### Review

# High-performance lignin-mimetic polyesters

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**Abstract** Liquid crystalline (LC) polymers were prepared by an in-bulk polycondensation of bioavaliable aromatic hydroxyl(carboxylic acid)s. *p*-Coumaric acid (4HCA) and its derivatives were selected as phytomonomers. The 4HCA homopolymer showed a thermotropic LC phase only in a state of low molecular weight. The copolymers of 4HCA with bile acids such as lithocholic acid (LCA) and cholic acid (CA) showed excellent cell compatibilities but low molecular weights. However, P(4HCA-*co*-CA)s allowed LC spinning to create molecularly oriented biofibers, presumably due to the chain entanglement that occurs during in-bulk chain propagation into hyperbranching architecture. P{4HCA-*co*-3,4-dihydroxycinnamic acid (DHCA)}s showed high molecular weight, high mechanical strength, high Young's modulus, and high softening temperature, which may be achieved through the entanglement by in-bulk formation of hyperbranching, rigid structures. P(4HCA-*co*-DHCA)s showed a smooth hydrolysis, in-soil degradation, and photo-tunable hydrolysis. Thus, P(4HCA-*co*-DHCA)s might be applied as an environmentally degradable plastic with extremely high performance.

Key words: Lignin, liquid crystals, polycondensation, polyesters, polyphenols.

Development of environmentally-benign polymers, which are derived from naturally occurring molecules and/or which degrade into environmentally atoxic molecules, is one effective method for solving environmental problems. **Bio-base** polyesters exhibiting smooth degradation have been widely studied as environmentally friendly polymeric materials. However, aliphatic bio-base polyesters such as poly(hydroxyalkanoate)s, poly(butylene succinate), and so on degrade too rapidly to actually be used. Ecoflex<sup>TM</sup> and Biomax<sup>TM</sup> are more durable and show greater performance levels than do the aliphatic bio-base polymers but the problems of environmental toxicity and availability of terephthalic acid are serious. Poly(lactic acid)s (PLA) have been remarkably well developed because of their high mechanical strength. However, it was estimated that these polyesters will become substitutes for only a small percentage of nondegradable plastics currently in use since application of the aliphatic polyesters is limited due to their poor level of thermoresistance in applications as an engineering plastic. Then, high performance environmentallybenign polymers that degrade into natural molecules are earnestly desired for improving human life. Nondegradable engineering plastics have a rigid component of a benzene ring and super engineering plastics have a continuous structure of benzene and hetero rings such as benzimide, benzoxazole, benzimidazole, or benzthiazole. Although no continuous

rigid structure in the polymer backbone exist in nature, the polysaccharides have many hetero rings. Although the polysaccharides sometimes show too low a degree of processability to be made into a useful material, they do have a tremendous amount of potential for use as high performance bio-base polymers since cellulose shows a very high Young's modulus (more than 10 GPa). Although the use of a high strength filler such as a bacterial cellulose<sup>9</sup> or modified lignin dramatically increases the plastic properties, the matrix polymers determine the intrinsic composite performance.

The introduction of an aromatic component into a thermoplastic polymer backbone is an efficient method for intrinsically improving material performance. Additionally, the continuous sequence of aromatic rings can be a mesogenic group. Molding in the thermotropic liquid crystalline (LC) state can induce molecular orientation giving anisotropy to the mechanical performance, which sometimes dramatically increases mechanical strength and Young's modulus. However, there has been no attempt to use an aromatic bio-based monomer as a constituent of a bio-base polymer. Here, we report on the preparation of various LC polyarylates derived mainly from polymerizable phytochemicals-in other words, "phytomonomers" widely present as lignin biosynthetic precursors<sup>13</sup>. One series of polyarylates showed environmental degradability and a performance level as high as an engineering plastic.

### Selection of Phytomonomers

The phenolic phytochemical family with the *p*-coumaryloyl group having a photosensitive phenylenevinylene and a polymerizable hydroxycarboxylic acid group, such as pcoumaric acid (4-hydroxycinnamic acid; 4HCA), ferulic acid (3-methoxy-4-hydroxycinnamic acid; MHCA), and caffeic acid (3,4-dihydroxycinnamic acid; DHCA), has been selected as biomonomers. These molecules are widely available in various plants with an essential pathway of lignin biosynthesis. 4HCA derivatives are used as allelopathic chemicals in plants and widely exist in soil. 4HCA is also available in several photosynthetic bacteria as a protein component. Rhodobacter capsulatus, Rhodobacter sphaeroides, and so on have photoactive yellow protein containing a 4HCA component as a photosensitive center. 4HCA showed an E-Z transformation by light irradiation ( $\lambda = 375$  or 435 nm) for the bacteria to swim away from the light. Furthermore, since their enzymatic synthetic roots from amino acids were well defined as being very simple, it is possible to mass-produce these phytomonomers. These phytomonomers were biodegraded by microbial action.

### First Thermotropic LC biohomopolymers

P4HCA (structure: Figure 1A) was obtained by the thermal polycondensation of 4HCA as follows. 4HCA was heated at 220°C for 24 h in the presence of anhydride acetic acid as a condensation reagent and sodium acetate as a catalyst for transesterification. The molten mixture gradually became viscous during the reaction period. After cooling, the product was dissolved in pentafluorophenol and purified by reprecipitation over methanol, then was washed with methanol by the Soxhlet extraction method for 24 h (yield: 90%). The product was a yellowish-white powder that was soluble in



P(4HCA-co-DHCA)s

Figure 1. Chemical structures of the polyesters.

pentafluorophenol to give a viscous solution, but was insoluble in water, ethanol, acetone, tetrahydrofuran, chloroform, and various aprotic amidic solvents. Infrared and <sup>1</sup>H NMR spectroscopy of P4HCA (molecular weight: 8000) confirmed the chemical structure of the target polymer.

In order to investigate the thermotropic properties of P4HCA, we performed crossed polarizing microscopic observations of samples sandwiched between two glass plates as the temperature was changed. The sample was a birefringent powder at 20°C. When the sample was heated at a rate of 10°C min<sup>-1</sup>, the sample melted at 215°C while maintaining its birefringence. In the temperature range of 215-280°C, we observed a schlieren texture with two and four brushes (Figure 2A), which was easily transformed into the dark-field view by sliding the cover glass. This finding indicated that P4HCA is macroscopically oriented by the application of shear stress. Therefore, P4HCA exhibits a nematic phase where the polymer chains are autonomously oriented but randomly located. The nematic liquid of P4HCA solidified at 200°C following cooling, and repeatedly appeared on successive changes in temperature. Unexpectedly, the nematic liquid also solidified at 280°C upon subsequent heating, showing transformation of the microscopic texture from the schlieren to a needle form,



Figure 2. (A) Schlieren texture in nematic phase of P4HCA. (B) L929 mouse fibloblasts extending on a P4HCA coated glass.



Figure 3. Typical photoreactions of cinnamoyl compounds.

which was widely seen in the crystals. The sample solidified at 280°C and no longer showed any transition with successive heating or cooling. The sample became pale yellow and insoluble in pentafluorophenol or other solvents. This transformation was accompanied by a 9.85% loss in weight, suggesting that the crystallization was due to decomposition. The heat solidification above 280°C implies that P4HCA may be applied to thermosetting resins as well as to LC thermoplastics. Xray diffraction studies of P4HCA in the crystalline state were made and the results suggested that the P4HCA chains are arranged hexagonally, with a distance of 1.0 nm, and that a group of P4HCA chains slide to neighboring groups at a distance of one half the length of the repeating unit. Since 4HCA is a photoresponsive molecule showing photoreactions in Figure 3, the photoreactivity of P4HCA was investigated in terms of its phase behavior. A P4HCA film processed by spin casting (2000 rpm) from its pentafluorophenol solution  $(1 \text{ wt\%}, 50 \mu \text{m})$  was UV-irradiated (wavelength: more than 280 nm) and the structure was investigated by IR spectroscopy and WAXD. UV irradiation in the crystalline state (25°C) for an hour did not produce a substantial change in IR spectra. In contrast, when the P4HCA film was UV irradiated in the LC state (220°C) for the same period, the IR peaks representing double bonds ( $v_{C=C}$ : 997 cm<sup>-1</sup> and 1283 cm<sup>-1</sup>) became smaller and carbonyl shoulders appeared at about  $1700 \,\mathrm{cm}^{-1}$ , suggesting that the vinylene group reacted.<sup>21</sup> The lack of UV reaction in the crystalline state suggests that the pelectrons of the two vinylene moieties of P4HCA cannot meet each other, while the vinylenes in the nematic state can react due to the mobility of the polymer rods along the n-direction. Since the interchain [2+2] cycloaddition photoreaction occurred from both the E- and Z-structures of P4HCA, it was hypothesized that the cyclobutane was effectively formed with UV irradiation in the LC condensed state. We confirmed the good cell compatibility of P4HCA by a cell adhesion test. After L929 fibroblasts were incubated on a P4HCA film for

24 h at 37°C, they adhered and extended (Figure 2B) as much as did cells grown on tissue culture polystyrene (TCPS). Therefore, P4HCA showed potential for applications as a novel biopolymer with photoreactivity and liquid crystallinity, which can induce structural transformation and change the molecular orientation.

In general, the main chain type of a thermotropic LC polymer is composed of more than two monomeric units<sup>22</sup> consisting of poly{4-hydroxybenzoic acid (HBA)co-5-hydroxynaphthoic acid (HNA)}, where HBA is a phytomonomer but HNA cannot be derived from flora or fauna. Although PHBA can be completely phyto-derived, PHBA is a highly crystallized polymer that shows no melting point. The HBA comonomer was incorporated in order to decrease chain rigidity to put the crystalline chain of PHBA in the thermotropic LC state. P4HCA was the first LC synthetic homopolymer derived from a phytomonomer, which was made by molecular weight control. Although the LC polymers generally showed high mechanical strength for engineering use owing to molecular orientation, P4HCA was very brittle because of its low molecular weight but has a significant advantage of smooth degradation. However, the high molecular weight P4HCA was highly crystallized and exhibited no LC phase.

# High-performance bio-base polymers from phytomonomers

The previous studies of P(4HCA-co-cholic acid)s showed that bulk polymerization of multifunctional monomers such as cholic acid can create LC-spun fiber even if the molecular weight is very low. It was proved theoretically and experimentally that the ABx-type multifunctional monomers gave hyperbranching architecture. The reason for successful LC-spinning may be that the hyperbranching architecture of the copolymers effectively induces chain entanglement to increase the melt viscosity. However, the low molecular weight, which may be due to the poor compatibility of 4HCA with the bile acids in the copolymerization, had a negative effect on the mechanical strength of the fibers.

We then tried to prepare hyperbranching LC polyarylates by the copolymerization of 4HCA with DHCA (structure: Figure 1B). The hyperbranching architecture with low molecular weight arms might handle both the degradability from the chain ends and the high mechanical performance. DHCA units can take the role of a branching point, and the oligo4HCA arms are rigid enough to show a LC phase. <sup>1</sup>H NMR spectroscopy in a mixed solvent of trifluoroacetic acid-d and dichloromethane- $d_2$  (1/5 v/v) demonstrated that the incorporation of both monomers into the polymer backbone and the copolymer composition, C= [DHCA]/[DHCA][4HCA], can be estimated by the integration ratio of the aromatic proton signals of the

individual units. The C value was close to the monomer composition in the feed. The molecular weights of the copolymers were estimated by GPC. The numberaverage and weight-average molecular weight ranged between Mn= $1.8 \times 10^{4} - 3.3 \times 10^{4}$  and Mw= $4.4 \times 10^{4} - 3.3 \times 10^{4}$  $9.1 \times 10^4$ , respectively. The polydispersity, Mn/Mw, ranged between 1.6-2.8 although the acetone-soluble fractions (Mw<5 Da) showed small values of Mn/Mw (<1.3). All of the copolymers were soluble in aprotic polar solvents such as DMF, thus denying the crosslinked network formation. If the poly(4HCA-co-DHCA)s were heated, they melted at specific temperatures to exhibit a thermotropic LC phase, where the schlieren texture was observed by crossed polarizing microscopy (Figure 4A). The melting temperatures (Tm) were higher than 220°C and the glass transition temperatures (Tg) ranged between 115–16°C, which were much higher than the values of the degradable bio-based polymers reported so far and high enough for engineering use {Tg of poly(bisphenol A carbonate), PC, is 145°C}, as shown in Table 1. Further heating induced a LC-crystal transition. which was characteristic of P4HCA. In the LC state, the samples behaved like a very soft elastomer,





Figure 4. (A) Schlieren texture in nematic phase of P(4HCA-*co*-DHCA). (B) Schematic illustration of the entangled copolymer chains.

presumably due to chain entanglement enhanced by the hyperbranching architecture (Figure 4B). The copolymers were successfully processed in the nematic state into various shaped molds (Figure 5) by pressure application. In the nematic state, the samples were molecularly oriented by elongation using a pair of tweezers. The degree of orientation ranged between 0.52-0.58 as confirmed by X-ray diffraction, which is relatively low as compared to other LC polymers, presumably due to the hyperbranching architecture. A mechanical bending test of the oriented samples showed the mechanical strength, s, Young's modulus, E, and maximal strain, e, ranging between 25-63 MPa, 7.6-16 GPa, and 1.2–1.3, respectively. The  $\sigma$  values of the poly(4HCA-co-DHCA)s with C=25-50 mol% were comparable to those of PC and all the conventional environmentally degradable polymers reported so far whereas E was much higher than they were.

The hydrolytic behavior of the copolymers was investigated by an acceleration test in an alkaline buffer of pH=10 at 60°C. The copolymers with a C of 45% or lower showed a slight weight loss of no more than 19% of the initial weight, which demonstrates the high durability. In contrast, the copolymers with a C of 77%



Figure 5. Compacts of P(4HCA-*co*-DHCA)s processed from the liquid crystalline melt.

and the DHCA homopolymer showed a rapid weight loss, with a half-life of about 15 days. In addition, GPC of the supernatant solution showed only a peak at a maximum of Mn=2000 and high performance liquid chromatography (HPLC) showed monomer peaks (retention time, RT: 15.562 min,  $\lambda_{max}$ : 225 and 310 nm) together with other peaks presumably assigned to oligomers (RT: 16.063 min,  $\lambda_{max}$ : 225, 297, and 310 nm). This result indicates that the weight loss was due to hydrolytic degradation; the circular pellets transformed into an amorphous shape accompanying the degradation. An increase in the DHCA composition enhanced the speed of hydrolysis, presumably due to the decreased degree of crystallization and the enhanced degradation from the chain ends by hyperbranching architecture. Since the copolymer with a C of 77% showed not only high values for the mechanical properties and thermotropic temperatures, but also hydrolytic degradability with a short half-life, it can be regarded as a hydrolytic engineering polymer that could be degraded into the original phytomolecules. Furthermore, some of the copolymer rectangles buried in soil for 10 months



Figure 6. The compact of P(4HCA-co-DHCA) copolymer of C=21% buried in soil for 10 months. (a) Macroscopic digital image. (b) FE-SEM image of the sample surface, showing the local cave-in with a micrometer size.

showed deformation (Figure 6A) and an 8–13% weight loss while PC buried alongside the copolymers in soil showed neither deformation nor weight loss. Moreover, scanning electron microscopic (SEM) photos of the deformed poly(4HCA-*co*-DHCA) samples demonstrate that the presence of many holes with a diameter of about 10 mm contrasts with the smooth surface of a hydrolytically degraded compact polymer, while PC buried alongside showed a flat surface without holes (Figure 6B). These findings could indicate an environmental degradation of the copolymer compacts by natural functions other than that of rainwater such as the action of microorganisms.

Figure 7 shows the photoreactivity of the poly(4HCAco-DHCA) copolymers. The time course of the photoreaction conversion was monitored by UV-visible absorption spectroscopy of the copolymer thin-film cast onto quartz. The absorption with a maximal peak at  $\lambda_{max}$ of 310 nm was reduced as the time of UV -irradiation was increased. In contrast, the absorption ( $\lambda_{max} = 225 \text{ nm}$ ) over the range of less than 250 nm increased by an increase in UV irradiation, resulting in the appearance of an isosbestic point at  $\lambda = 250$  nm. UV irradiation for longer than 20 seconds made the copolymers insoluble in the solvent. Spectroscopic studies such as <sup>1</sup>H NMR and IR demonstrated that UV irradiation of the copolymers at ambient temperature induced a [2+2] cycloaddition of the vinylene units, forming the cyclobutane cross-linkage in the polymeric chains (Figure 7). The photoreaction increased the  $\sigma$  and E values to maximum values of 104 MPa and 19 GPa, respectively, by photoreaction, presumably due to the cross-linkage formation. The changes in e values were negligible. In contrast, the thermotropic temperatures were maintained regardless of the photoreaction. Photoconversion from aromatic into aliphatic carboxy ester showed a shortening of the degradation half-life from more than 30 days to only 12 days. In particular, the copolymers with C of 77% and 100% showed a very short half-life of only 5 days.



Figure 7. UV-absorption change of P(4HCA-*co*-DHCA) membrane by UV-irradiation.

Furthermore, the period of UV irradiation controlled the speed of hydrolysis. The cyclobutane formation could attenuate the ester carbonyl conjugation with the phenylenevinylene to make it more polar and easier to degrade randomly, and the cross-linking barely affected degradation from the chain ends. Since the  $\lambda_{max}$  of the UV absorption peak of the copolymer was 310 nm (UV-B), which is scarcely present in sunlight reaching the ground atmosphere, the hydrolysis was not spontaneously accelerated.

### Hybridization

Poly(4HCA-co-DHCA)s were hyperbranch polymers which have many bulky branches rigid-rod, just like as lignin. Then we tried to hydridize the copolymers with celluloses to increase their mechanical properties<sup>33</sup>. Since the direct mixing may be difficult for hybridization with other macromolecules, we made a polymerizationsimultaneous hybridization, i.e. 4HCA and DHCA were copolymerized in the presence of celluloses. Here the feed composition of 4HCA/DHCA was fixed at 60/40 mol mol<sup>-1</sup>. The reaction solution increased its viscosity gradually and became dark brown. The color was darker than the resins prepared without celluloses, presumably due to the impurities such as ligning contaminating celluloses. However infrared (IR) analyses demonstrated that ester linkages between 4HCA and/or DHCA was successfully formed.

Kenaf fibers were very stiff and too long and thick to hybridize with the copolymers. Millimeterscaled broken pieces of kenaf fibers dispersed over the resins after polymerization- simultaneous hybridization. The dispersion gave inhomogeneity functioning as mechanically-weak points bad for performance of hybrid and in fact the mechanical strength of resins was decreased after hybridization using this type of kenaf fibers. Then we milled kenaf hybrids before use. Since the fibers were very stiff, it was difficult to reduce their size using mechanical mill with some blades even if liquid nitrogen was used for freezing the fibers. Using a ceramic pestle gave one of the best methods for grinding down the kenaf fibers into nanometer-scaled fibers. Scanning electron microscopic image illustrated the existence of nanofibers 1-5 nm in thickness and 20-200 nm in length. In this study, the nanofibers were used for fillers reinforcing the copolymer resins. Moreover we tried to cinnamovlation of cellulose fiber aiming to increase the miscibility of the fiber with the copolymers. The ground fibers were dispersed into dimethylacetamide (DMAc), and then cynnamoyl chloride was added. The reaction mixture was stirred overnight to give darkbrown powdery nanofibers. The cinnamoylation of the nanofiber surface were confirmed by IR analyses and here abbreviated as c-kenaf.

Effects of hybridization of the copolymers with the

nanofibers were investigated in terms of mechanical properties and melting behaviors. The hybrids were successfully processed into rectangular compacts in brass template by hot pressing. The mechanical strength of the resins was measured by three-points bending tests. The mechanical strengths of the non-oriented copolymer resins without the fillers were 31 MPa which increased to 41 MPa by hybridization using the kenaf nanofiber (10 wt%). The kenaf nanofibers have a reinforcing effect on the hyperbranching copolymers. We tried to prepare the hybrids just by mixing the melting copolymer with the nanofibers. However, the mechanical strengths were not increased through the hybridization methods. These results indicated that the hyperbranching chains were difficult to interact with the celluloses as imagined above, while the chains might entangle with the celluloses during the propagating of the copolymer chains from monomers.

Dynamic mechanical properties were measured in order to determine the softening temperature of the resins as well as the viscoelasticity. The copolymer resins and every hybrid showed two peaks of Tan  $\delta$  around -50and 150°C (Figure 8A). One at lower-temperature can be assigned to local relaxation and the other at highertemperature can be assigned to glass transition. While the relaxation at around 50°C did not change regardless of hybridization, softening temperature increased from 139 to 154°C with increasing the composition of kenaf nanofibers up to 10 wt%. This result indicated that the cellulose directly interact with the hyperbranch copolymers on the molecular level e.g. cross-linking physically. The interaction may be based on hydrogen and/or p-hydrogen interaction of phenols with hydroxyls of sugar units. However, kenaf nanofibers aggregated through their own strong interchain interaction to form apparent nanofiber networks, which reduced miscibility of copolymer chains with nanofibers to show the left shoulders of Tan d peaks. The softening temperature of the hybrid with the c-kenaf nanofiber was slightly higher than that of the corresponding hybrid with normal nanofiber. The cinnamoylation can increase the interaction of the nanofibers with hyperbranch polymers, as expected, presumably due to the high compatibility between cinnamoyl groups of nanofibers and copolymers. Moduli in torsion and complex viscosities at room temperature increased by hybridization, presumably due to the reinforcement by kenaf networks. However, one can see the difference in complex viscosity in the melt state (around 200°C) between kenaf and c-kanef hybrids, as shown in Figure 8B. From these results, we can summarize the effects of cinnamovlation of kenaf nanofibers; the cinnamovlation could enhance the interaction of the copolymers with kenaf nanofibers to increase the softening temperature, while it could weaken the kenaf interchain interactions to reduce



Figure 8. Dynamic mechanical analyses of rectangular compacts of poly(4HCA-*co*-DHCA) (60/40) hybrids with kenaf cellulose. (A) Temperature dependence of loss tangent, Tan d. (B) Temperature dependence of complex viscosities, h\*.

moduli and viscosities of hybrids.

### Conclusion

We successfully prepared high performance bio-base polymers, poly(4HCA-*co*-DHCA)s, with phototunable hydrolytic properties that could lead to the development of novel, environmentally friendly engineering plastics for use in automobiles, aircraft, electronic devices, and other materials. We finally propose that the positive use of ABx-type multifunctional phytomonomers that widely exist as amino acids, glycolipids, and other metabolites will take on the new purposes of highly functional and highly efficient bio-base polyesters and/or polyamides with their hyperbranching architecture.

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