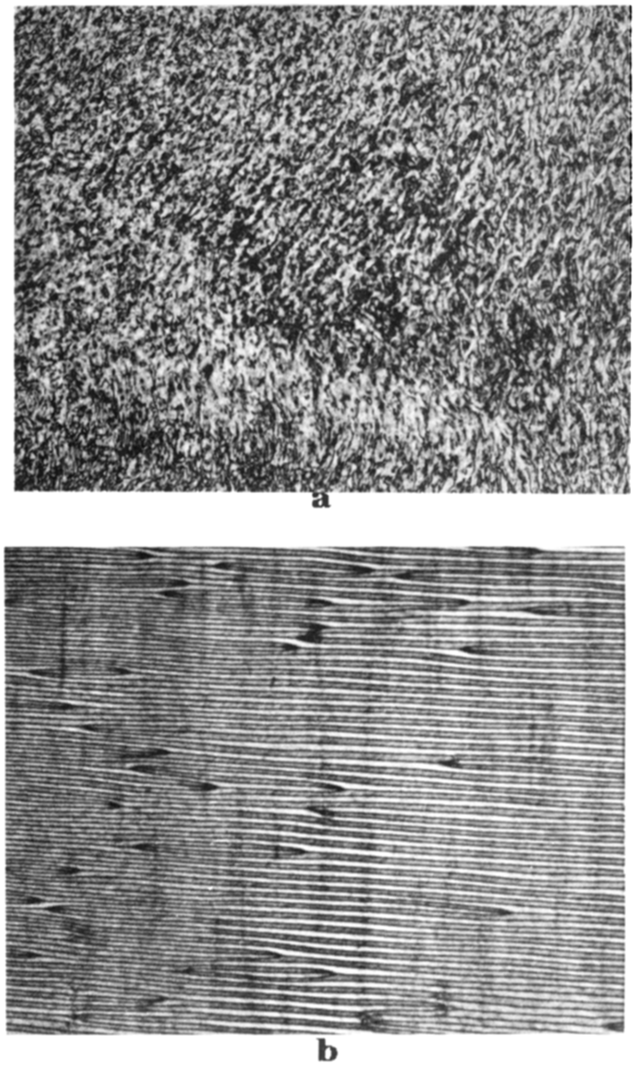


Figure 6. Photomicrographs of as-prepared PGHCA-6 under polarized light microscopy: (a) taken with crossed polars at 218 °C (magnification 625×); (b) taken with crossed polars at room temperature for the quenched sample that was sheared at 245 °C, where the shear direction is vertical (magnification 625×).

Solubility. The resulting terpolyester was insoluble in most of the common organic solvents such as THF, $CHCl_3$, $CHCl_2CHCl_2$, DMF, DMSO, etc. It was sufficiently soluble in *p*-chlorophenol and partially soluble in a 1/1 mixture (by weight) of $CHCl_2CHCl_2$/phenol. It was interesting to note that a completely transparent solution could not be developed in trifluoroacetic acid unless a small amount of chloroform (about 10% in weight) was added. In other words, the mixture of TFA/$CHCl_3$ is a good solvent for PGHCA. This favorable polymer solubility suggested that the resulting polymers are copolymers and not simple mixtures of each homopolymer either from PHBA or from PHCA.[18,24] This, particularly, could be additional evidence indicating that GA was indeed incorporated into the copolymer main chain since merely the PHBA/PHCA (50/50) copolymer was not soluble in *p*-chlorophenol at all.[18]

Water Absorption and Hydrolysis Degradation. Since the novel thermotropic copolyester is designed to be degraded in the biological environment, the water absorption process of the polymer was first investigated. Figure 7 exemplifies the water uptake behavior for the terpolymers having different molecular weights either at 37 °C or at 60 °C. Here it should be mentioned that a strong hydrolysis condition, such as a higher pH and temperature (60 °C) than would naturally occur, was employed for accelerating the hydrolysis in order to have a rapid understanding of its biodegradability. Besides, a totally aromatic liquid crystalline polyester derived from terephthalic acid (TPA)/4,4′-dihydroxydiphenyl

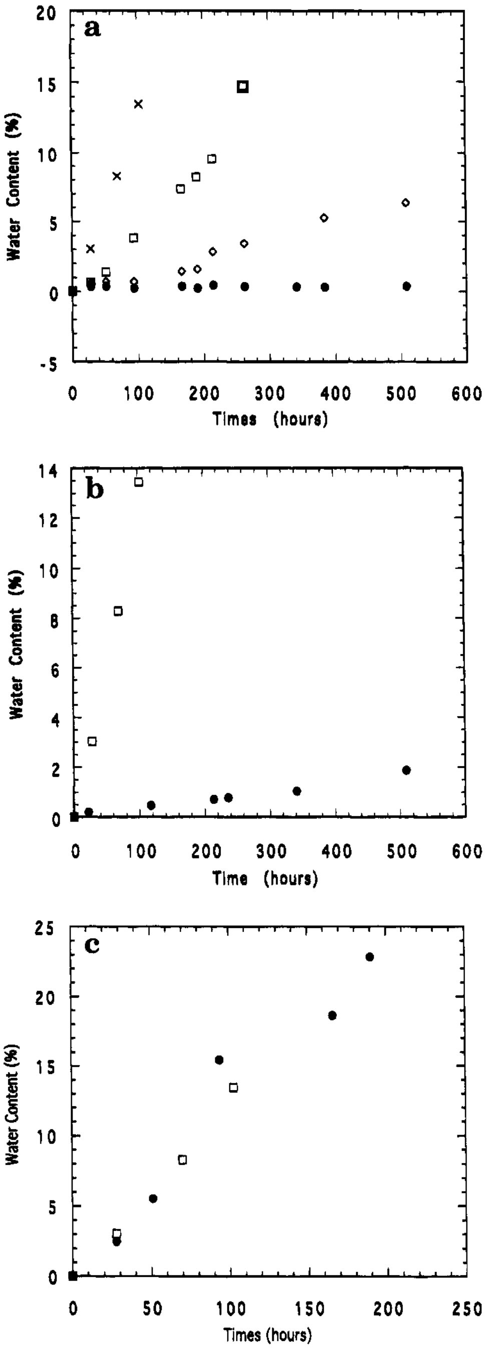


Figure 7. (a) Water absorption vs degradation times for PGHCAs with different molecular weights in a buffer solution of pH 10 at 60 °C: (◇) PGHCA-06; (□) PGHCA-13; (×) PGHCA-15; (●) LCP-34. (b) Water absorption vs degradation times for PGHCA-15 films in a buffer solution of pH 10 at different temperatures: (●) PGHCA-15 at 37 °C; (□) PGHCA-15 at 60 °C. (c) Water absorption vs degradation times for PGHCA-15 films in buffer solutions of pH 7 and pH 10 at 60 °C: (●) PGHCA-15 in pH 7; (□) PGHCA-15 in pH 10.

ketone (BHBPK)/1,3-dihydroxybenzene (mHQ)/4-hydroxybenzoic acid (PHBA), here noted as LCP-34, was used as a control.

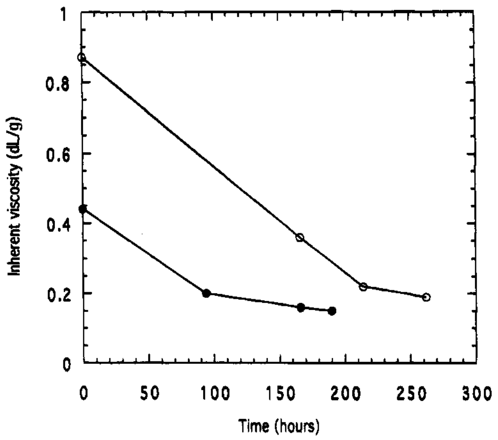


Figure 8. Inherent viscosity change vs degradation times for PGHCA films in buffer solutions of pH 7 or pH 10 at 60 °C: (○) PGHCA-13 in pH 10/60 °C; (●) PGHCA-15 in pH 7/60 °C.

Table 3. Changes of the FTIR Absorbance Ratio for PGHCA-15 Films

	hydrolysis time (h)[a]		
A_1/A_2	0	94	190
A_{1787}/A_{1601}	0.55	0.14	0.04
A_{1735}/A_{1601}	2.34	1.56	1.15
A_{1632}/A_{1601}	0.62	0.55	0.83

[a] In a buffer solution of pH 7.0 at 60.0 °C; the inherent viscosity of PGHCA-15 is 0.51 dL/g in TFA/CHCl$_3$ at 25 °C.

This *in vitro* degradation was assumed to be associated with the water uptake, which is markedly different depending on the pH value of a buffer solution, the temperature, and the molecular weight of the polymer as shown in Figure 7. Unlike those nondegradable polyesters such as LCP-34 which usually attained its water absorption equilibrium with a water content of only 1% in several hours, PGHCA displayed an unique water absorption behavior: under the present conditions its absorption equilibrium was never reached, but the water absorption pattern is strongly dependent on the molecular weight of the copolymer. The lower the molecular weight, the more rapidly water absorbed. Hence, it is believed that there is another stronger interaction between water and the polymer chain then the simple diffusion. It is a chemical reaction—a reaction of water and the ester bonds in the copolyester—which leads to the degradation of the polymer.

Furthermore, it is also evident that increasing the molecular weight could lower its hydrolysis ability. In other words, under the same degradation conditions, the copolymer with a relatively low molecular weight would display a faster degradation behavior. However, it is surprising that there was no significant change in degradation kinetics with change in pH (Figure 7c) since polyesters are usually known to be base-sensitive. A similar phenomenon was also observed by Reed et al.[5] from GA/LA copolyester.

In addition to the water absorption behavior of the copolymer, there is much concern about the change of its actual molecular weight. The results indicated that the thermotropic copolyester (PGHCA) indeed demonstrated an improved degradability in comparison with LCP-34, which showed only as little as 0.1% weight loss after 500 h of degradation in a buffer solution of pH 10 at 60 °C, whereas PGHCA lost about 2% of its original weight under the same conditions. Although this mass loss is small, its inherent viscosity was seen to decrease dramatically from 0.87 to 0.22 for PGHCA-13 after 262 h of degradation in a buffer solution of pH 10 at 60 °C as shown in Figure 8. This mass loss behavior is quite different with the 50/50 GA/LA copolymer, in which the mass loss occurred simultaneously with molecular weight loss, and the major loss in each took over the 2–4 week period.[5] The decline of the inherent viscosity clearly shows that the copolymer decreases in water over a period of several days under the testing conditions, which at least could be direct evidence for the

Table 4. Thermal Stability of PGHCA Films after the Hydrolysis Degradation

	temp after different wt losses (°C)			
hydrolysis time (h)[a]	1%	5%	10%	50%
0	317	352	367	531
70	118	291	308	460
103	67	283	303	447

[a] In a buffer solution of pH 7.0 at 60.0 °C.

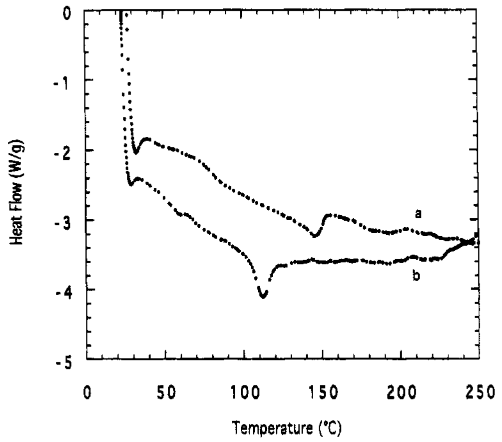


Figure 9. DSC traces of original and degraded PGHCA-6 films: (a) original film; (b) degraded in pH 10/60 °C/500 h.

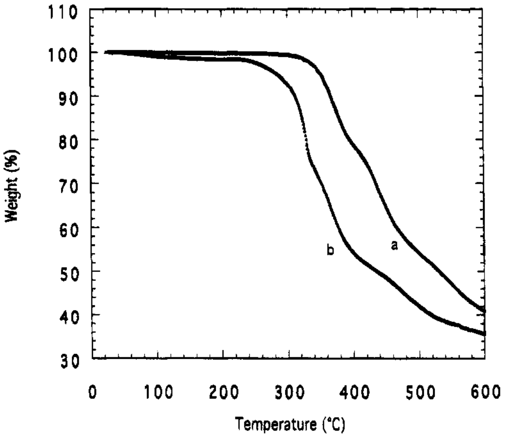


Figure 10. Dynamic TGA traces of original and degraded PGHCA-6 films: (a) original film; (b) degraded in pH 10/60 °C/384 h.

scission of the main chains of the copolymer during the hydrolysis. This fact, on the other hand, suggested that the hydrophilic poly(glycolic acid) (PGA) units had been incorporated onto the main chain of the copolymer as revealed previously by FTIR and NMR, but they seemed to be distributed separately along the main chains. Low-MW PGHCA-15 showed a similar but faster degradation behavior.

Previous studies on water absorption and inherent viscosity (molecular weight) clearly showed that the hydrophilicity was greatly improved by the incorporation of GA segments. The higher the molecular weights, the lower the water absorption at fixed temperature and pH, and the higher temperature could accelerate the water absorption. It is reasonable, therefore, to conclude that the novel thermotropic copolyester is degradable. However, to gain insight into the nature of the degradation, several additional experiments from structure examination (FTIR and WAXD) to property evaluation (DSC, TGA, and DMA) were carried out for the degraded samples.

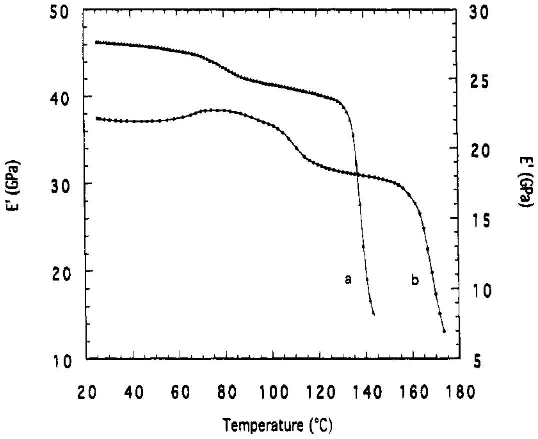


Figure 11. Dynamic mechanical analysis spectra of original and degraded PGHCA-6 films: (a) original films; (b) degraded in pH 10/60 °C/500 h and then dried at 105 °C/4 h/vacuum.

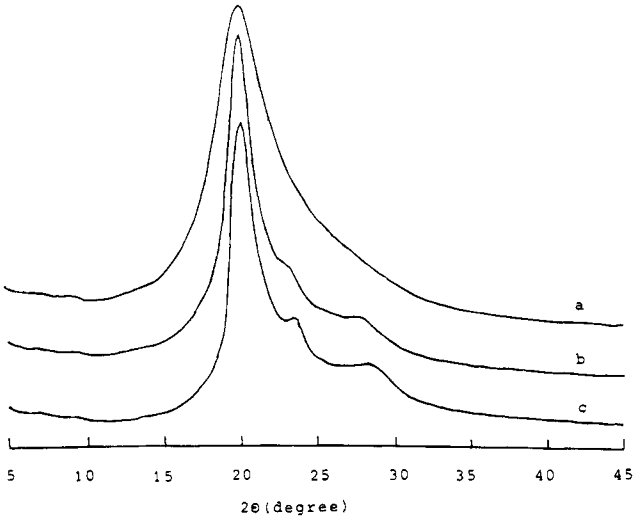


Figure 12. WAXD patterns of PGHCA-15 films after degradation in a buffer solution of pH 7 at 60 °C for various periods of time: (a) original film; (b) degraded for 94 h in pH 7/60 °C; (c) degraded for 190 h in pH 7/60 °C.

Identification of Degraded Copolymer. Generally, the degradation of polymer was a result of the depression of the molecular weight and was characterized by the property loss. In PGHCA, it was found that the mechanical properties were strongly determined by the degradation even though no obvious weight loss was observed until the specimen became quite brittle. FTIR and TGA measurements give further evidence that chemical degradation occurred during the water absorption process and that the degradation resulted from hydrolysis of the ester bonds in the copolyester. Tables 3 and 4 illustrate the results from FTIR analysis. The rapid decrease of the characteristic absorbancies of both the GA carbonyl band and PHBA or PHCA carbonyl bands with increasing hydrolysis times means that the ester bond breaking took place. It should also be mentioned that the presence of degradable GA segments could induce the degradation of the aromatic ester bonds as indicated by the lowering of A_{1735}/A_{1601}. The WAXD analysis (Figure 12) on the degraded samples suggested that the hydrolytic degradation could lead to a reduction of its amorphous fraction because an apparent enhancement of the ordered degree is observed with the increasing of the hydrolysis time.

Degradation of the polymer not only alters the chain structure as revealed above but usually would lead to a

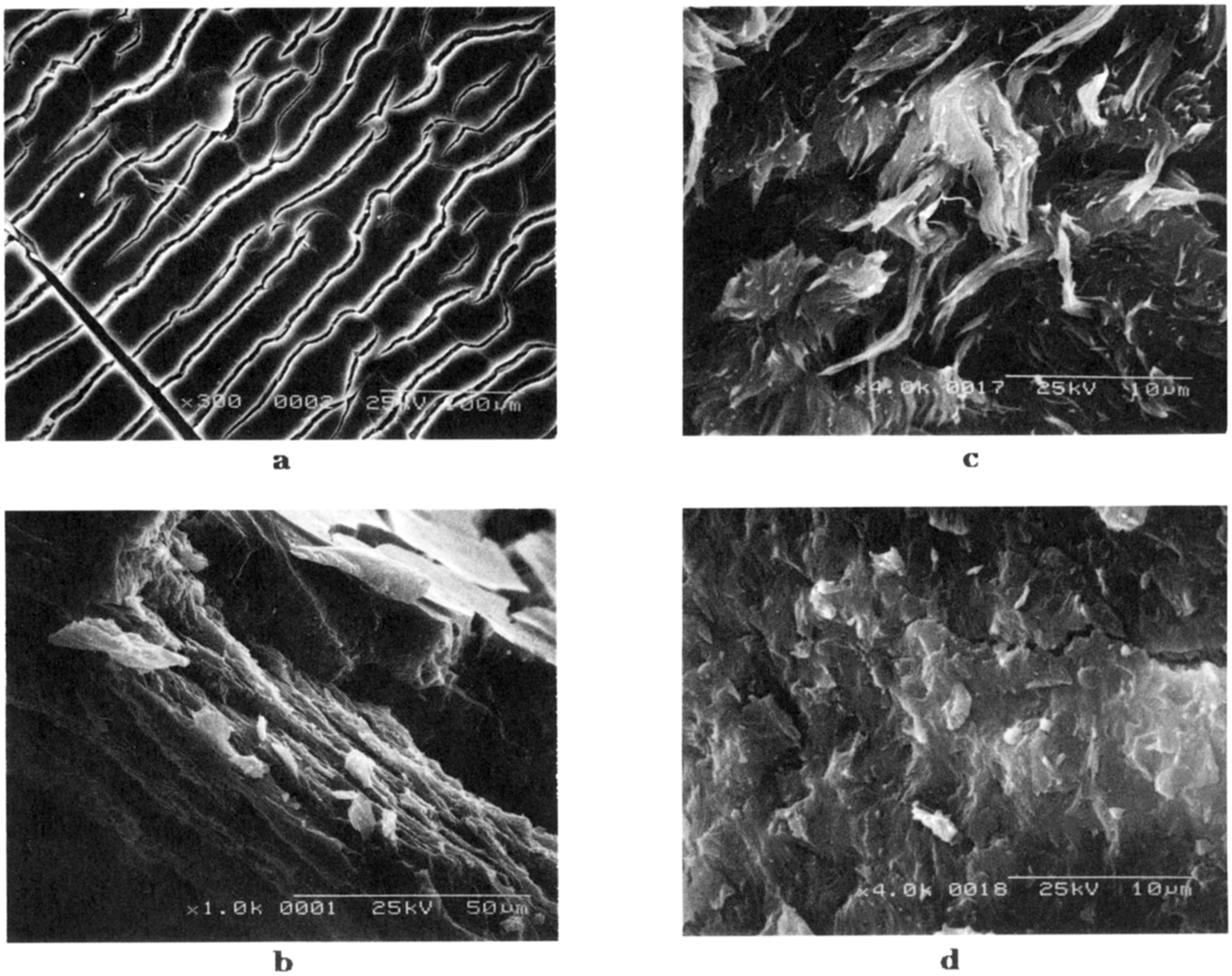


Figure 13. SEM micrographs of original and degraded PGHCA films: (a) surface, degraded PGHCA-15 film in pH 10/60 °C for 103 h; (b) cross section, degraded PGHCA-15 film in pH 10/60 °C/103 h; (c) cross section, original PGHCA-13 film; (d) cross section, degraded PGHCA-13 film in pH 10/60 °C/214 h.

significant reduction of properties. Here only the changes in the thermal property are discussed. The influence of the degradation on the mechanical property is under investigation.

DSC measurements were performed to clarify the relationship between the changes in sequence distribution and packing structure of the copolyester. The DSC curves of a degraded PGHCA-15 film, subject to treatment in a buffer solution of pH 10 at 60 °C, are shown in Figure 9. Obviously, the DSC pattern of PGHCA-15 before hydrolysis showed one clear glass transition near 80 °C and a broad melting endotherm with a maximum at 150 °C. It was observed that the melting transition shifted toward lower temperature, the peak width became narrower, and the corresponding area was almost unchanged, indicating a crystal with a more perfect packing and a smaller size in the degraded copolymer. Besides, a lower T_g or sometimes a multi-T_g could also be also detected with the passage of hydrolysis time. This fact means that the molecular weight of the copolymer decreases by scission of the main chain and also that the hydrolysis by water occurs preferentially in the amorphous regions of the copolymer.

The dynamic thermal gravimetric analysis of PGHCAs having different molecular weights (Figure 10 and Table 4) clearly shows that the longer the degradation time, the less the thermal stability due to the formation of the lower molecular weight ones after hydrolysis degradation.

Figure 11 gives a DMA spectrum for the degraded PGHCA film with high molecular weight, which was hydrolyzed in a buffer solution of pH 10 at 60 °C for 500 h, and then the film was dried at 105 °C for 4 h under vacuum to remove any residue of water. The broad transition ranging from 60 to 90 °C was attributed to the glass transition. In addition, two melting transitions (105 and 160 °C) appeared, which suggested the nature of a multicomponent structure. This finding agreed with the previous NMR result and also was further supported by WAXD analysis, as shown in Figure 12. Obviously, the degree of crystallinity or the ordered structure was increased after the degradation. In other words, the relative content of the rigid aromatic segments in the copolyester was increasing.

In Figure 13, scanning electron micrographs of the degraded PGHCA films, both surface and fractured cross sections, are given. It is visible that numerous cracks developed on the two surfaces of the film, which made the films become quite brittle after a certain period of degradation. Consequently, it is impossible to measure their mechanical property. Moreover, from the morphology of the degraded film it seems the degradation occurred predominately in the corn (Figure

13b). This phenomenon is similar to that observed in some aliphatic degradable polyesters by Vert et al.[7] For this thermotropic degradable copolyester, the higher orientation of macromolecules near the skin than near the corn region due to its liquid crystalline nature made a tighter molecular packing at the skin region, and accordingly the degradation occurred favorably in the corn. Parts c and d of Figure 13 revealed that the fibrous structure could be completely destroyed after a longer period of hydrolysis or degradation of copolyester.

Conclusion

A new method to enhance the copolycondensability of aromatic hydroxy acid (PHBA) with α-hydroxy acid (GA) by the introduction of a promoting comonomer, PHCA, is first presented. High molecular weight liquid crystalline polyesters with a potential biodegradable property have been successfully prepared via this method. The as-prepared terpolyester with $T_g = 82$ °C and $T_{kn} = 150$ °C possessed fair thermal stability and good mechanical strength. The *in vitro* hydrolysis degradation of these novel thermotropic ternary copolyesters having different molecular weights has been investigated in buffer solutions of pH 7 or pH 10 at 37 or 60 °C in the absence of an enzyme, respectively. The copolyester showed improved hydrophilicity in comparison with conventional aromatic thermotropic liquid crystalline polyesters. The degradation was evident by a dramatic depression of 60–70% of the inherent viscosity after different periods of degradation depending on the molecular weight and temperature. Further evidence from the analysis on the structures by FTIR and WAXD, morphology by SEM, and properties by DSC, TGA, and DMA on the degraded product supported the theory that the novel thermotropic ternary copolyester is degradable.

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