Synthesis of Liquid Crystalline Monomers and Side-chain Polymers Containing 2-Phenylbenzoxazole in Mesogenic Unit

Sehoon Kim, Jiwon Sohn, and Soo Young Park*

Dept. of Fiber and Polymer Science, Seoul National University, Seoul 151-742, Korea
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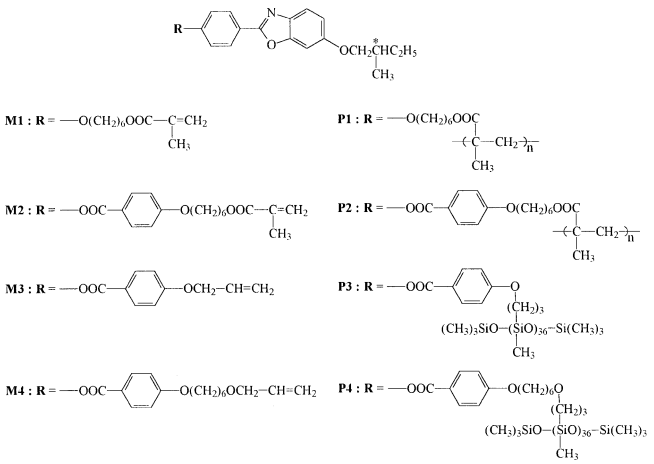
2-Arylbenzoxazole derivatives are characterized by the anisotropic molecular shape with an efficient π-electron conjugation along the molecular long axis. Due to the efficient π-electron conjugation and consequent high-yield photoluminescence, 2-arylbenzoxazole derivatives are well-known as fluorescent materials and laser dyes. On the other hand, anisotropic molecular shape is potentially useful to the liquid crystallinity of this class of compounds. Low molecular weight liquid crystals[1] and several liquid crystalline polymers[2~4] containing 2-phenylbenzoxazole in the mesogenic unit were already reported. However, none of the works reported to date aimed at the syntheses of highly fluorescent liquid crystals, which are promising materials for the polarized emission devices. It was considered that the properly designed 2-arylbenzoxazole structure is an excellent candidate for the fluorescent liquid crystal due to its ambidextrous potential.

As a first step of this approach, we report the synthesis of fluorescent liquid crystalline monomers and polymers with benzoxazole-based mesogenic core and (S)-2-methylbutoxy tail (shown in Scheme 1).

Among the various synthetic routes to 2-arylbenzoxazole, the dehydrative cyclization of *o*-(acylamino)phenols is most general.[5~7] When benzoic acid and *o*-aminophenol are activated either thermally or by means of some reagents such as polyphosphoric acid,[8] polyphosphate ester[9] or boric acid,[10] direct cyclization occurs. Alternative route is the oxidative ring-closure of phenolic Schiff's bases by various oxidizing agents such as $Pb(OAc)_4$ or MnO_2.[1,4,11] The choice of synthetic route should be investigated very carefully, since the success of reaction depends strongly on the chemical structure of reactants, and in many cases, modifications are required for high yield.

In this work, we investigated the synthetic route to the particular 2-arylbenzoxazole compounds shown in Scheme 1.



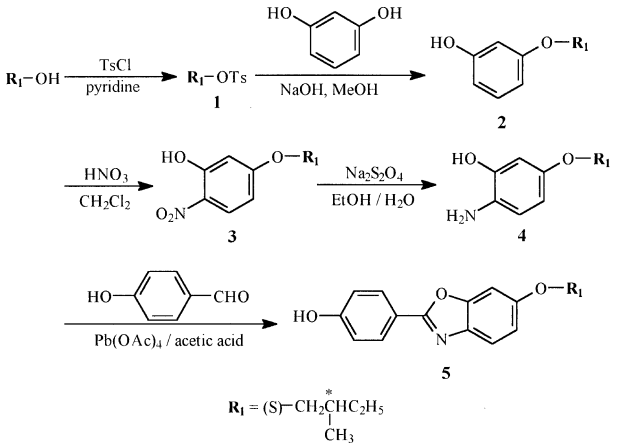
Scheme 1. Benzoxazole-based monomers and polymers synthesized in this work.

Results and Discussion

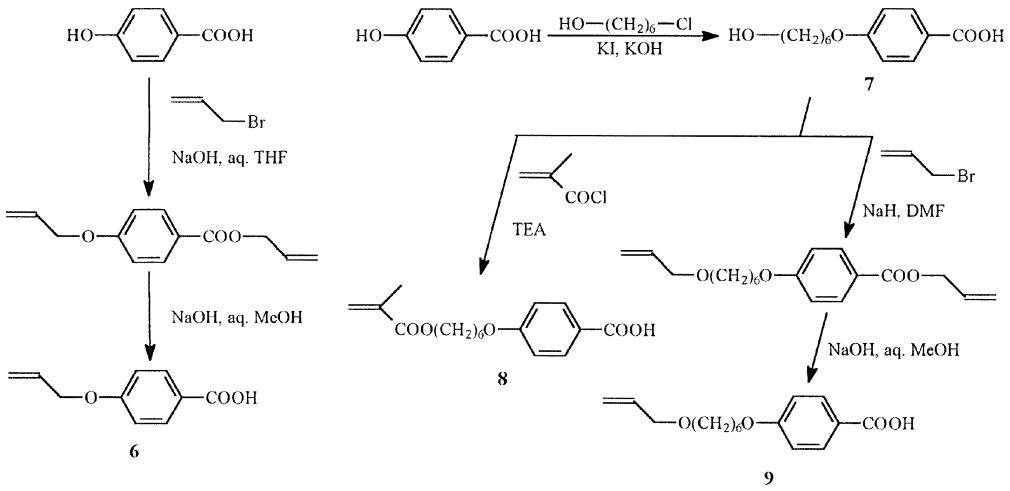
Synthetic routes to the compounds shown in Scheme 1 are depicted in Schemes 2-4, and the details of synthetic procedures are described in experimental part. All the compounds were fully identified by IR, ^{1}H NMR, mass spectroscopy, and elemental analysis. All of them exhibited high-efficiency blue photoluminescence in solution and liquid crystalline state (λ_{em}: 380-400 nm).

As shown in Scheme 2, phenol derivative with chiral tail (**2**) were prepared by S_N2 reaction of resorcinol with tosylated product of (S)-2-methylbutanol. Nitration of **2** gave 2-nitrated phenol (**3**) with 34% yield, together with 4-nitrated and 2,4-dinitrated by-products. Reduction of **3** using sodium dithionite, which is less expensive reducing agent than metal hydrides, gave **4** with 61% yield.

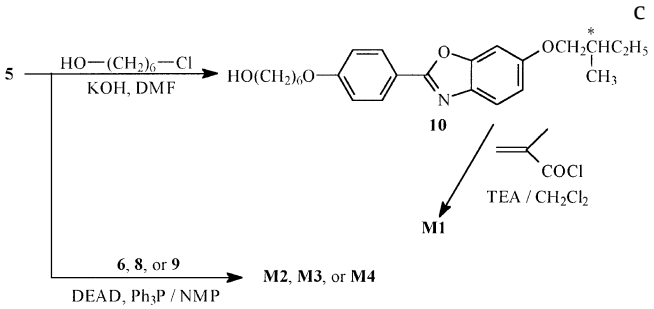
To obtain 2-phenylbenzoxazole (**5**), two methods were attempted: (1) preparation of phenolic Schiff's base, followed by its oxidative ring closure (general method); (2) direct cyclization under mild condition in the presence of lead(IV) acetate as oxidizing agent (modified method in this work). Schiff's base method failed because the imine linkage of Schiff's base from **4** and 4-hydroxybenzaldehyde is very unstable and the separation was very difficult, while direct



Scheme 2. Synthesis of 2-phenylbenzoxazole derivative (**5**) containing chiral tail.



Scheme 3. Syntheses of *p*-substituted benzoic acid derivatives.



Scheme 4. Syntheses of methacrylate and allyloxy monomers.

yclization of the two reactants successfully gave **5** with 55% yield without separate step of Schiff's base formation.

Benzoic acid derivatives were prepared as shown in Scheme 3, which are required for the synthesis of monomers (**M2**-**4**) as the counterparts against **5**. The syntheses of **7** and **8** were reported by Dubois *et al.*[12] Compounds **6** and **9** were prepared by the same method for 4'-allyloxybiphenyl-4-carboxylic acid, reported by Akiyama *et al.*[13]

All monomers were derived from hydroxy-substituted 2-phenylbenzoxazole (**5**), as shown in Scheme 4. Monomers (**M2**-**4**) with the extended mesogen, 4-benzoxazol-2-yl-phenyl ester, were obtained by the esterification between **5** and benzoic acid derivatives (**6**, **8**, and **9**). The esterifications were achieved in 53-74% yield by means of Mitsunobu reaction using diethyl azodicarboxylate (DEAD) and triphenylphosphine.

Free radical polymerizations of methacrylate monomers (**M1**, **M2**) were carried out using 2,2'-azobisisobutyronitrile (AIBN), affording polymethacrylates (**P1**, **P2**). The conversions were 54-58% and inherent viscosities were measured to be 0.11-0.12 dL/g. Polysiloxanes (**P3**, **P4**) were prepared through polymer reaction between poly(methylhydrosiloxane) (PMHS) and allyloxy monomers (**M3**, **M4**) in highly anhydrous condition with 55-60% conversions. IR and ^{1}H NMR spectra showed 100% substitution of monomers on Si-H units. In IR spectra of **P3** and **P4**, there was no Si-H absorption at 2160 cm^{-1}. The absence of Si-H peak at 4.7 ppm in ^{1}H NMR spectra also confirmed the full substitution.

Table 1. Phase transition temperature of monomers and polymers

compound	Phase transition temperature (°C)
	2nd heating
	cooling
M1	K ambient temperature I
P1	g 36 I
M2	I 29 g K 80 N* 86 I[a]
P2	g 44 Sm 135 N* 143 I
M3	I 141 N* 133 Sm 39 g K 110 N* 130 I
P3	I 128 N* 81 K g 36 N* 99 I
M4	I 95 N* 31 g IL 69 Sm 75 N* 90 I
P4	I 87 N* 70 Sm 30 IL g 6 Sm 133 I
	I 131 Sm 3 g

K: crystal, N*: cholesteric, I: isotropic, Sm: smectic phase, g: glassy, IL: isotropic liquid crystalline phase, a: exotherm due to polymerization appears just above clearing temperature.

Liquid crystallinity of monomers and polymers was observed by DSC and polarized optical microscopy, and the transition temperatures are summarized in Table 1. **M1** and **P1** with 2-phenylbenzoxazole mesogen did not show any mesomophic behavior above room temperature. According to Pavluchenko and coworkers,[1] 2-phenylbenzoxazole with short and long alkyl chain in both end points, exhibited monotropic nematic phase. In cases of **M1** and **P1**, however, introduction of bulky chiral group caused the broadening of molecular geometry and prevented liquid crystallinity.

The monomers and polymers (**M2**-**4**, **P2**-**4**) with extended mesogen, 4-benzoxazol-2-yl-phenyl ester, showed liquid crystalline phases such as cholesteric (N*) and smectic (Sm) phase. Especially, **M4** exhibited no texture between the crossed polarizers in the temperature range below smectic

phase, as if it were isotropic liquid (denoted by isotropic liquid crystalline in Table 1). To know the exact nature of this phase, X-ray diffractometry measurement is in progress.

In conclusion, direct cyclization between 2-aminophenol part and benzaldehyde counterpart in the presence of lead(IV) acetate, was successful to synthesize hydroxy-substituted 2-phenylbenzoxazole. From the obtained benzoxazole derivative (**5**), we synthesized benzoxazole-based fluorescent monomers and polymers, and confirmed their liquid crystallinity. The detailed characterization of liquid crystallinity will be reported elsewhere with the fluorescent properties including polarized emission.

Experimental Section

Thin layer chromatography (TLC) was carried out with TLC aluminium sheet (Merck, Silica gel 60 F_{254}). Elemental analysis data were obtained with LECO CHNS-932. Infrared spectra were measured on Bomem FT-IR spectrophotometer. ^{1}H NMR spectra were recorded on a Jeol JNM-LA300 (300 MHz) using $CDCl_3$ or acetone-d_6. Low resolution mass spectroscopic data were obtained using JMS AX505WA by EI (electron impact) mode. Inherent viscosities were measured using Ubbelohde viscometer at a concentration of 0.5 g/dL in NMP at 30 °C. Thermal analyses of mesomorphic transitions were performed on Perkin-Elmer DSC 7 at the heating or cooling rate of 5 °C/min using dry ice in isopropyl alcohol as a coolant. Microscopic observations were made with Nikon Optiphot 2-POL polarizing microscope equipped with a Mettler FP 80 heating stage at the heating or cooling rate of 5 °C/min.

Reagent grade reactants were obtained from chemical suppliers and used as received. Poly(methylhydrosiloxane) (M_W = 2270, DP = 36) was purchased from Aldrich Chem. Co., Methacryloyl chloride was distilled under reduced pressure prior to use. AIBN was recrystallized from methanol at room temperature. Solvents for all reactions were dried by the standard methods. Monomers **M3** and **M4** were prepared by the same method described for **M2**.

***p*-Toluenesulfonic acid (S)-2-methylbutyl ester (1)**. 20 g of (S)-2-methylbutanol (0.227 mol) was dissolved in 30 mL of pyridine, followed by dropwise addition of 43.3 g of *p*-toluenesulfonyl chloride (0.227 mol) dissolved in 130 mL of pyridine under magnetic stirring in ice bath. After stirring for additional 3 h at room temperature, the mixture was poured into excess of cold water and neutralized with hydrochloric acid, followed by extraction with diethyl ether. The extract was washed several times with water and dried with anhydrous magnesium sulfate. The removal of solvent by rotary evaporation afforded 54 g of crude **1** as a colorless oily liquid which was quite pure as judged by TLC and IR: 98% yield; IR (NaCl window, cm^{-1}) no OH absorption, 1359 (SO_2, asymmetric), 1190 (SO_2, symmetric).

3-[(S)-2-Methylbutoxy]-phenol (2). 47.3 g of resorcinol (0.43 mol) and 17 g of sodium hydroxide (0.43 mol) were dissolved in 200 mL of methanol. After reflux for 30 min, 52 g of **1** dissolved in 60 mL of methanol was added dropwise very slowly, followed by additional reflux for 4 h. The reaction mixture was cooled, poured into excess of water, and acidified with 2 N hydrochloric acid. After extraction with diethyl ether, the extract was washed with water and dried with anhydrous magnesium sulfate. Excess of diethyl ether was removed by rotary evaporation and the residue was purified by column chromatography on silica gel with methylene chloride/*n*-hexane (vol. ratio 1/3) as eluent to afford 25 g **2** as brown oily liquid: 65% yield; IR (NaCl window, cm^{-1}) 3370 (OH), 1287, 1146 (C-O); ^{1}H NMR ($CDCl_3$, ppm) 0.8-0.92 (m, 6H, aliphatic H's), 1.1-1.79 (m, 3H, aliphatic H's), 3.65 (ddd, J = 6.3, 9, 27 Hz, 2H, C_{Ar}-O-CH_2-), 5.58 (s, 1H, C_{Ar}-OH), 5.31-5.42 (m, 3H, aromatic H's), 6.99-7.05 (m, 1H, aromatic H).

5-[(S)-2-Methylbutoxy]-2-nitrophenol (3). 20 g of **2** (0.11 mol) was dissolved in 280 mL of dried methylene chloride and stirred in water bath. 5.6 mL of fuming nitric acid (about 0.12 mol) diluted in 100 mL of dried methylene chloride was added dropwise. After additional stirring for 30 min, excess of solvent was distilled off and the residue was purified by column chromatography on silica gel with methylene chloride/*n*-hexane (vol. ratio 1/3) as eluent to give 8.5 g of **3** as dark yellow oily liquid: 34% yield; IR (NaCl window, cm^{-1}) 3183 (OH), 1534 (NO_2, asymmetric), 1330 (NO_2, symmetric); ^{1}H NMR ($CDCl_3$, ppm) 0.93-1.03 (m, 6H, aliphatic H's), 1.24-1.9 (m, 3H, aliphatic H's), 3.85 (ddd, J = 6.2, 9.06, 24.9 Hz, 2H, C_{Ar}-O-CH_2-), 6.49-6.53 (m, 2H, aromatic H's), 8.01 (d, J = 10 Hz, 1H, aromatic H), 11.04 (s, 1H, C_{Ar}-OH); m/z (EI) calcd for $C_{11}H_{15}NO_4$, 225.10, found 225.

2-Amino-5-[(S)-2-methylbutoxy]-phenol (4). Detailed procedure is described in ref. 14: 61% yield; mp 90-95 °C; IR (KBr pellet, cm^{-1}) 3354, 3311 (NH_2), 3500-2200 (OH), no nitro peaks.

4-{6-[(S)-2-Methylbutoxy]-benzoxazol-2-yl}-phenol (5). 3.5 g of **4** (17.8 mmol) and 3 g of 4-hydroxybenzaldehyde (24.6 mmol) were suspended in 150 mL of glacial acetic acid. After stirring for 30 min at room temperature, 9 g of lead(IV) acetate was gradually added. And then, the mixture was gently boiled for 20 min, cooled immediately and poured into cold water. The precipitate was collected by filtration and purified by column chromatography on silica gel with ethyl acetate/*n*-hexane (vol. ratio 1/4) as eluent to afford 2.9 g **5** as a pink solid: 55% yield; mp 150 °C; IR (KBr pellet, cm^{-1}) 3450-2500 (OH); ^{1}H NMR ($CDCl_3$, ppm) 0.88-1.06 (m, 6H, aliphatic H's), 1.25-1.94 (m, 3H, aliphatic H's), 3.84 (ddd, J = 6.36, 8.75, 27 Hz, 2H, $C_{benzoxazole}$-O-CH_2-), 6.92-6.97 (m, phenyl 2H, benzoxazole 1H), 7.09 (d, J = 2.19 Hz, benzoxazole 1H), 7.58 (d, J = 8.58 Hz, benzoxazole 1H), 8.07 (d, J = 8.61 Hz, phenyl 2H); m/z (EI) calcd for $C_{18}H_{19}NO_3$, 297.14, found 297.

4-Allyloxybenzoic acid (6). Synthetic procedure is described in detail for 4'-allyloxybiphenyl-4-carboxylic acid in ref. 13: 66% yield; mp 153 °C; IR (KBr pellet, cm^{-1}) 3400-2400 (OH, carboxylic acid), 1676 (C=O), 1254 (C-O); ^{1}H NMR ($CDCl_3$, ppm) 4.55 (dt, J = 1.52, 5.27 Hz, 2H, C=C-CH_2-O-), 5.23-5.4 (m, 2H, CH_2=C-), 5.9-6.1 (m, 1H,

C=CH-), 6.89 (d, J = 8.98 Hz, 2H, aromatic H's), 7.99 (d, J = 8.98 Hz, 2H, aromatic H's); Elem. anal. calcd. for $C_{10}H_{10}O_3$: C 67.41, H 5.66. Found: C 68.66 H 6.49.

4-(6-Allyloxyhexyloxy)-benzoic acid (9). 1.7 g of sodium hydride (40 mmol, 60% dispersion in mineral oil) was added to the mixture of 4 g of **7** (16.8 mmol) and 5.1 g of allyl bromide (42 mmol) in 50 mL of DMF. The reaction mixture was stirred overnight at room temperature and neutralized with 2 N hydrochloric acid. Then it was poured into excess of brine and the precipitate was collected by filtration, affording crude allyl 4-(6-allyloxyhexyloxy)benzoate which was reasonably pure as judged by TLC. The solution of the crude product in 70 mL of methanol was poured into the mixture of 5 g of sodium hydroxide in 30 mL of water and refluxed for 1 h. Methanol was distilled off and the mixture was acidified with 2 N hydrochloric acid. After filtration, the precipitate was washed with water and purified by column chromatography on silica gel with ethyl acetate/*n*-hexane (vol. ratio 1/1) as eluent to give 3.28 g of **9** as a white solid: 70% yield; IR (KBr pellet, cm^{-1}) 2940 (CH, aromatic), 2863 (aliphatic), 1676 (C=O), 1258 (C-O); ^{1}H NMR ($CDCl_3$, ppm) 1.4-1.85 (m, 8H, aliphatic H's), 3.45 (t, J = 6.6 Hz, 2H, -O-CH_2-), 3.96-4.05 (m, 4H, C=C-CH_2-O-, C_{Ar}-O-CH_2-), 5.16-5.3 (m, 2H, CH_2=C-), 5.86-5.97 (m, 1H, C=CH-), 6.93 (d, J = 8.7 Hz, 2H, aromatic H's), 8.04 (d, J = 8.7 Hz, 2H, aromatic H's); Elem. anal. calcd. for $C_{16}H_{22}O_4$: C 69.04, H 7.97. Found: C 71.60 H 8.33.

6-(4-{6-[(S)-2-Methylbutoxy]-benzoxazol-2-yl}-phenoxy)-hexan-1-ol (10). 2 g of **5** (6.7 mmol) was dissolved in 50 mL of DMF and 1 g of crushed potassium hydroxide (17.9 mmol) was added to the mixture. After 1 h of stirring at room temperature, 4.6 g of 6-chlorohexan-1-ol (33.7 mmol) was added to the mixture and subsequently stirred at room temperature for one day. The mixture was poured into excess of brine and extracted with ethyl acetate. After removal of the excess ethyl acetate under reduced pressure, the residue was purified by column chromatography on sili-ca gel with ethyl acetate/*n*-hexane (vol. ratio 1/3) as eluent to afford 1.4 g of **10** as a pink solid: 53% yield; mp 59 °C; IR (KBr pellet, cm^{-1}) 3348 (OH); ^{1}H NMR ($CDCl_3$, ppm) 0.95-1.06 (m, 6H, aliphatic H's), 1.25-1.94 (m, 11H, aliphatic H's), 3.68 (t, J = 6.4 Hz, 2H, HO-CH_2-), 3.84 (ddd, J = 6.27, 9, 27 Hz, 2H, $C_{benzoxazole}$-O-CH_2-), 4.04 (t, J = 6.4 Hz, 2H, C_{phenyl}-O-CH_2-), 6.94 (dd, J = 2.2, 8.8 Hz, benzoxazole 1H), 7 (d, J = 8.97 Hz, phenyl 2H), 7.08 (d, J = 2.2 Hz, benzoxazole 1H), 7.59 (d, J = 8.8 Hz, benzoxazole 1H), 8.13 (d, J = 8.97 Hz, phenyl 2H); m/z (EI) calcd for $C_{24}H_{31}NO_4$, 397.23, found 397.

2-Methacrylic acid 6-(4-{6-[(S)-2-methylbutoxy]-benzoxazol-2-yl}-phenoxy)-hexyl ester (M1). 0.3 g of **10** (0.76 mmol) and 0.14 mL of triethylamine (1.52 mmol) were dissolved in 5 mL of dried methylene chloride. To this mixture, 0.16 g of methacryloyl chloride was added at 0 . After the additional stirring for 10 h, 20 mL of methylene chloride was added, and washed with excess of dilute sodium bicarbonate solution. The solvent was distilled off, then the residue was purified by column chromatography on silica gel with ethyl acetate/*n*-hexane (vol. ratio 1/3) as eluent to give 0.31 g of **M1** as a reddish brown solid: 88% yield; IR (KBr pellet, cm^{-1}) 1717 (C=O), 1169 (C-O); ^{1}H NMR ($CDCl_3$, ppm) 0.95-1.06 (m, 6H, aliphatic H's), 1.25-1.94 (m, 11H, aliphatic H's), 1.95 (s, 3H, C=C-CH_3), 3.84 (ddd, J = 6.27, 9, 27 Hz, 2H, $C_{benzoxazole}$-O-CH_2-), 4.04 (t, J = 6.4 Hz, 2H, C_{phenyl}-O-CH_2-), 4.17 (t, J = 6.5 Hz, 2H, -COO-CH_2-), 5.56 (s, 1H, CH_2=C), 6.11 (s, 1H, CH_2=C), 6.94 (dd, J = 2.2, 8.7 Hz, benzoxazole 1H), 7 (d, J = 8.79 Hz, phenyl 2H), 7.08 (d, J = 2.2 Hz, benzoxazole 1H), 7.59 (d, J = 8.7 Hz, benzoxazole 1H), 8.13 (d, J = 8.79 Hz, phenyl 2H); m/z (EI) calcd for $C_{28}H_{35}NO_5$, 465.25, found 465.

4-[6-(2-Methacryloyloxy)-hexyloxy]-benzoic acid 4-{6-[(S)-2-methylbutoxy]-benzoxazol-2-yl}-phenyl-ester (M2). 0.5 g of **5** (1.68 mmol), 0.62 g of **8** (2 mmol), and 0.6 g of triphenylphosphine (2.3 mmol) were dissolved in 12 mL of calcium hydride-dried 1-methyl-2-pyrrolidinone (NMP). Thereafter, 0.4 g of diethyl azodicarboxylate (DEAD, 2.3 mmol) diluted in 1 mL of NMP was added dropwise to the mixture at 0 °C, followed by additional stirring for 12 h. After the reaction, it was poured into excess of brine and the precipitate was collected, dried, and recrystallized from ethanol to give 0.6 g of **M2** as a pale pink needle: 61% yield; IR (KBr pellet, cm^{-1}) 1730 (C=O, benzoate), 1715 (C=O, methacrylate), 1267, 1167 (C-O); ^{1}H NMR ($CDCl_3$, ppm) 0.95-1.06 (m, 6H, aliphatic H's), 1.16-1.91 (m, 11H, aliphatic H's), 1.95 (s, 3H, C=C-CH_3), 3.78-3.92 (m, 2H, $C_{benzoxazole}$-O-CH_2-), 4.06 (t, J = 6.23 Hz, 2H, C_{phenyl}-O-CH_2-), 4.18 (t, J = 6.5 Hz, 2H, -COO-CH_2-), 5.56 (s, 1H, CH_2=C), 6.11 (s, 1H, CH_2=C), 6.96-7 (m, benzene 2H, benzoxazole 1H), 7.11 (d, J = 2.04 Hz, benzoxazole 1H), 7.38 (d, J = 8.43 Hz, phenyl 2H), 7.63 (d, J = 8.79 Hz, benzoxazole 1H), 8.16 (d, J = 8.61 Hz, benzene 2H), 8.27 (d, J = 8.43 Hz, phenyl 2H); m/z (EI) calcd for $C_{35}H_{39}NO_7$, 585.27, found 585.

4-Allyloxybenzoic acid 4-{6-[(S)-2-methylbutoxy]-benzoxazol-2-yl}-phenyl ester (M3). 74% yield; IR (KBr pellet, cm^{-1}) 1732 (C=O), 1260, 1200 (C-O); ^{1}H NMR (acetone-d_6, ppm) 0.94-1.06 (m, 6H, aliphatic H's), 1.26-1.93 (m, 3H, aliphatic H's), 3.92 (ddd, J = 6.23, 9.25, 26.18 Hz, 2H, $C_{benzoxazole}$-O-CH_2-), 4.72 (dd, J = 1.47, 3.66 Hz, 2H, C=C-CH_2-), 5.28-5.49 (m, 2H, CH_2=C-), 6.04-6.15 (m, 1H, C=CH-), 7.02 (dd, J = 2.3, 8.79 Hz, benzoxazole 1H), 7.14 (d, J = 8.97 Hz, benzene 2H), 7.29 (d, J = 2.3 Hz, benzoxazole 1H), 7.49 (d, J = 8.79 Hz, phenyl 2H), 7.62 (d, J = 8.79 Hz, benzoxazole 1H), 8.15 (d, J=8.97 Hz, benzene 2H), 8.27 (d, J = 8.79 Hz, phenyl 2H); m/z (EI) calcd for $C_{28}H_{27}NO_5$, 457.19, found 457.

4-[6-Allyloxy-hexyloxy]-benzoic acid 4-{6-[(S)-2-methylbutoxy]-benzoxazol-2-yl}-phenyl-ester (M4). The crude product was first recrystallized from ethanol and second from ethyl acetate/*n*-hexane (vol. ratio 1/2): 53% yield; IR (KBr pellet, cm^{-1}) 1721 (C=O), 1252 (C-O); ^{1}H NMR ($CDCl_3$, ppm) 0.95-1.07 (m, 6H, aliphatic H's), 1.26-2 (m, 11H, aliphatic H's), 3.46 (t, J = 6.5 Hz, 2H, -C-O-CH_2-), 3.78-3.91 (m, 2H, $C_{benzoxazole}$-O-CH_2-), 3.98 (d, J = 5.49 Hz,

2H, C=C-CH_2-), 4.06 (t, J = 6.5 Hz, 2H, C_{phenyl}-O-CH_2-), 5.17-5.31 (m, 2H, CH_2=C-), 5.88-5.98 (m, 1H, C=CH-), 6.95-7 (m, benzene 2H, benzoxazole 1H), 7.11 (d, J = 2.2 Hz, benzoxazole 1H), 7.37 (d, J = 8.79 Hz, phenyl 2H), 7.63 (d, J = 8.79 Hz, benzoxazole 1H), 8.16 (d, J = 8.97 Hz, benzene 2H), 8.27 (d, J = 8.79 Hz, phenyl 2H); m/z (EI) calcd for $C_{34}H_{39}NO_6$, 557.28, found 557.

Polymethacrylates P1, P2. The solution of 0.6 mmol of monomer (**M1** or **M2**) and 0.03 mmol of AIBN in 5.6 mL of sodium-dried THF was sealed in an ampule after several freeze-pump-thaw cycles under reduced pressure. Then the ampule was heated to 65 °C and kept for 24 h under stirring. After cooling, the solution was added very slowly into 200 mL of methanol and the precipitate was collected by filtering. It was purified by several reprecipitation from methylene chloride into methanol until the residual monomer was not detected in TLC: 54-58% conversion; ^{1}H NMR ($CDCl_3$, ppm) no vinyl proton peak of monomers at 5.56 and 6.11 ppm.

Polysiloxanes P3, P4. 0.44 mmol of monomer (**M3** or **M4**) and poly(methylhydrosiloxane) (PMHS) (0.4 mmol (Si-H)) were dissolved in 0.5 mL of sodium-dried toluene. A drop of 5% hexachloroplatinic acid (H_2PtCl_6) in isopropyl alcohol was added to the mixture, and it was heated to 110 °C under nitrogen atmosphere. Reaction was allowed to continue for 20 h. After cooling, the solvent was distilled off and the crude product was purified by reprecipitation from methylene chloride into cold methanol: 55-60% conversion.

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