

Syntheses of hyperbranched liquid-crystalline biopolymers with strong adhesion from phenolic phytomonomers*

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Abstract: A novel thermotropic liquid-crystalline (LC) biocopolymer, poly{*trans*-3-methoxyl-4-hydroxycinnamic acid (MHCA: ferulic acid)-*co-trans*-3,4-dihydroxycinnamic acid (DHCA: caffeic acid)}, was synthesized by a thermal acidolysis-polycondensation of MHCA and DHCA, efficiently catalyzed by Na₂HPO₄. When the MHCA composition of poly(MHCA-*co*-DHCA) was 60, 75, and 90 mol %, the copolymers showed a nematic LC phase although individual homopolymers such as polyMHCA and polyDHCA did not exhibit LC phase. Poly(MHCA-*co*-DHCA)s showed high molecular weight (M_w) ranged between M_n 2.6×10^4 to 3.7×10^4 and M_w 8.2×10^4 to 13.1×10^4 , respectively, high glass-transition temperature (T_g) with the range of 115 to 140 °C and high degradation temperature T_{10} from 315 to 356 °C. In the adhesive test of copolymers against the surface of carbon substrate, the copolymers showed high shear strength at fracture.

Keywords: adhesives; hyperbranched polymers; liquid-crystalline biopolymers; phenolic phytomonomers.

INTRODUCTION

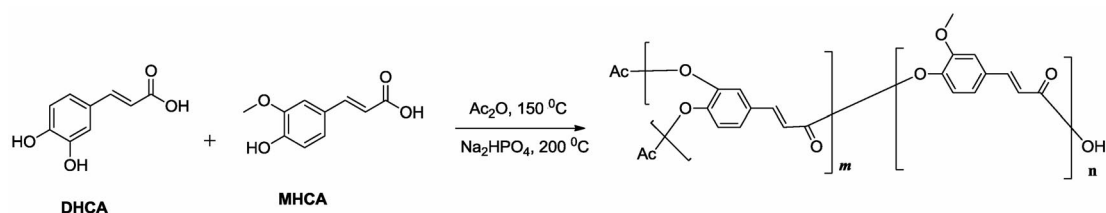
Biopolyesters exhibiting smooth degradation have been widely studied as environmentally friendly polymeric materials [1]. However, aliphatic ecopolyesters such as poly(hydroxyalkanoate)s [2], poly(butylene succinate) [3], and so on degrade too rapidly to actually be used [4]. EcoflexTM and BiomaxTM are more durable and show greater performance levels than the aliphatic ecopolymers, but the problems of environmental toxicity and availability of terephthalic acid are serious. Poly(lactic acid)s (PLAs) have been remarkably well developed because of their high mechanical strength [5]. However, it was estimated that these polyesters will become substitutes for only a small percentage of non-degradable plastics currently in use because application of the aliphatic polyesters is limited due to their poor level of thermoresistance in applications. The ongoing search for high-performance biopolymers is motivated by their potential to mitigate environmental impact and thus contribute to improving quality of life.

The introduction of an aromatic component into a thermoplastic polymer backbone is an efficient method for intrinsically improving heat-resistance performance [6]. Additionally, the continuous sequence of aromatic rings can be a mesogenic group. Liquid-crystalline (LC) polymers are easily oriented at the molecular level to create materials with ultrahigh-strength, a high modulus, and other ori-

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entation-related functions [7,8]. However, almost all commercial high-performance aromatic LC polymers are made from non-renewable resources and non-degradable ones such as poly(*p*-phenylene terephthalamide) (Kevlar™) and poly(*p*-phenylene-2,6-benzobisoxazole) (Zylon™), which have a high proportion of rigid aromatic moieties, showed lyotropic LCs that could induce preparation of highly oriented fibers [9,10]. Our group has studied polymers from aromatic biobased monomers [11,12], especially phenolic phytonomers containing a *p*-coumaryl group such as *p*-coumaric acid (4-hydroxycinnamic acid; 4HCA) and caffeic acid (3,4-dihydroxycinnamic acid; DHCA), which are known to be biodegraded but their renewability is not very high. In this study, we use ferulic acid (3-methoxy-4-hydroxycinnamic acid; MHCA) which is mass-produced from rice brans deposited in high quantity in the world and then is highly renewable. However, polyMHCA homopolymer was not processable by heating or dissolution [13]. Here, we report the preparation of new highly heat-resistant LC hyperbranched biopolymers [poly(MHCA-*co*-DHCA)] from MHCA efficiently catalyzed by Na₂HPO₄ (Scheme 1).



Scheme 1 Syntheses of the polymers of poly(DHCA-*co*-MHCA)s.

EXPERIMENTAL SECTION

Materials

Ferulic acid [MHCA; Tsuno Food Industrial Co., Ltd.] and caffeic acid [DHCA; Tokyo Chemical Industry (TCI)] were used without further purification. The acetic anhydride and sodium acetate (Wako Pure Chemical Industries, Ltd.) were used as received. The acetone and methanol (Wako Pure Chemical Industries, Ltd.) used as a wash solvent were used as received. Trifluoroacetic acid (TFA-*d*) and dichloromethane (DCM-*d*) used for NMR analyses were purchased from Wako Pure Chemical Industries, Ltd. and were used as received.

General procedure for polycondensation of poly(DHCA-*co*-MHCA)s

Poly(MHCA-*co*-DHCA) with a DHCA composition of 40 mol % was synthesized by a two-step reaction by a thermal polycondensation of MHCA and DHCA in one bottle by the following procedure. The mixture of DHCA (20 g, 111 mol) and MHCA (32 g, 167 mmol) was heated at 150 °C and mechanically agitated for 2 h in the presence of a condensation reagent acetic anhydride (60 mL) and a transesterification catalyst such as disodium hydrogen phosphate (1 wt %). The mixture was further heated to 200 °C and agitated for 8 h. The resulting sample was taken out and precipitated over a mixture of acetone and methanol. The precipitates were filtered and washed with acetone, and then dried at 50 °C for 10 h. The white or yellow powders of the copolymers were produced. The homopolymer of each monomer and other copolymers were prepared by the analogous procedures with this copolymer.

Measurements

The molecular weights (M_w) of the poly(DHCA-*co*-MHCA)s were determined by gel permeation chromatography (GPC; Shodex GPC-101 with a connection column system of 803 and 807) that was cali-

brated with polystyrene standards (eluent: dimethylformamide, DMF). The NMR spectra were obtained on a Bruker DRX 500 spectrometer operating at 400.13 MHz for ^1H NMR. A mixed deuterated solvent of TFA-*d*/DCM-*d*₂ was used. The thermal properties were analyzed by differential scanning calorimetry (DSC; EXSTAR6100, Seiko Instruments, Inc.) and thermogravimetric analysis (TGA; SSC/5200 SII Seiko Instruments, Inc.). Samples were scanned from 20 to 200 °C at a scanning rate of 10 °C/min under a nitrogen atmosphere with a flow rate about 80 mL/min. Glass transition temperatures (T_g) were measured using data generated during the second heating cycle. The thermal degradation behavior of the samples was observed from the TGA curves by heating from 50 to 500 °C at a rate of 10 °C/min under a nitrogen atmosphere with a flow rate about 200 mL/min. The shear adhesive test was measured by a tensile testing machine (3365-L5, Instron, Canton, MA, USA).

Observation of liquid crystallinity by a crossed-polarizing microscope

Samples were sandwiched between two carbon plates and heated at a rate of 10 °C/min from 25 °C by a Mettler Toledo FP82HT Hot Stage (Greifensee, Switzerland). Phase transitions such as melting temperatures (T_m) were observed.

Preparation of adhesive bonding specimen

The carbon substrates were obtained from the Nilaco Corporation (Tokyo, Japan) and used as received. The carbon plates were 50 mm long, 10 mm wide, and 8 mm thick. The adhesive poly(DHCA-*co*-MHCA)s specimen was prepared by sandwiching the resin between two carbon plates at a range of 200–240 °C, 5 atm for 5 min using a hot press. The bonding area was 10 mm long and 10 mm wide. The bonding samples were then cooled to room temperature under atmospheric conditions.

RESULTS AND DISCUSSION

Molecular design and synthesis

We previously demonstrated that a *p*-coumaryl oligomeric segment with an appropriate length was mesogenic to give a good processability, though a too long one induced the stable crystal formation [11]. However, polyMHCA is not LC [13] presumably due to a structural trade-off from the methoxy side group requiring the long backbone. The appropriate disordering of the long backbone by copolymerization of MHCA with a *p*-coumaryl derivative comonomer probably imparts polyMHCA LC property. On the other hand, the Flory theory shows that the polymerization of AB₂-type multifunctional monomers such as DHCA with one functional group (A) of one type and two groups (B) of another type created a hyperbranched architecture without cross-linkage. In our previous research on DHCA and 4HCA to make hyperbranching LC polymers, we were prompted to design hyperbranching polymers by using DHCA [11]. Then we selected DHCA as a comonomer with MHCA to prepare LC poly(DHCA-*co*-MHCA) [13]. Since these monomers have bulky groups neighboring to hydroxyls, we tried to find suitable catalysts, for the production of copolyesters poly(MHCA-*co*-DHCA)s with well-defined structures, from alkaline salts such as Na₂HPO₄, NaH₂PO₄, KH₂PO₄, and NaHCO₃. We first tried Na₂HPO₄ and CH₃COONa as catalyst, based on our previous work they showed efficient catalytic activity for polyester [11c,14]. CH₃COONa can catalyze the polymerization with high M_w , however, showing multimodal GPC peaks indicative of a heterogeneous structure, presumably due to difficulty in controlling the side reactions. However, Na₂HPO₄ efficiently catalyzed those reactions generating polymers with M_w 6.4×10^4 and monomodal GPC peaks with a very narrow M_w distribution, which increased gradually with reaction time. Other catalysts such as NaH₂PO₄, KH₂PO₄, and Na₂HCO₃ only yielded oligomers with M_w of between M_w 6.9×10^3 to 8.2×10^3 , after the same polymerization time of 4 h at 200 °C. Thus, we chose Na₂HPO₄ as the most efficient catalyst to make a series of copoly-

mers with in-feed compositions of MHCA (C_{MHCA}) of 90, 75, 60, 50, 40, and 25 mol % (Table 1). The M_n values were in a narrow range of 26 000–37 000, whereas the M_w values were over a wide range of 82 000–131 000. GPC showed an obvious broadening of the M_w distribution and multimodal peaks appear, accompanying the disappearance of monomodal for extended reaction times, suggesting the formation of hyperbranched architecture [14].

Table 1 Synthetic conditions of poly(DHCA-*co*-MHCA)s and their thermal performance.^a

C_{MHCA}^b (mol %)	M_w (g/mol)	M_n (g/mol)	M_w/M_n	T_g^d (°C)	T_{10}^e (°C)	T_m^d (°C)	Yield ^c (wt %)
90	87 000	26 100	3.33	140	315	200	87
75	131 000	31 400	4.16	132	332	210	80
60	82 000	27 000	3.04	128	337	245	86
50	97 600	23 200	4.21	125	342	260	77
40	106 000	37 200	2.85	115	351	255	79
25	121 000	32 400	3.72	123	356	195	83

^aReactions were carried out in the presence of Na_2HPO_4 (1 wt % to total weight of monomers) and acetic anhydride at 150 °C for 2 h under atmosphere pressure and then at 200 °C under vacuum until the reaction mixture became solid for about 8 h.

^bMHCA molar composition to the total monomers in feed.

^cPurification by precipitation of DMF solution into acetone and methanol.

^dThermotropic properties were measured by DSC (10 °C min⁻¹), and the softening behavior was confirmed by a crossed-polarizing microscope equipped with a hot stage (temperature-controlled to $\pm 0.1^\circ$ accuracy)

^e10 % weight-loss temperature, T_{10} , was measured by TGA under nitrogen (10 °C min⁻¹).

Structural characterizations of copolyesters poly(DHCA-*co*-MHCA)s

The structures of these hyperbranching copolyesters were characterized by Fourier transform-infrared (FT-IR), ¹H NMR, which demonstrated the formation of a targeted polyester structure. A representative ¹H NMR spectrum from a poly(DHCA-*co*-MHCA) (C_{MHCA} : 60 mol %) is shown in Fig. 1. A series of peaks marked as a, a', a'', b, and b' in a chemical shift range of δ 7.13–7.82 ppm were assigned to individual aromatic protons as shown in the chemical structure over the top of the spectrum. Broad peaks marked as d and d' in δ 6.81 ppm and c and c' in δ 8.08 ppm were assigned to the double-bond protons of α -CH and β -CH, respectively. The large peak in 2.47–2.50 ppm corresponds to the acetyl groups at the end of the hyperbranched architecture, and at the non-polymerized side groups of the DHCA units. The integral strength ratio of the vinylene protons 2 H to the aromatic ones 3.0 H agreed well with the proton ratio in the realistic copolymer structure, showing no side reaction such as heat breakage of the vinylene group. The integral strength of the methoxyl protons was estimated at 1.78 H based on the aromatic proton signals (3.0 H), which also agreed with the calculated value (1.8 H) from the molar composition of the acetyl groups. The aromatic protons marked as a' and a'', which are adjacent to the O-substituted carbons of DHCA, showed multiple signals, suggesting the coexistence of coumaryloyl ester and unreacted acetyl ester. FT-IR spectrum of the same sample further confirmed the target structure, the characteristic carbonyl stretching bond of the ester group at 1762 and 1728 cm⁻¹ was formed and the vinylene group kept well (Fig. S1).

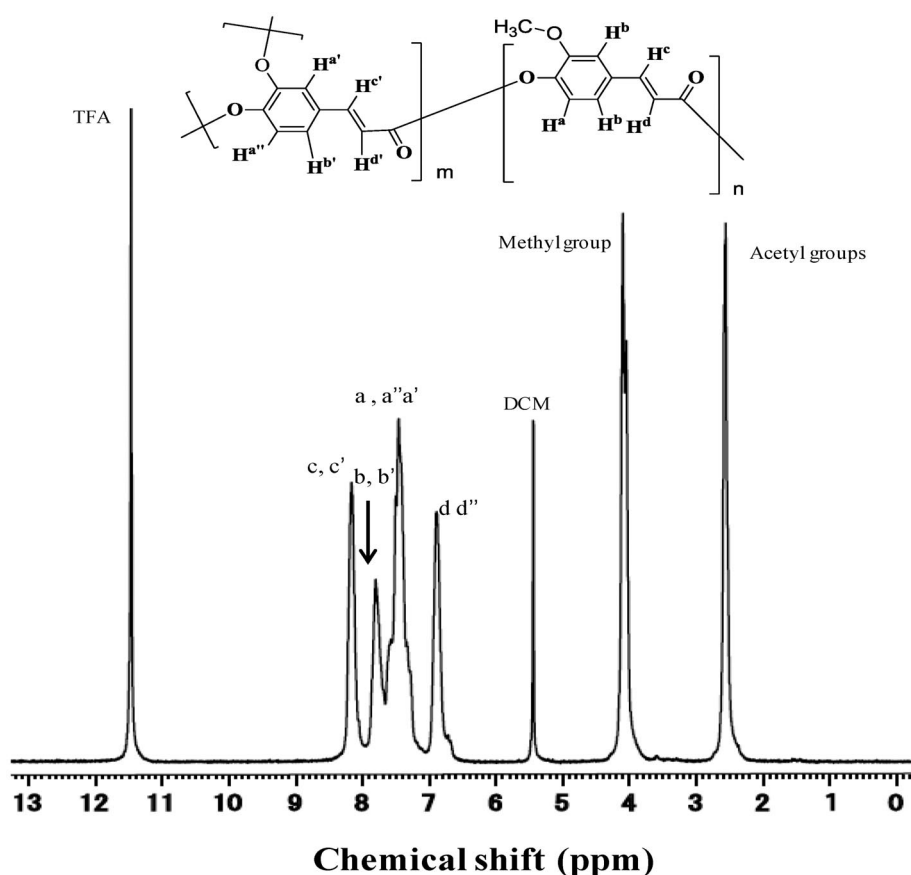


Fig. 1 ^1H NMR spectrum of poly(DHCA-co-MHCA) with an in-feed monomer composition of $C_{\text{MHCA}} = 60$ mol %.

Thermotropic properties of poly(4HCA-co-LCA)s

Thermal behaviors such as the glass transition and pyrolysis of the copolymers poly(DHCA-co-MHCA)s were investigated. The T_g value of poly(MHCA-co-DHCA) with an in-feed composition of $C_{\text{MHCA}} = 60$ mol % increased with polymerization time in initial 8 h, then no significant change in T_g from 8 to 10 h (Fig. S2), the similar phenomenon was seen in our previous study on poly(4HCA-co-DHCA)s [14]. This is because the T_g value is strongly dependent on the M_w initially and the effect of further M_w increases on the decrease in the chain-end composition were trivial, and thus the T_g noticeably changed from 2 to 8 h and then only slightly increased from 8 to 10 h. Next, we measured T_g vs. C_{MHCA} in poly(MHCA-co-DHCA)s with a different composition of MHCA at the same polymerization time of 8 h (data in Table 1). T_g ranged between 115 and 140 °C for these copolymers with various compositions of MHCA in the copolymers poly(MHCA-co-DHCA)s. The T_g values were much higher than the values of degradable biobased polymers reported so far [15] and high enough for engineering use (representative DSC chart: Fig. S3). The T_g tends to decrease with increase of composition of DHCA in the copolymers, which probably results from increase of flexibility of the polymer chains. The 10 % weight-loss temperature for various compositions of poly(DHCA-co-MHCA)s, T_{10} , ranged between 315 and 356 °C, which suggested this polymer has high heat-resistance property for use in engineering thermoplastics.

The thermotropic properties were also investigated by crossed-polarizing microscopic observation. The results of the microscopic observation showed almost the same results as the DSC analysis. The T_g of the copolymers ranged between 115 and 140 °C. PMHCA showed a T_m at 230 °C and then solidified again over 280 °C. In the copolymers, the T_m increased with decreasing C_{MHCA} and then decreased, its highest value at 260 °C with $C_{MHCA} = 50$ mol %. Figure 2 shows the phase diagram of poly(DHCA-*co*-MHCA)s of various compositions. Polarizing optical microscopy indicated that in poly(DHCA-*co*-MHCA)s with $C_{MHCA} = 60$ mol % and higher showed clear birefringence and fluidity in their melted state, thus demonstrating the formation of the LC structure. String textures of the LCs shown in the representative photograph (inset of Fig. 3A) were hypothetically derived from the nematic

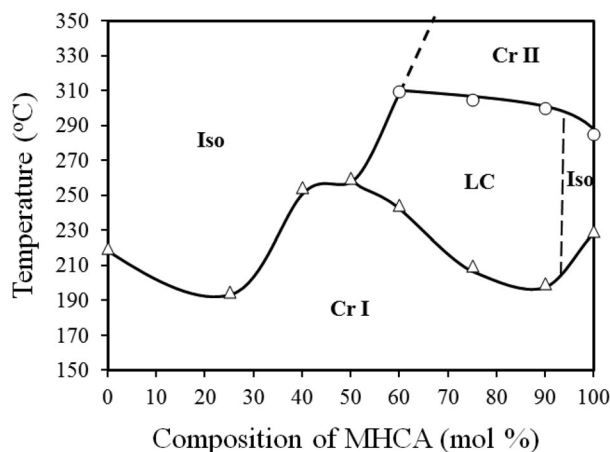


Fig. 2 Phase diagram of poly(DHCA-*co*-MHCA)s of various compositions. “Iso” refers to isotropic phase, “Cr” refers to crystalline phase, and “LC” refers to liquid-crystalline phase.

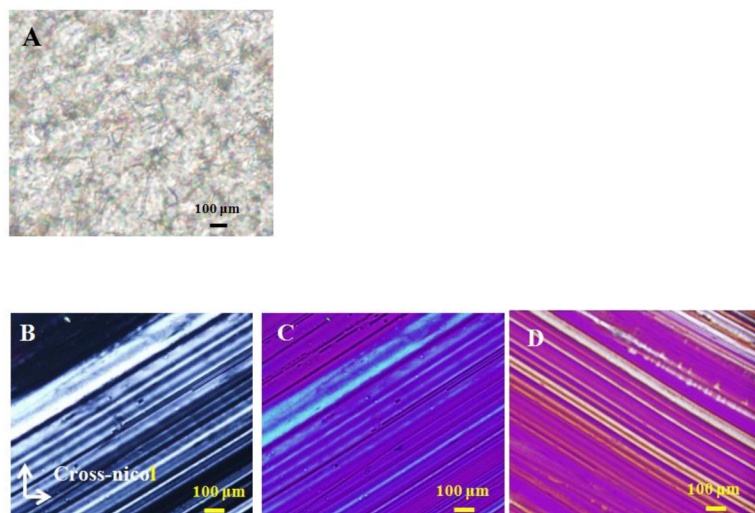


Fig. 3 Crossed-polarized optical microscope images of poly(DHCA-*co*-MHCA)s with an MHCA composition of 60 mol %, (A) taken at 250 °C, and (B–D) taken at room temperature after being sheared at 250 °C. (C,D) The image was taken under a first-order retardation plate ($\lambda = 530$ nm). If image (C) was rotated at 90 °C, image (D) was obtained.

phase. However, the nematic fluid solidified at 300 °C on average, showing a transformation from the microscopic texture typical of the nematic form to that of the crystalline upon subsequent cooling and heating, and they no longer appeared with successive heating and cooling cycles. This phenomenon was also found in our previous study on P4HCA homopolymer [11a]. It may be involved in the chemical conversion of the polymer unit, such as decomposition or acetyl group additions to double bonds. As a whole, the phase diagram showed that the melting point of the copolymers can be controlled by a change in the composition, while retaining their LC properties. In addition, one can see that the LC property transformation can be controlled by adjusting the percentage of monomer, although both of the homopolymers have not shown LC phenomenon at heating and cooling.

In LC melts state, poly(DHCA-*co*-MHCA)s were very viscous, then they can be easily spun to give the fibers in this state; the surface of the copolymer melts in the LC state was picked up with a pair of tweezers and pulled to yield fibers with a diameter of about 100–300 μm (Fig. 4A). Figure 4B shows microscope pictures of the fibers taken under a crossed polarizer. The fibers were bright when they made a ±45° angle to both the polarizer and analyzer, and the fibers clearly showed blue and orange colors in the presence of a color-sensitive plate ($\lambda = 530$ nm) depending on the sign of the angle. On the other hand, the film cross-nicol shear experiment was done for poly(DHCA-*co*-MHCA) with $C_{MHCA} = 60$ mol %, under cross-nicol polarimetry at 250 °C, which suggested the mechanical orientation of the sample was demonstrated by shearing (Figs. 3B–D) [15,16]. It shows an orientation of the polymer main-chains along the shear direction.

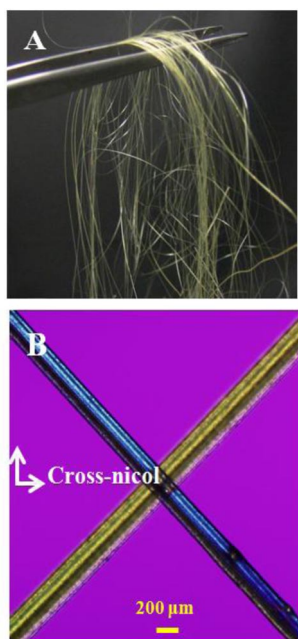


Fig. 4 (A) Fibers spun from LC melt of poly(DHCA-*co*-MHCA) with $C_{MHCA} = 60$ mol % in-feed; (B) crossed-polarized microscopic photos of the fibers under first-order retardation plate (530 nm).

Solubility

The solubility of the poly(DHCA-*co*-MHCA) with different C_{DHCA} values in various kinds of solvent was evaluated (Table 2). The MHCA homo-polymer polyMHCA is insoluble in any single solvent examined here and only partly soluble in the mixture solution of TFA and DCM. In the poly(DHCA-

co-MHCA)s with C_{MHCA} values from 25 to 60 mol %, the polymers prepared showed superior solubility than higher C_{MHCA} from 75 to 90 mol % (such as in DMF). For those polymers with composition lower than 60 % of C_{MHCA} , they were soluble in DMF at shorter polymerization times, whereas the ones prepared for the longer polymerization times were only partly soluble (more than 10 h, not shown here). Overly dense branching chains might restrict the chain mobility and solubilization of the polymer chains. The poly(DHCA-*co*-MHCA)s with C_{MHCA} values of 25 to 40 %, as well as polyDHCA can be completely dissolved in DMF, even if the polymerization time was very long, thus resulting in a very high M_w . However, all the copolymers with various composition of C_{DHCA} can be dissolved in the mixture solution of TFA and DCM, which supported the formation of hyperbranched architecture, not a cross-linked network.

Table 2 Solubility of homo- and copolymers poly(DHCA-*co*-MHCA) with different in-feed compositions of MHCA.^a

Solvent	Monomer		C_{MHCA} (mol %) ^b							
	DHCA	MHCA	0	25	40	50	60	75	90	100
Water	○ ^c	○ ^c	X	X	X	X	X	X	X	X
Methanol	○	○	X	X	X	X	X	X	X	X
Acetone	○	○	X	X	X	X	X	X	X	X
Acetonitrile	○	○	X	X	X	X	X	X	X	X
Chloroform	X	X	X	X	X	X	X	X	X	X
TFA + DCM	○	○	○	○	○	○	○	○	○	○
THF	○	○	X	X	X	X	X	X	X	X
Toluene	X	X	X	X	X	X	X	X	X	X
NMP	○	○	○	○	○	○	○	±	±	X
DMSO	○	○	○	○	○	○	±	±	±	X
DMF	○	○	○	○	○	○	○	±	±	X

^aMarks “○”, “X”, “±” mean soluble, insoluble, and partly soluble, respectively.

^b C_{MHCA} refers to the composition of MHCA in copolymer.

^cDissolved in water by heating.

Adhesive properties

The LC structure of the copolymers can affect their mechanical performance under shearing. Then we investigated mechanical test under shearing using the thin specimens (thickness < 50 μm) of poly(DHCA-*co*-MHCA)s sandwiched between two carbon plates and hot-pressed at a range of 200–240 °C. Four polymers with 25, 50, 60, and 75 mol % of C_{MHCA} were chosen for the mechanical test. As shown in the upper illustration of Fig. 5a, the edges of the carbon substrate were glued by polymers and opposite sides were pulled by tester. The force applied to the specimen was monitored, and the stress was defined as the force divided by the bonding area. The stresses at fracture for four copolymers are summarized in Fig. 5b. Evidently, the stresses at fracture, σ , of LC copolymers with C_{MHCA} of 60 and 75 mol % were 14.5 and 15.0 MPa, respectively, which are higher than those of non-LC copolymers with C_{MHCA} of 25 and 50 mol % (9.8 and 10.3 MPa, respectively). The fractured samples were covered on almost 50 % area of both substrate surfaces, meaning that the stresses at fracture were dominated by not only the mechanical toughness of the polymer resin but also the adhesion force of the polymers to substrates. It should be noted that the strong adhesive capability of these polymers with various composition is superior to that of conventional instant superglue 4 MPa (Aron Alpha, Toagosei Co., Ltd.) [17]. It might be a result of strong hydrogen bonding between the polymer ends and carbon surfaces; the hyperbranched copolymers contain a number of end catechols, which also exist in 3,4-dihydroxyphenylalanine, through which the marine shellfish stick firmly to rock

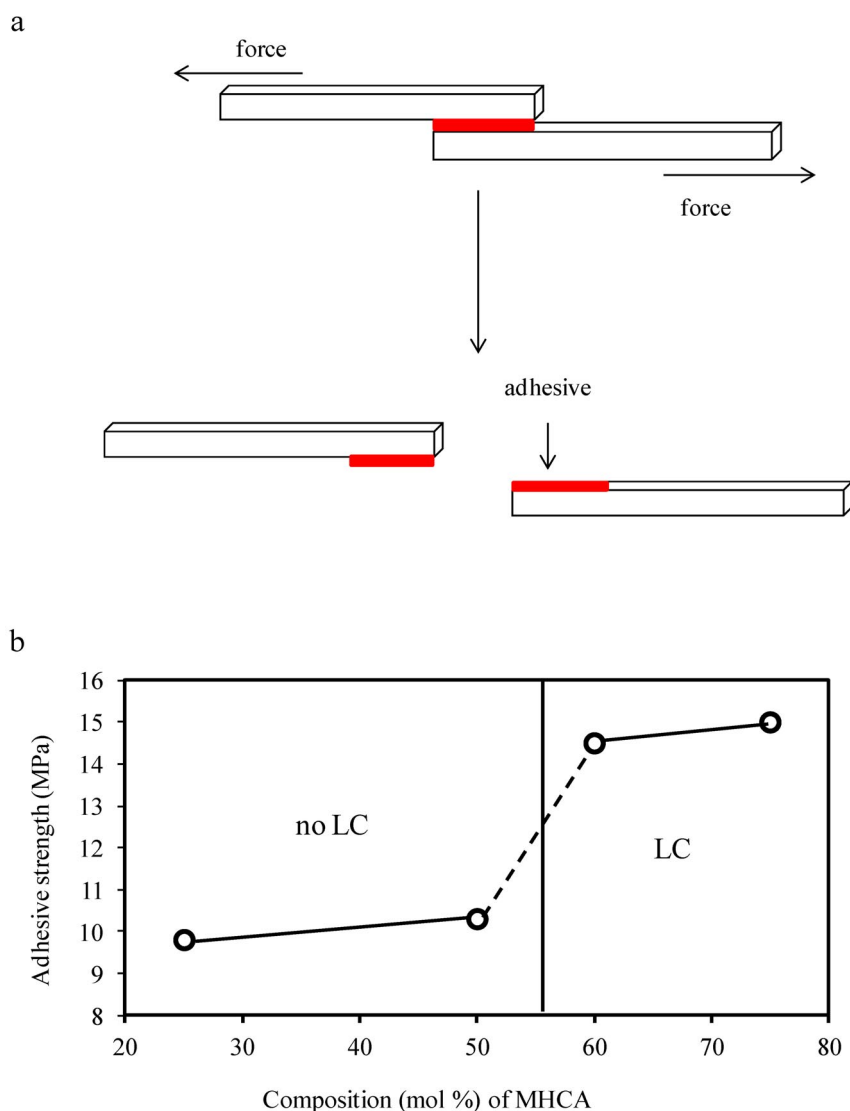


Fig. 5 (a) Polymer glue was sandwiched between two substrates and pulled to failure. (b) Mechanical fracture strength, σ , of poly(DHCA-*co*-MHCA)s resin glued substrates on carbon substrate.

surfaces [18]. LC alignment of the polymer branches might support the multiple-hydrogen bonding with the polar moiety of the substrate surface. Thus, we prepared a bioderived LC resin with high adhesive property.

SUMMARY

We have described syntheses of novel thermotropic LC copolymers, poly(MHCA-*co*-DHCA)s, by a thermal acidolysis-polycondensation of rice bran-derived MHCA and DHCA. When the MHCA composition in poly(MHCA-*co*-DHCA)s was 60, 75, and 90 mol %, the copolymers showed an LC phase. Poly(MHCA-*co*-DHCA)s showed high M_w , high heat-resistant temperature, and strong adhesive properties. More interestingly, the effects of LC alignment of the copolymers on the adhesive lead to much

stronger adhesion than that of non-LC polymers. The strong adhesive capability of these polymers with various compositions is superior to that of conventional instant superglue. It is expected that poly(DHCA-co-MHCA)s may be useful for applications as environmental plastics and adhesive materials.

SUPPLEMENTARY INFORMATION

Supplementary figures are available online (<http://dx.doi.org/10.1351/PAC-CON-12-05-12>).

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