Polyesters of 2-Pyrone-4,6-Dicarboxylic Acid (PDC) Obtained from a Metabolic Intermediate of Lignin

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2-Pyrone-4,6-dicarboxylic acid (PDC), a chemically stable metabolic intermediate of lignin, was for the first time utilized to prepare polyesters. Condensation polymerization at about 200 °C with 1,2-ethanediol, 1,3-propanediol or bis(2-hydroxyethyl) terephthalate was effectively promoted by the catalytic amount of Sb₂O₃. The corresponding polyesters, P(PDC2), P(PDC3) or P(PDCB)_x (x: PDC unit content, and $x \leq 0.5$), became insoluble when the number-average molecular weight exceeded about 4×10^3 . Due to the pseudo-aromatic nature of PDC ring, these polyesters were thermally stable up to 210 °C. From the measurements of strain-stress characteristics, Yong's modulus of P(PDC2) or P(PDC3) was as high as 250 MPa and 2 times larger than that of amorphous PET. The accelerated hydrolysis of P(PDC2) or P(PDC3) in basic, acidic, and pure water at 60 °C gave 60–100% degradation in 1.5–3 weeks. The degradability could be controlled by changing the PDC content “x” in the case of P(PDCB)_x, because the lactone ring cleavage as well as ester hydrolysis were considered to be the major events in the main-chain scission.

KEY WORDS: Biomass / Hydrolysis / Lignin / Mechanical Strength / Polyester /

Biomass-based polymers – plastics, fibers, and rubbers – have attracted keen interests, because the demands of society targeting to “carbon-neutral” sustainable chemistry became urgent issues.^{1–8} Green plastics categorized to poly(hydroxy alkanate)s such as poly(lactic acid) and poly(hydroxy butyrate) as well as polyesters from glycols and dibasic acids such as poly(tetramethylene succinate) are the commercialized instances.⁹ Because such polyesters contain no aromatic rings and are composed of alkylene main-chain, lack of mechanical strength and heat-resistant properties are their common disadvantages.¹⁰

It is significant to prepare (pseudo-)aromatic, functional and degradable small molecules from biomass,^{11–14} and we have recently established the preparation protocol of a novel dibasic acid, 2-pyrone-4,6-dicarboxylic acid (PDC), from the lignin bio-metabolic intermediates by using transformed bacterium.¹⁵ PDC consists of the polar pseudo-aromatic ring system and two carboxylic acids, of which molecular shape is akin to isophthalic acid.^{16,17} Therefore, we decided to introduce the pseudo-aromatic ring into polyester main-chains for the improvement of mechanical strength and heat-resistant properties of the bio-based polymers. In the present paper, the direct polycondensation at an elevated temperature between PDC and diols, such as 1,2-ethanediol (ED), 1,3-propanediol (PD), and bis(2-hydroxyethyl) terephthalate (BHT), was examined, and the resulting (co)polyesters, abbreviated as P(PDC2), P(PDC3), and P(PDCB)_x (x: PDC unit content, and $x \leq 0.5$) (formulae, see Chart 1), respectively, were characterized by thermal

analysis, tensile strength measurements, and hydrolysis tests.

EXPERIMENTAL

Materials

All reagents were obtained from the Kanto Chemical Co., Wako Chemicals Industries Ltd., and Tokyo Kasei Co., and used without further purification. 2-Pyrone-4,6-dicarboxylic acid (PDC) was prepared from protococatechuate *via* the metabolic pathway of *Sphingomonas paucimobilis* SYK-6 as reported previously.¹⁵

Measurements

Thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC) measurements were carried out on a Rigaku Thermo plus TG8120 and DSC8230, respectively, under nitrogen flow, at a heating rate of 10 °C min^{−1} from 20 °C to 1000 °C for TGA and from 20 °C to 180 °C for DSC. ¹³C NMR spectra were measured on a JEOL AL400 MHz spectrometer at 20 °C. Chemical shifts are reported in ppm downfield from SiMe₄, using the solvent's residual signal as an internal reference. Infrared spectra (IR) were recorded on a JASCO FT/IR-4100 spectrometer. Number average molecular weights (M_n) of the polyesters were estimated by a JASCO 980 Gel Permeation Chromatography, calibrated by polystyrene standards. Elemental analyses of the polyesters were carried out on a Yanaco MT-5 elemental analyzer. Strain-stress (S-S) curves of the polymer films were measured at 21 ± 2 °C in an

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Chart 1. Chemical structure of PDC and synthetic route of P(PDC_m) [*m* = 2, 3] and P(PDCB)_x.

atmosphere of dry nitrogen by using a Tensilon testing machine (Auto COM/AC-50A, TS Engineering Co.). Young's moduli were estimated from the initial (less than 0.5% elongation) slopes of S-S curves. X-Ray diffraction patterns were measured by using a Rigaku X-ray diffractometer RU-200A.

Oligomerization

Oligo(PDC2) and oligo(PDC3) were prepared by the direct polycondensation of equimolar mixture of PDC and 1,2-ethanediol (ED) or 1,3-propanediol (PD) in the presence of 0.5 mol % (with respect to both monomers) of Sb₂O₃ catalyst. In the case of oligo(PDCB)_x, the mixture of PDC and bis-(2-hydroxyethyl) terephthalate (BHT) in the molar ratio of 50/50–5/95 (for the preparation of copolyesters with *x* = 0.50–0.05, respectively) and 0.5 mol % of Sb₂O₃ as a catalyst was similarly charged. With vigorous stirring, the monomer mixtures were preheated to 140 °C to obtain homogeneous molten solution. Further reaction at 200 °C for given periods (shown as 1st stage in Table I) solidified the charged mixtures, resulting in the corresponding oligomers. After cooling to room

temperature, the solid oligomers were crashed and ground into 400 mesh fine powders. The powdery oligomers (*M_n* = 2–4 × 10³), thus obtained stoichiometrically, were mostly soluble (90–95%) in THF, acetone, DMF, and DMSO.

Oligo(PDC2). ¹³C NMR (DMSO-*d*₆, 100 MHz, 20 °C): δ 64 (–CH₂CH₂–), 108 (pyroneδC), 122 (pyroneβC), 144 (pyroneγC), 148 (pyroneεC), 158 and 159 (carboxylates), 163 (pyroneαC).
Oligo(PDC3). ¹³C NMR (DMSO-*d*₆, 100 MHz, 20 °C): δ 28 (–CH₂CH₂CH₂–), 63 (–CH₂CH₂CH₂–), 107 (pyroneδC), 121 (pyroneβC), 143 (pyroneγC), 148 (pyroneεC), 158 and 159 (carboxylates), 163 (pyroneαC).

Oligo(PDCB)_{0.50}. ¹³C NMR (DMSO-*d*₆, 100 MHz, 20 °C): δ 61–64 (methylenes), 108 (pyroneδC), 122 (pyroneβC), 129 and 133 (phenylene), 142 (pyroneγC), 148 (pyroneεC), 158 and 159 (all carboxylates), 164 (pyroneαC).

Polymerization and Sample Preparation

The oligomers were subjected to post-polymerization in thin film states. The oligomer powders were sandwiched between Kapton® films (0.1 mm-thick polyimide from du Pont-Toray Co.) with a 0.3 mm-thick Teflon spacer and hot-pressed under 10 MPa at 200 °C for 5 min. After quenched by cold nitrogen flow from liquid nitrogen overflow, the oligomer films were peeled off and further polymerized at 200 °C *in vacuo* for given periods (shown as 2nd stage in Table I).

PET (commercial reagent from Tokyo Kasei Co., *M_n* = 23 × 10³) films were similarly prepared by hot-pressing the 400 mesh powders at 180 °C and quenching.

Thus obtained P(PDC2), P(PDC3), P(PDCB)_x, and PET films were used for mechanical strength measurements. For other measurements such as the elemental analysis, these film samples were crashed into particles by shaking them with SUS

Table I. Preparation of the (co)polyester films

(co)polyester	Reaction period at 200 °C/h	
	1st stage	2nd stage
P(PDC2)	0.50	3.0
P(PDC3)	0.50	3.0
P(PDCB) _{0.50}	1.0	3.0
P(PDCB) _{0.40}	1.0	3.0
P(PDCB) _{0.30}	3.0	3.0
P(PDCB) _{0.20}	3.0	6.0
P(PDCB) _{0.15}	3.0	6.0
P(PDCB) _{0.10}	3.0	6.0

balls at liquid nitrogen temperature. In the case of X-ray diffraction measurements and thermal analyses, the film samples were cut into small pieces.

Hydrolysis Test of Film Samples

The 0.3 mm-thick (co)polyester films were cut into about 100 mg test pieces and were subjected to the accelerated hydrolysis tests at 60 °C in 50 mL of 0.10 M aq. NaOH, 0.05 M aq. H₂SO₄, and distilled water without agitation. In the case of distilled water, the aqueous phase was exchanged with fresh water in every 12 h to avoid the acidification of the solution. After the given periods, the remaining portions of the film samples were collected by filtration, washed with 0.01 M aq. H₂SO₄ followed by distilled water for the samples soaked in aq. NaOH or with distilled water for the samples soaked in other solutions, then dried at 100 °C *in vacuo*. The weight loss of the samples was calculated as the remaining weight relative to the initial weight. Polymer fragments solubilized in the solutions were attempted to collect by evaporating the aqueous solution after the dialysis through a 24 Å-pore cellophane membrane.

RESULTS AND DISCUSSION

Polycondensation and Film Preparation

Since PDC is soluble in 1,2-ethanediol (ED), 1,3-propanediol (PD) or molten bis(2-hydroxyethyl) terephthalate (BHT) at an elevated temperature of >120 °C, these mixtures with Sb₂O₃ were preheated to 140 °C to obtain homogeneous solutions and were then subjected to the further reactions.

The polycondensation between PDC and ED or PD at 200 °C commenced rapidly because of the strong acidic nature of PDC¹⁸ and the presence of Lewis acid, Sb₂O₃, that accelerated the elimination of water. Typically within 30 min, the pre-molten and homogeneously mixed systems solidified. At this 1st stage (see Experimental and Table I) the contents turned into oligomers with $M_n = 2\text{--}4 \times 10^3$ (measured by GPC, calibrated by polystyrene standards), being mostly soluble (90–95%) in THF, acetone, DMF, and DMSO. Elevation of the temperature shortened the reaction period, but discoloration occurred. ¹³C-NMR spectra of the oligomers with $M_n \approx 4 \times 10^3$ (corresponding to X_n , number-average degree of polymerization, ≈ 20) supported the designated structures. Upon esterification, the chemical shifts of carboxylate carbons evidently shifted upfield. For instance, when oligo(PDC2) is produced, the carboxylate carbons of PDC at 160.8 and 160.9 ppm moved to about 158 and 159 ppm, respectively.¹⁸ The oxyethylene carbons, on the contrary, shifted downfield from 62.8 to about 64 ppm. The carbonyl stretching vibrations in the IR spectra also showed the dramatic change from 1757 cm⁻¹ (lactone) and 1743 and 1726 cm⁻¹ (two carboxylates) for PDC to 1722 cm⁻¹ (all carbonyls overlapped) for oligo(PDC2). This fusion of the carbonyl vibrations is usually seen in the esterification of PDC even for small molecular-weight compounds such as PDC dimethyl ester. The elemental analysis also supported the structure

of oligo(PDC2). The yield of oligo(PDC2) was essentially stoichiometric, as usually experienced in such polycondensation, except for mechanical losses.

The polycondensation between PDC and PD at 200 °C commenced similarly as in the case of oligo(PDC2). After the 1st stage polycondensation, oligo(PDC3) with $M_n = 2\text{--}4 \times 10^3$, which was mostly soluble (90–95%) in THF, acetone, DMF, and DMSO, was obtained stoichiometrically. The spectral changes in the ¹³C-NMR and IR spectra upon oligomerization were very similar to those of the PDC-ED system.

When the further polycondensation of oligo(PDC2) or oligo(PDC3) was continued as it was, the development of M_n became very slow. Because the tenacious plug, that was not a complete solid but a very tough elastomer even at an elevated temperature, did not allow water molecules to escape from inside, the system has plausibly hit the ceiling condition of esterification (polymerization)–hydrolysis (depolymerization) equilibrium. Therefore, after the solidified oligomers were once ground into 400 mesh powders, they were spread on a Teflon-coated SUS plate and the further post-polymerization was examined *in vacuo* at 200 °C for 3–6 h. The resulting polyesters were obtained as pale yellow plates of coagulated powders. Nothing could be extracted from the crashed polyester plates with acetone or other media. Thus, the obtained P(PDC2) and P(PDC3) were insoluble, infusible, and hard solids in this case, and their intractability upon shaping into thin films or textiles raised difficulties in the characterization of the physical properties. To overcome this problem, we explored the film preparation conditions and finally succeeded in the optimization. The 400 mesh oligomer powders were hot-pressed into 0.3 mm-thick films under 10 MPa at 200 °C for 5 min in advance, and were subjected to post-polymerization at 200 °C for given periods listed as the 2nd stage in Table I. Although P(PDC3) gave uniform thin films of about 0.3 mm thickness under the optimized conditions, P(PDC2) afforded uneven films with small bubble cells presumably caused by water vapor during the post-polymerization. Attempts to obtain better films by decreasing the post-polymerization temperature and/or the evacuation speed were unsuccessful. This is because the post-polymerization of P(PDC2) did not commence at <180 °C and the steep evolution of water vapor was essential once it commenced.

These film samples could be crashed into particles by shaking them with SUS balls at liquid nitrogen temperature. Nothing was extracted from the particles with acetone or other media, indicating the progress of polycondensation. The elemental analysis results of these polyester particles listed in Table II are in good agreement with the values estimated for the designated structures or the structures based on the initial feed ratios of starting materials.

The self-polycondensation of BHT with eliminating ED molecules in the presence of Sb₂O₃ catalyst is the well-known process to manufacture poly(ethylene terephthalate), PET.¹⁹ Addition of PDC to the system, namely leading to copolycondensation between PDC and BHT, yielded P(PDCB)_x ($0.10 \leq x \leq 0.50$) by eliminating water and/or ED molecules

Table II. Elemental analysis of the polyesters

Polyester	Feed ratio [PDC]/[BHT]	Elemental analysis, found (calcd. ^a)/wt/wt %		
		C	H	O
P(PDC2)	—	51.29 (51.46)	2.94 (2.88)	—(45.68)
P(PDC3)	—	53.41 (53.58)	3.66 (3.60)	—(42.82)
P(PDCB) _{0.50}	0.50/0.50	56.86 (56.72)	3.46 (3.51)	—(39.77)
P(PDCB) _{0.40}	0.40/0.60	57.77 (57.84)	3.72 (3.64)	—(38.52)
P(PDCB) _{0.30}	0.30/0.70	59.12 (58.97)	3.77 (3.78)	—(37.25)
P(PDCB) _{0.20}	0.20/0.80	60.15 (60.13)	3.96 (3.91)	—(35.96)
P(PDCB) _{0.15}	0.15/0.85	60.90 (60.71)	4.03 (3.98)	—(35.31)
P(PDCB) _{0.10}	0.10/0.90	61.21 (61.30)	4.06 (4.05)	—(34.65)

^aCalculated according to the designated structure based on the initial feed ratio of the starting materials.

(Chart 1). Here x represents the content of oxyethyleneoxy-carbonyl[(2-pyranone)-4,6-diyl]carbonyl repeating unit, and, as explained later, is almost the same as the PDC content estimated from the initial feed ratio of the starting materials. When the molten mixture of PDC and BHT, well agitated at 140 °C to keep homogeneity, was heated to 200–240 °C for 10–180 min in the presence of Sb_2O_3 , the system became very viscous to stoichiometrically yield the corresponding oligomers with $M_n = 1\text{--}4 \times 10^3$, which are soluble in THF, acetone, DMF, and DMSO. Polymerization time vs. M_n plots in the case of $x = 0.50$ are illustrated in Figure 1. As expected, the polymerization rate increased as an increase in the temperature. However, the higher temperature tended to develop discoloration, and hence the polymerization temperature of PDC-BHT systems was also settled to be 200 °C where white oligomers could be obtained. Because of the bulkiness of BHT compared to ED and PD, the polycondensation of PDC and BHT commenced more slowly than the combinations of PDC-ED and PDC-PD. Especially in order to prepare P(PDCB)_x with $x < 0.5$, the necessity to eliminate ED molecules besides water might be another reason of the slower propagation. Therefore, as listed in Table I, the reaction period of 1st stage was prolonged to 1.0 ($x = 0.50$)–3.0 h ($x = 0.10$). In the case of $x < 0.10$, oligomerization at 200 °C was too slow on the practical timescale. Heating to 260–280 °C was necessary to accelerate the reaction, but due to the noticeable discoloration,

the discussion of P(PDCB)_x with $x < 0.10$ is omitted in the present article.

The yield of oligo(PDCB)_x was essentially stoichiometric except for mechanical losses. The ^{13}C -NMR spectra of the oligomers with $M_n \approx 4 \times 10^3$ (corresponding to $X_n \approx 20$) supported the progress of copolymerization.

The P(PDCB)_x films were prepared from the powdery oligo(PDCB)_x by the same procedure as those of P(PDC2) and P(PDC3) films, *i.e.*, the hot-pressing followed by the post-polymerization (2nd stage reaction) *in vacuo* at 200 °C. Unlike P(PDC2), every P(PDCB)_x gave uniform films. Since all films were infusible and insoluble in organic solvents, they were crashed into particles by shaking with SUS balls at liquid nitrogen temperature. Nothing was extracted from the particles with acetone or other media, again indicating the progress of the polycondensation. The elemental analysis results of these particles listed in Table II were in fairly good agreement with the values calculated for the structures, supporting that the initial feed ratios of the starting materials were maintained. This suggested that the initial feed ratio of PDC could be qualitatively used for the x values representing the content of oxyethyleneoxycarbonyl[(2-pyranone)-4,6-diyl]carbonyl repeating unit in the copolymers.

Thermal Properties

Thermal stability of the polyesters carrying oxyethyleneoxy unit, namely P(PDC2), P(PDCB)_x , and PET, was investigated by TGA at a heating rate of 10 °C min^{−1} under nitrogen atmosphere (Figure 2). Because of the ester linkage breakdown, every polyester sample including PET showed the steep weight loss at about 400 °C. In the case of PDC polyesters, prior to the ester linkage breakdown, the weight loss started at about 250 °C similarly to PDC,¹⁸ and this tendency became more significant with increasing x .

Formation of char or the thermal degradation residue was seen at high temperature such as 700 °C for PDC polyesters, while nothing remained in the case of PET. It should be noted that the quantity of char was greater for the polyesters with the higher content of PDC unit, *i.e.*, $\text{P(PDCB)}_{0.50}$ and P(PDC2). About 25% of the initial weight of P(PDC2) remained at this

Figure 1. Relationship between M_n and polymerization time for $\text{P(PDCB)}_{0.50}$.

Figure 2. TG curves of the polyesters at a heating rate of 10 °C min⁻¹ under N₂.

Figure 3. The 1st and 2nd heating scans of DSC of P(PDCB)_{0.10} at 10 °C min⁻¹ under N₂.

temperature. Such high char yield was often observed for intumescent flame-resistant plastics.²⁰ The present PDC polyesters actually exhibited flame-resistant properties and the results will be reported elsewhere. The TGA curve of P(PDC3) was very similar to that of P(PDC2) except for the slightly smaller amount of the residue at 700 °C.

In the DSC thermograms, the endothermic peaks due to the melting of the crystalline portions were observed for P(PDCB)_x with $x = 0.10$ – 0.20 . A typical example of the DSC curves of P(PDCB)_{0.10} is illustrated in Figure 3. The onset melting temperature (T_m) was 238 °C, about 25 °C lower than that of PET,²¹ probably due to the shorter crystalline segment by copolymerization. This transition could be detected only in the 1st heating cycle of DSC. In the 2nd heating cycle after heating to 250 °C in the 1st cycle, it disappeared completely. Since the sample was discolored after the 1st cycle, this was considered to be caused by the side reactions such as partial crosslinking.

Polarized optical microscope observation revealed the existence of the crystalline portions in the PET and P(PDCB)_{0.10}–_{0.20} films. From the X-ray diffraction analyses according to Ruland's method,²² the typical crystallinity of PET, P(PDCB)_{0.10}, P(PDCB)_{0.15}, P(PDCB)_{0.20}, and P(PDCB)_{0.30} films was determined to be about 0.35, 0.28, 0.20, 0.05, and 0, respectively.

Figure 4. T_g values of PET and P(PDCB)_x as a function of PDC content.

In both 1st and 2nd cycles of Figure 3, the glass transition temperature (T_g) was seen at about 80 °C. The onset T_g values of PET and P(PDCB)_x films estimated from the 1st DSC heating scan were plotted as a function of x , and the relationship was illustrated in Figure 4. The reported onset T_g value of PET [= P(PDCB)_{0.0}] was 61 °C,²³ consistent with the present observation. The T_g values increased as an increase in x , and it reached 103 °C at $x = 0.50$. Because PDC possesses a noncentrosymmetric 2*H*-pyranone ring carrying electron-withdrawing two carboxylate groups at 4,6-positions, its high polarizability brings about strong intermolecular interactions. Therefore, the polyesters with higher PDC contents, P(PDC2) and P(PDC3), did not show T_g values below the degradation temperature of 250 °C, probably because of the strong interchain interactions.

Film Properties

PET and (co)polyester films of about 0.3 mm thickness obtained by the post-polymerization at 200 °C *in vacuo* were cut into about 5 × 20 mm blades and were subjected to the strain-stress (S-S) measurements by a Tensilon testing machine in dry nitrogen at 21 ± 2 °C and the results were shown in Figure 5. The central 10 mm length of the blades was the testing area. Because PET and P(PDCB)_x with $x < 0.20$ exhibited relatively low T_g , these blades showed the yield point at the strain of about 5% with the maximum stress of about 46–59 MPa (Figure 5 and Table III). Beyond the yield points, these samples showed further ductility up to the strain of about 70% with the almost constant stress of 35 MPa for PET and 45 MPa for P(PDCB)_{0.15}, reflecting their viscoelastic properties. Since these (co)polyesters are partly crystalline, their mechanical properties might fluctuate with the crystallinity. As for PET, for instance, the tensile strength of about 54 MPa was reported in the literature where the sample was fractured after the elongation to the strain of 175%.²⁴ The copolyester blades with $x \geq 0.20$ were rigid and had little crystallinity due to the higher content of polar PDC unit. They displayed the breakdown at the strain of 5–6% without yield points. With increasing x , the maximum fracture stress became larger to reach 74 MPa for P(PDCB)_{0.50} and 89 MPa for P(PDC3) (Table III). From the initial slopes of S-S curves of

Figure 5. Strain-stress curves of the polyesters, recorded at $21 \pm 2^\circ\text{C}$ in air.

Table III. Mechanical properties of the (co)polyester films

Sample	Maximum fracture stress/MPa	Young's Modulus/MPa
PET	46.4 ^a 54 ^b	1.34×10^2
P(PDCB) _{0.15}	58.5 ^a	1.35×10^2
P(PDCB) _{0.20}	57.8	1.32×10^2
P(PDCB) _{0.30}	65.9	1.44×10^2
P(PDCB) _{0.40}	63.1	1.52×10^2
P(PDCB) _{0.50}	74.4	1.53×10^2
P(PDC3)	89.1	2.47×10^2

^aMaximum stress at the yield point. ^bTensile strength at break (elongation ratio = 1.75). Data taken from ref 24.

Figure 5, Young's modulus was roughly estimated and also summarized in Table III. The rigid nature of P(PDC3) was characterized by the high Young's modulus of about 250 MPa, 2-fold larger value than that of PET. Unfortunately Izod or Charpy impact strength measurements could not be examined, because the non-fusible characteristics of P(PDC2), P(PDC3), and the copolymers with $x \geq 0.20$ did not allow to prepare thick test pieces and the present post-polymerization procedure merely enabled the preparation of thin films.

In the biometabolic system, PDC is hydrolyzed to its ring-opened structure of (*E*)-3-hydroxycarbonyl-5-oxo-2-hexenedioic acid, then rapidly hydrated to the intermediate specimen of 3-hydroxy-3-hydroxycarbonyl-5-oxo-hexanedioic acid, and finally degraded by the enzymatic oxidation into two kinds of

α -ketocarboxylic acids, 2-oxopropionic acid (pyruvic acid) and 2-oxobutanedioic acid (oxalacetic acid), that are introduced into the TCA cycle.¹⁵ Therefore, the present (co)polyesters are expected to be hydrolyzed or further hydrated into hydrophilic fragments (Chart 2). In the present examination, the accelerated hydrolysis tests of 0.3 mm-thick film pieces were carried out at 60°C in 0.10 M aq. NaOH, 0.05 M aq. H_2SO_4 , and distilled water ($\text{pH} = 5.5\text{--}6.0$).

Figure 6a, 6b, and 6c illustrates the results of the hydrolysis tests in aq. NaOH, aq. H_2SO_4 , and water, respectively. The alkali hydrolysis completely solubilized the polyesters, P(PDC2) and P(PDC3), within 10–12 d. As nothing remained after the evaporation of the dialyzed alkali solution, these polyesters were thought to degrade to low molecular weight fragments initialized by the hydrolysis of main-chain ester linkage. Since the ring-opening (and the subsequent hydration) reaction of PDC nuclei might be the initial events as mentioned above, the resulting side-chain anionic polyesters would promote the further hydrolysis reaction.

The alkali hydrolysis of P(PDCB)_x was depressed as compared to the polyesters, P(PDC2) and P(PDC3). It took about 3 weeks for P(PDCB)_{0.50} to reach the weight loss of 85–90%. With decreasing x from 0.50 to 0.30, the hydrolysis rate became much slower. Although the weight loss of P(PDCB)_{0.30} after 30 d was only a few %, the hydrolysis reaction turned out to steadily occur in the film. As shown in Figure 7, the film was swollen and torn off after 18 and 30 d, respectively, and T_g of

Chart 2. Anticipated degradation pathway of PDC nuclei in the polymers.

Figure 6. Weight loss of the polyesters upon hydrolysis at 60°C (a) in 0.10 M aq. NaOH, (b) in 0.05 M aq. H₂SO₄, and (c) in distilled water.

the film decreased from 88 to 75 °C, indicating the main-chain scission by ester hydrolysis. Again nothing remained after the evaporation of the dialyzed alkali solution, suggesting that these copolyesters were degraded to low molecular weight fragments. In the case of $x \leq 0.20$, no noticeable weight loss was found after 30 d (not shown).

The acid hydrolysis was slower as compared to the alkali hydrolysis (Figure 6b). Within 30 d the weight loss of P(PDC2) and P(PDC3) reached the relatively high value of 90–100%. No large fragment that could not migrate through the dialysis membrane was found in each solution. On the other hand, the very low weight loss of <10% was observed for P(PDCB)_{0.50} due to the hydrophobic nature of terephthalate units. Since a T_g

Figure 7. Change of the appearance and T_g of P(PDCB)_{0.30} upon alkali hydrolysis.

decrease of P(PDCB)_{0.50} in accordance with the soaking period was not observed in this case, a slight weight loss by soaking the sample for a long time was possibly caused by the extraction of the oligomer portion. In the case of $x \leq 0.40$, no noticeable weight loss was found after 30 d (not shown).

It is noteworthy that the weight loss of P(PDC2) and P(PDC3) after 30 d-soaking reached 80–90% even by the hydrolysis in distilled water. Again no large fragment that could not migrate through the dialysis membrane was found in each solution. Negligibly small weight loss was recorded for P(PDCB)_{0.50}. As no T_g decrease in accordance with the soaking period was found, the copolyesters were essentially inert to hydrolysis in the neutral pH range.

From these results, it can be concluded that the hydrolyzability of PDC-(co)polyesters is controlled by changing the constitution. In alkali solution, PDC-(co)polyesters are all hydrolyzable and the hydrolysis rate increases in the order of P(PDCB)_{0.30} < P(PDCB)_{0.50} < P(PDC2) and P(PDC3). In acidic or neutral solutions, only P(PDC2) and P(PDC3) are hydrolyzable and the copolyesters are essentially inert to hydrolysis.

CONCLUSION

(Co)polyesters carrying PDC nuclei were successfully prepared by the ordinary polycondensation procedure in the presence of Sb₂O₃ catalyst. Copolyesters with high PDC contents were rigid and had little crystallinity due to the polar pseudo-aromatic nature of the PDC ring. Significantly, P(PDC3) exhibited the very high Young's modulus of about 250 MPa, 2-fold larger value than that of PET. Polyesters, P(PDC2) and P(PDC3), were efficiently hydrolyzed in basic, acidic, and neutral aqueous solutions, a result that offers the potential use for bio-degradable materials. Because the hydrolysis of copolyesters became slower with the decrease

in the PDC content, the stability and (bio-)degradability were revealed to be tunable by the constitution of the copolyesters.

Acknowledgment. This research was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology, Japan (#18208028), the COE Research Initiative Program of Future Nano-Science and Technology, TUAT, and the 34th Award for Encouragement by the Agricultural Chemical Research Foundation, Japan (T. M.). We thank Prof. S. Kajita (Tokyo University of Agriculture and Technology) for useful discussion.

Received: October 4, 2007

Accepted: October 22, 2007

Published: November 27, 2007

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