Selected Papers

Synthesis and Chiral Recognition Ability of a Poly(phenylenevinylene)-Encapsulated Amylose Derivative

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Poly(*p*-phenylenevinylene) (PPV) was found to be encapsulated in amylose during the polymerization of the precursor monomer in an aqueous solution. The resulting amylose–PPV composite can be further chemically modified by introducing various substituents into the hydroxy groups of the amylose using isocyanates and acetic anhydride. Here we report on the chemical modification of the amylose–PPV composite with 3,5-dimethylphenyl isocyanate in order to obtain a novel chiral packing material for resolving enantiomers by high-performance liquid chromatography (HPLC). The obtained 3,5-dimethylphenylcarbamated amylose–PPV was soluble in pyridine and exhibited a lyotropic liquid crystalline phase in a concentrated pyridine solution. The chiral recognition ability of the 3,5-dimethylphenylcarbamated amylose–PPV was different from that of amylose tris(3,5-dimethylphenylcarbamate) having no PPV rods in the helical cavity of the amylose and can resolve many racemic compounds into enantiomers. Among racemic compounds, cyclic dibenzamide and dibenzanilide derivatives were resolved on the 3,5-dimethylphenylcarbamated amylose–PPV better than amylose tris(3,5-dimethylphenylcarbamate). The difference in the enantioseparation abilities of these amylose-based chiral stationary phases for HPLC is discussed based on the difference in their helical structures.

A pair of enantiomers of chiral drugs often exhibits different biological and physiological activities in a living system. Therefore, direct chromatographic enantioseparation, particularly by high-performance liquid chromatography (HPLC), has become the most popular and practically useful method not only for the analysis of enantiomer compositions but also obtaining pure enantiomers in large quantity, and chiral HPLC is now recognized as the essential technology for research and development of chiral drugs in the pharmaceutical industry.[1] The design and development of a chiral stationary phase (CSP) capable of effective chiral recognition for a broad range of enantiomers is of key importance for chromatographic enantioseparation, and therefore a number of CSPs have been developed.[2] Among more than a hundred commercially available CSPs, the most widely used CSPs are the derivatives of polysaccharides,[2l–2q] such as cellulose and amylose. In particular, the 3,5-dimethylphenylcarbamates of cellulose and amylose show an extremely high chiral recognition ability for many racemates[1i,2q] and are commercialized.

On the other hand, native polysaccharides, such as amylose,[3] schizophyllan,[4] and curdlan,[5] adopt a one-handed helical structure and possess a one-dimensional chiral hydrophobic cavity inside their helical structures, in which a variety of guest molecules can be encapsulated as a result of hydrophobic interactions, thus forming unique inclusion complexes. We recently found that poly(*p*-phenylenevinylene) (PPV), a typical π-conjugated polymer used as the emissive layer in light-emitting diodes[6] could be encapsulated in amylose during the polymerization of the precursor monomer in an aqueous media.[7] Although PPV is totally insoluble in solvents, the resulting amylose–PPV (APPV) composite was soluble in dimethyl sulfoxide (DMSO) and formed a lyotropic liquid crystalline (LC) phase in a concentrated DMSO solution.[7]

Amylose has reactive hydroxy groups and further modification of the exterior APPV by introducing various substituents into the hydroxy groups through macromolecular reaction is possible while maintaining its rotaxane-like structure.[8] In this study, we performed the chemical modification of APPV using 3,5-dimethylphenyl isocyanate and evaluated its chiral recognition ability as a CSP for HPLC. The resolving ability of the 3,5-dimethylphenylcarbamated APPV was compared with that of amylose tris(3,5-dimethylphenylcarbamate) (ADMPC) having no PPV rods in the helical cavity of the amylose and the effect of the different helical structures on their chiral recognition abilities was discussed.

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Experimental

Instruments. The NMR spectra were measured using a Varian VXR-500S spectrometer (Varian, Palo Alto, CA) operating at 500 MHz for ^{1}H using TMS as the internal standard. The IR spectra were recorded using a JASCO FT/IR-680 spectrometer (JASCO, Hachioji, Japan). The absorption and photoluminescence spectra were measured in a 1.0-cm quartz cell on a JASCO V-570 spectrophotometer and a JASCO FP 6500 spectrofluorometer, respectively. The polarizing optical microscopic observations were carried out with an E600POL polarizing optical microscope (Nikon, Tokyo, Japan) equipped with a DS-5 M CCD camera (Nikon) connected to a DS-L1 control unit (Nikon). The thermogravimetric (TG) analyses were conducted on a SEIKO EXSTAR6000 TG/DTA 6200 (Seiko Instruments Inc., Chiba, Japan) under a heating rate of 10 °C min^{-1} in a nitrogen flow of 200 mL min^{-1}. Elemental analyses were performed by the Nagoya University Analytical Laboratory in School of Bioagricultural Sciences.

The chromatographic separations of enantiomers were performed using a JASCO PU-2080 Plus liquid chromatograph equipped with Multi UV–vis (JASCO MD-2010 Plus) and polarimetric (JASCO OR-2090 Plus, Hg–Xe without filter) detectors at room temperature. A solution of a racemate was injected into the chromatographic system using a Rheodyne Model 7725i injector (20 μL loop).

Materials. Anhydrous *N*,*N*-dimethylacetamide (DMA) and pyridine (water content <0.005%) were purchased from Wako (Osaka, Japan) and stored under nitrogen. 3,5-Dimethylphenyl isocyanate was obtained from Tokyo Kasei (TCI, Tokyo, Japan) and LiCl was from Kishida (Osaka, Japan). The solvents used in the chromatographic experiments were of HPLC grade. Amylose (DP = ca. 300) was kindly supplied by Daicel Chemical Industries (Tokyo, Japan). The racemates[9] were commercially available or were prepared by the usual methods. Porous spherical (3-aminopropyl)triethoxysilanized silica gel (Daiso gel SP-1000-7-APSL, A-silica) with a mean particle size of 7 μm and a mean pore diameter of 100 nm was kindly supplied from Daiso Chemical (Tokyo, Japan).

Synthetic Procedure for Modified APPV with 3,5-Dimethylphenyl Isocyanate (APPV–PC). Amylose–PPV composite (APPV) (200 mg, 1.15 mmol), which had been prepared according to the previously reported method,[7] was dispersed in DMA–pyridine (8/5, v/v, 10.4 mL) containing LiCl (106 mg, 2.49 mmol) at 80 °C under nitrogen, and 3,5-dimethylphenyl isocyanate (0.80 mL, 8.5 mmol) was then added dropwise to the mixture. After being stirred at 80 °C for 18 h, the reaction mixture was cooled to room temperature and then poured into a large amount of methanol and the resulting yellow precipitate was collected by centrifugation, washed with methanol, and dried in vacuo at room temperature overnight to give APPV–PC in 86% yield (607 mg).

IR (KBr, cm^{-1}): 3323 (ν_{N-H}), 1720 ($\nu_{C=O}$). ^{1}H NMR (500 MHz, pyridine-d_5, 70 °C): δ 1.99 (s, 6H, CH_3), 2.05 (s, 6H, CH_3), 2.36 (s, 6H, CH_3), 4.23–5.02, 5.63, 5.88 (br, 7H, glucose protons), 6.46–7.72 (br, 9H, aromatic), 9.37 (br, 1H, NH), 9.71 (br, 2H, NH). Found: C, 66.27; H, 6.25; N, 7.08%. Calcd for $(C_6H_7O_5)_{9.00}(C_8H_6)_{0.99}(C_{12}H_{15}ClS)_{0.01}(C_9H_{10}NO)_{27}$: C, 66.18; H, 6.17; N, 6.83%.

Polarized Microscopy Studies. A small amount of APPV–PC (ca. 2 mg) was placed on a slide glass plate and then a small amount of pyridine (ca. 5 μL) was dropped close to the composite. A cover glass was placed on the sample and the specimen was subjected to polarized optical microscopy observations with a Nikon E600POL polarized microscope. A clear birefringent texture was observed at the interface between the isotropic solution and solid states.

Preparation of Chiral Columns. A typical experimental procedure is described below. The APPV–PC dissolved in pyridine was coated on the A-silica according to the previously reported method.[10] The solvent was then evaporated under reduced pressure. The weight ratio of the APPV–PC to silica gel was ca. 20:80. After fractionating the packing materials with sieves, the obtained column packing material was packed into a stainless-steel tube (25 cm × 0.20 cm (i.d.)) by conventional high-pressure slurry packing using a Chemco Slurry-Packing Apparatus Model 124A (Chemco, Osaka, Japan).[11] The plate number of the column was 2200 for benzene with hexane–2-propanol (90:10, v/v) as the eluent at a flow rate of 0.1 mL min^{-1}. The dead time (t_0) was estimated using 1,3,5-tri-*tert*-butylbenzene as the nonretained compound.[12]

Molecular Modeling of APPV–PC. The molecular modeling and molecular mechanics (MM) calculations were conducted with the Compass force field,[13] as implemented in the MS Modeling software (version 4.4, Accelrys, San Diego, CA) operated using a PC running under Windows XP. The initial left-handed 8_1-helical structure of 3,5-dimethylphenylcarbamated amylose including a PPV molecule (APPV–PC) (40 repeating monomer unit) was constructed using the Polymer Builder module in the MS Modeling software. First, a repeating unit of 3,5-dimethylphenylcarbamated amylose was taken from the reported 4_3-helical structure of ADMPC[14] and was allowed to construct 40-mer with a left-handed 8_1-helical structure. We also constructed a 14-mer of PPV using the Polymer Builder module. The dielectric constant was set to 1.0. The geometry optimizations were carried out without any cutoff by the smart minimizer. First, the starting PPV conformation was subject to the steepest decent optimization to eliminate the worst steric conflicts. Second, subsequent optimization until the convergence using a conjugate gradient algorithm was performed. The fully optimized PPV was obtained by further energy minimization using the Newton method with the 0.1 kcal/mol/Å convergence criterion. The resulting PPV 14-mer was then manually inserted into the cavity of the left-handed 8_1-helical 3,5-dimethylphenylcarbamated amylose (40-mer) so as to form a 3,5-dimethylphenylcarbamated amylose–PPV inclusion complex (APPV–PC). The APPV–PC was then energy minimized as follows. First, the APPV–PC was energy minimized by the steepest descent and conjugated gradient methods and finally the Newton method with the 0.1 kcal/mol/Å convergence criterion, while the geometric parameters for the PPV and amylose backbone of the APPV–PC were fixed. The PPV chain was then energy minimized by the same method, while the geometries of the exterior 3,5-dimethylphenylcarbamoyl residues of the APPV–PC were fixed. The obtained structure was further energy minimized by the same method without fixing geometric parameters, giving the fully optimized structure of APPV–PC.

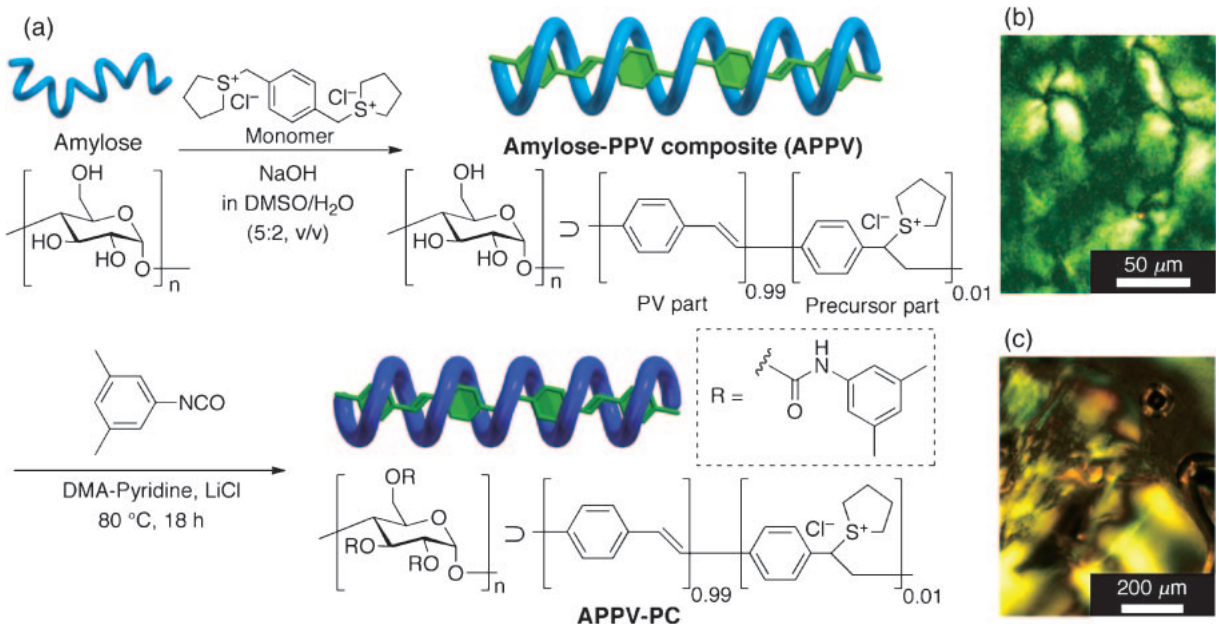

Figure 1. (a) Schematic illustration of the synthesis of amylose–PPV composite (APPV) and its derivative modified with 3,5-dimethylphenyl isocyanate (APPV–PC). The core PPV polymer contains approximately 1 mol % of the precursor units.[7] (b, c) Polarized optical micrographs of a nematic LC phase of APPV in a concentrated DMSO solution (b) and a lyotropic LC phase of APPV–PC in a concentrated pyridine solution (c) taken at ambient temperature (ca. 25 °C).

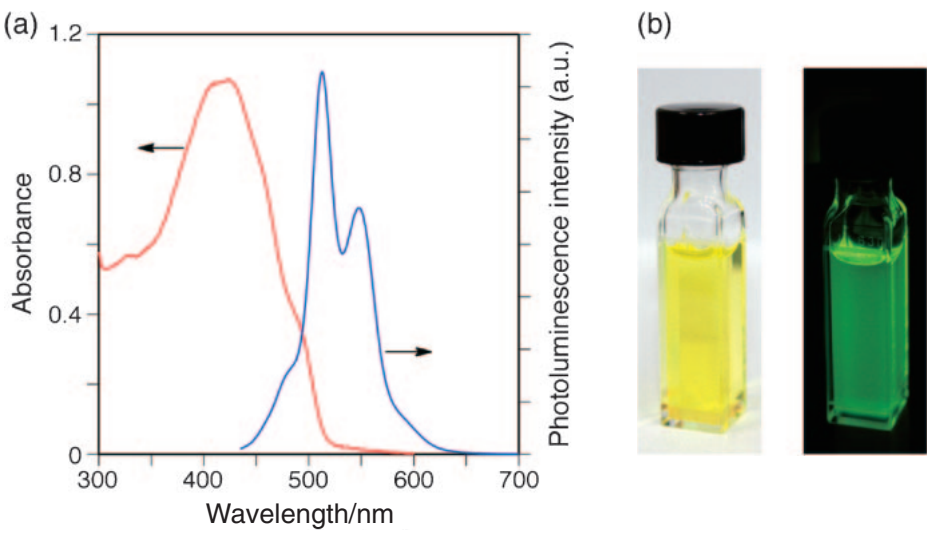

Figure 2. (a) Absorption (red line) and photoluminescence (blue line) (excitation wavelength = 425 nm) spectra of APPV–PC in pyridine. (b) Photographs of APPV–PC in pyridine under white (left) and UV light at 365 nm (right).

Results and Discussion

The APPV was prepared according the previously reported method[7] and was allowed to react with an excess amount of 3,5-dimethylphenyl isocyanate in a mixture of DMA and pyridine containing LiCl at 80 °C as outlined in Figure 1a.[8] The obtained 3,5-dimethylphenylcarbamated APPV (APPV–PC) was soluble in pyridine and mostly soluble in DMSO and $CHCl_3$. ^{1}H NMR spectra and elemental analysis showed that the hydroxy groups of the exterior amylose were almost quantitatively converted into the phenylcarbamate moieties. APPV–PC showed a green luminescence under UV light at 365 nm. The absorption and photoluminescence spectra of APPV–PC in pyridine were similar in pattern to those of the original APPV (Figure 2), indicating that the PPV was encapsulated in the amylose helical cavity and the APPV retains its rotaxane-like inclusion structure even after the exterior amylose hydroxy groups were converted to the 3,5-dimethylphenylcarbamates.

Amylose is a flexible polymer and shows no LC phase. However, once the rigid-rod PPV is threaded into the amylose tube, the resulting rotaxane-like APPV becomes a rod-like structure to form a lyotropic nematic LC phase in a concentrated DMSO solution, as supported by its clear Schlieren texture (Figure 1b). After chemical modification, the APPV–PC maintained its rod-like feature and showed a

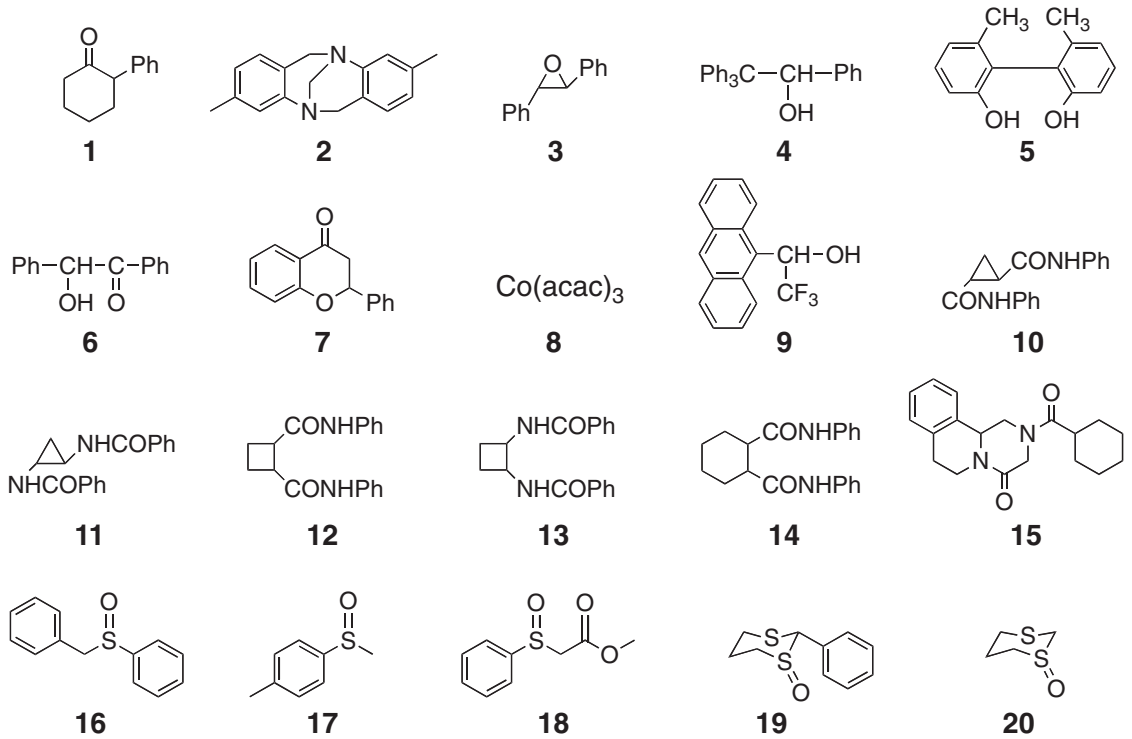

Figure 3. Structures of racemates **1**–**20**.

similar lyotropic LC phase in a concentrated pyridine solution (Figure 1c) as previously prepared APPV derivatives modified with an alkyl isocyanate and acetic anhydride.[8]

The APPV–PC was then coated on (3-aminopropyl)triethoxy silanized silica gel (particle size 7 μm, pore size 100 nm) to be used as a chiral packing material. The packing material thus obtained was packed into a stainless-steel column (25 cm × 0.20 cm (i.d.)) by conventional high-pressure slurry packing[11] and its chiral recognition ability was evaluated with 20 racemates shown in Figure 3.

The results of the chromatographic resolutions of a variety of racemic compounds **1**–**20** are summarized in Table 1 and Figure 4. For comparison, the resolution results on a commercially available amylose-based chiral column, Chiralpak AD, which consists of amylose tris(3,5-dimethylphenylcarbamate) (ADMPC) are also shown.[9] Chiralpak AD is one of the most frequently used CSPs. These amylose-based CSPs generally showed a similar trend in the enantioseparation, but significant differences were observed in the resolution of some racemates. Figure 5a shows a chromatogram of the resolution of the racemic *trans*-cyclopropanedicarboxanilide (**10**) on a column packed with the APPV–PC using hexane–2-propanol (90:10, v/v) as the eluent. The peaks were detected with a UV detector and identified with a polarimetric detector. The enantiomers were eluted at retention times of t_1 and t_2 showing complete separation. The capacity factors, k_1' $[=(t_1 - t_0)/t_0]$ and k_2' $[=(t_2 - t_0)/t_0]$, were 2.08 and 6.59, respectively. The separation factor, α $[=k_2'/k_1']$ and the resolution factor R_S $[=2(t_2 - t_1)/(w_1 + w_2)]$, were estimated to be 3.17 and 6.23, respectively. The racemate **10** was also resolved on ADMPC under the same eluent system (Figure 5b), but the enantioselectivity ($\alpha = 3.17$) of APPV–PC for **10** was much

Table 1. Chromatographic Resolution of Racemates **1**–**20** on APPV–PC and ADMPC (Chiralpak AD)

Racemates	APPV–PC[a]			ADMPC[b]		
	k_1'	α	R_s	k_1'	α	R_s
1	0.44	ca. 1 (−)	—	0.61	ca. 1 (−)	—
2	0.38	1.49 (+)	1.14	0.53	1.58 (+)	2.30
3	0.30	2.69 (+)	3.36	0.42	3.04 (+)	6.67
4	1.59	2.05 (+)	5.07	2.65	1.98 (+)	5.48
5	3.45	1.50 (−)	3.32	2.46	2.11 (−)	6.38
6	2.13	1.15 (−)	1.07	3.14	1.21 (−)	2.07
7	0.68	ca. 1	—	0.93	1.12 (+)	0.77
8	0.22	ca. 1 (−)	—	0.25	ca. 1 (−)	—
9	1.03	ca. 1	—	1.30	1.15 (+)	0.75
10	2.08	3.17 (+)	6.23	3.25	2.01 (+)	3.59
11	1.18	1.44 (−)	1.88	1.36	1.08 (+)	0.12
12	1.24	1.41 (−)	1.23	1.46	2.01 (−)	3.21
13	1.03	3.28 (−)	3.42	1.65	1.59 (−)	1.96
14	0.53	1.40 (−)	1.23	0.78	1.63 (−)	1.96
15	3.86	1.25 (+)	1.24	7.17	1.18 (+)	0.82
16	1.42	ca. 1 (+)	—	2.94	ca. 1 (+)	—
17	1.17	1.17 (+)	0.20	2.04	ca. 1 (+)	—
18	2.48	ca. 1 (+)	—	4.50	ca. 1 (+)	—
19	2.59	2.06 (+)	4.50	4.56	1.90 (+)	3.45
20	1.75	1.34 (−)	2.18	5.68	1.61 (−)	2.67

a) Conditions: column, 25 cm × 0.20 cm (i.d.); eluent, hexane–2-propanol (90:10, v/v); flow rate, 0.1 mL min^{-1}. The signs in parentheses represent the optical rotation of the first-eluted enantiomers. b) Conditions: column, 25 cm × 0.46 cm (i.d.); eluent, hexane–2-propanol (90:10, v/v); flow rate, 0.5 mL min^{-1}. Data of **1**–**10** on ADMPC were taken from Ref. 9.

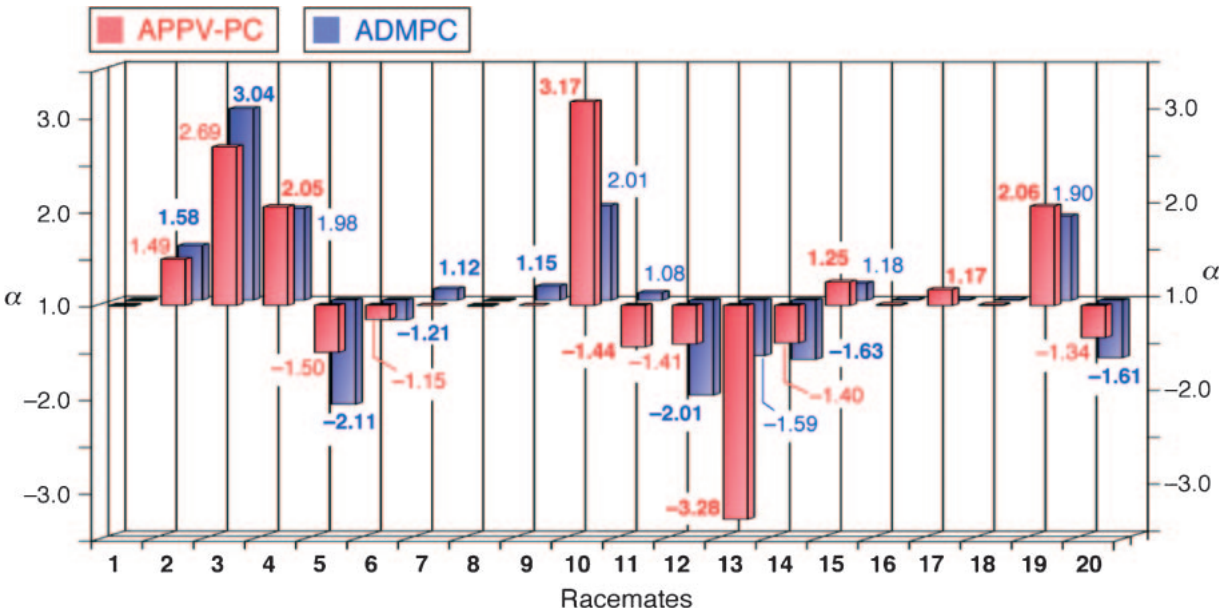

Figure 4. Histograms of the separation factors (α) on APPV–PC (red bars) and ADMPC (blue bars). For chromatographic conditions, see Table 1.

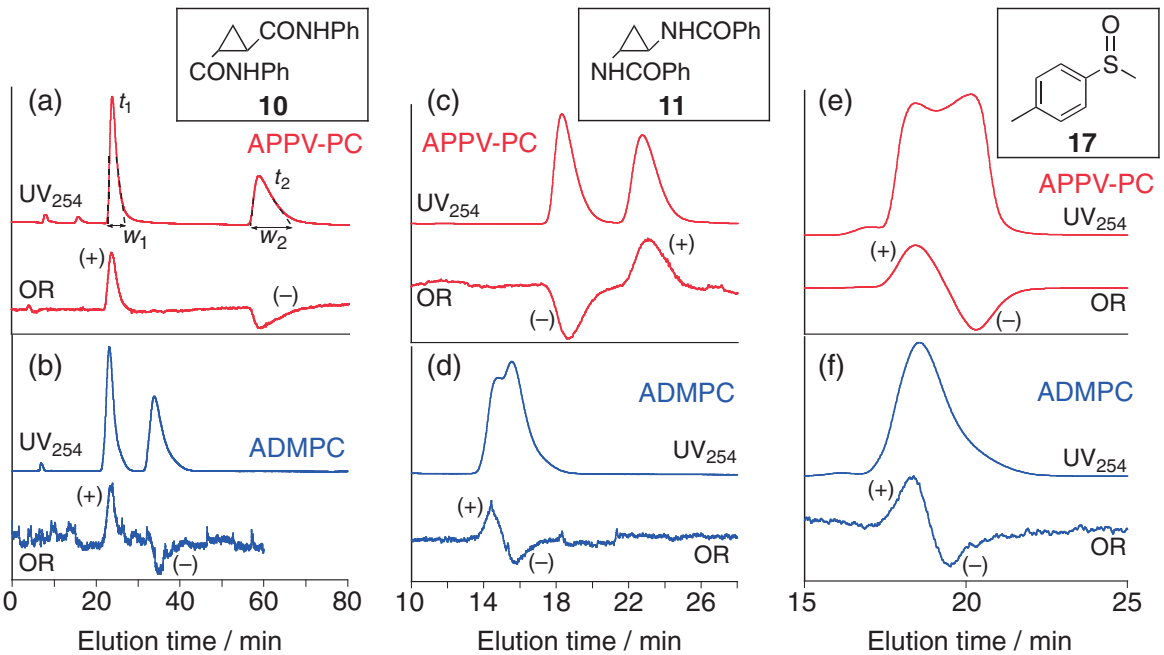

Figure 5. Chromatograms for the resolution of **10** (a and b), **11** (c and d), and **17** (e and f) on APPV–PC (column = 25 cm × 0.20 cm (i.d.), flow rate = 0.1 mL min^{-1}, red lines) and ADMPC (column = 25 cm × 0.46 cm (i.d.), flow rate = 0.5 mL min^{-1}, blue lines), respectively.

greater than that of ADMPC ($\alpha = 2.01$). Similar results were obtained in the separation of cyclic dibenzamide racemates **11** and **13**. The optical resolving ability of APPV–PC for **11** and **13** ($\alpha = 1.44$ and 3.28, respectively) was higher than that of ADMPC ($\alpha = 1.08$ and 1.59, respectively). Interestingly, the racemate **11** was partially separated on the ADMPC with the elution order of enantiomers such that the (+)-isomer eluted first followed by the (−)-isomer, while the reversed elution order was observed on the APPV–PC (Figures 5c and 5d). Moreover, the APPV–PC exhibits better resolution for some sulfoxide compounds than the ADMPC. For example, the APPV–PC resolved methyl *p*-tolyl sulfoxide (**17**), which was hardly separated on the ADMPC (Figures 5e and 5f). These results suggest that ADMPC and APPV–PC may possess a different helical structure, although the exterior amylose hydroxy groups were completely modified to convert to the identical 3,5-dimethylphenylcarbamates.

The native amylose is known to adopt a left-handed helix with a ca. 0.8 nm pitch of six glucose units per turn (6_1 helix) and possesses a chiral hydrophobic cavity with a ca. 0.5 nm

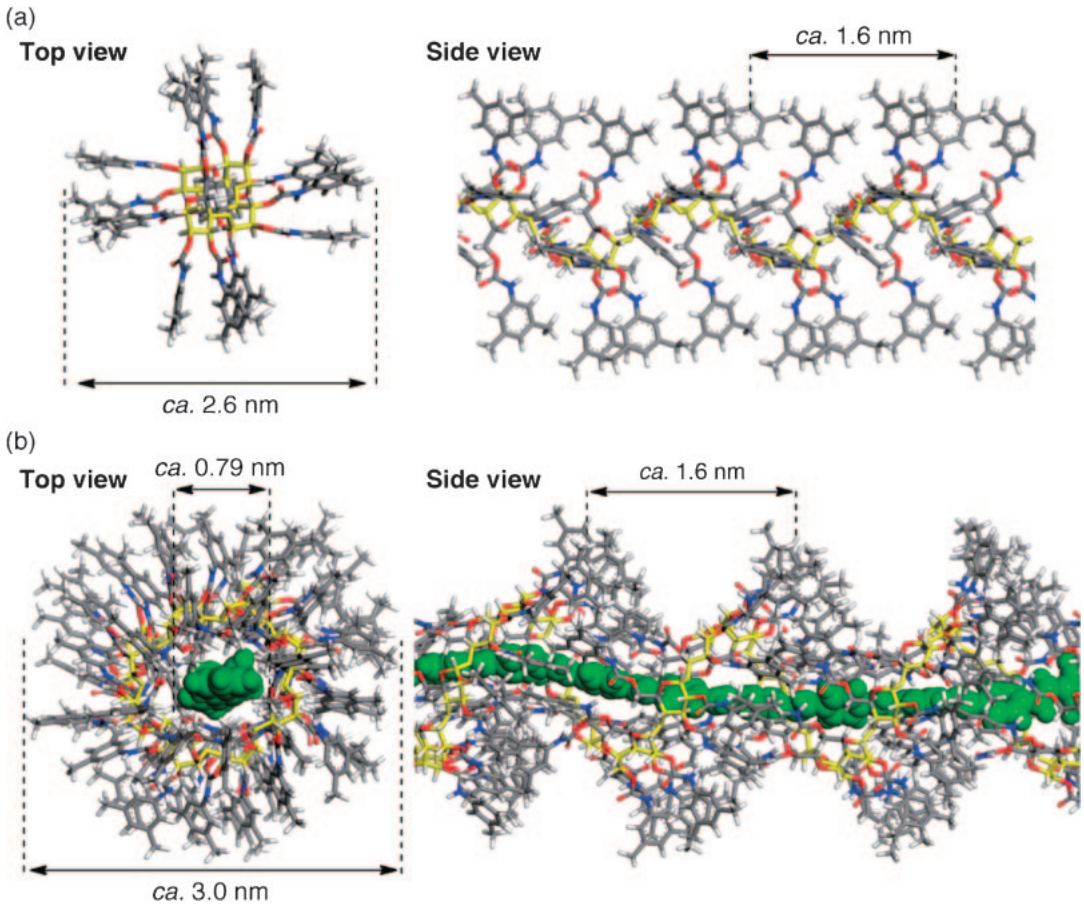

Figure 6. Possible structures of ADMPC (a) and APPV–PC (b). The structures are shown using the cylinder model. The PPV (green) is shown using the space-filling model for clarity. The carbon atoms of amylose are shown in yellow colors. The structure of ADMPC was taken from Ref. 14.

diameter,[15] while the exterior amylose of the APPV probably adopts an 8_1-helical structure (eight glucose units per turn) with an internal diameter of a ca. 0.8 nm to accommodate a PPV molecule. Recently, Okamoto et al. reported that the most plausible helical structure of ADMPC was a left-handed 4_3 helix on the basis of 2D NMR measurement of ADMPC in solution combined with computer modeling (Figure 6a).[14] This model suggests that there is no cavity inside the ADMPC helix, but a chiral helical groove with polar carbamate groups exists along the main chain. Although the APPV–PC and ADMPC are composed of the same amylose skeleton, their helical structures appear to be different from each other, since the APPV–PC accommodated a rod-like PPV molecule in the interior helical cavity, which would likely give rise to a conformational change of the main-chain helix as well as the arrangement of exterior phenylcarbamate residues of the APPV–PC. The observed difference in their chiral recognition abilities as CSPs including the reversed elution order for the enantiomers **11** may be ascribed to the difference in their higher-ordered helical structures of the amylose helices. Figure 6b shows a possible structure of APPV–PC obtained by molecular mechanics calculations. The calculated structure revealed that the external diameter of APPV–PC (ca. 3.0 nm) is slightly larger than that of ADMPC (ca. 2.6 nm), the helical pitch of APPV–PC and ADMPC is almost the same value (ca. 1.6 nm), and the pendant phenylcarbamate residues of APPV–PC are packed more closely to each other. The polar carbamate groups in ADMPC and APPV–PC are preferably located inside, and the hydrophobic aromatic groups are placed outside the polymer main-chains so that polar enantiomers can preferentially interact with the carbamate residues in the groove through hydrogen bond formation, which may be one of the major driving forces for their efficient recognition of enantiomers. However, we have no concrete evidence for the exact structure of the APPV–PC. A further detailed structural analysis including X-ray diffraction and 2D NMR measurements should be necessary and work along this line is now in progress.

Conclusion

In this study, we prepared a novel chiral packing material composed of a rod-like PPV-encapsulated amylose tris(3,5-dimethylphenylcarbamate) (APPV–PC) through macromolecular reaction. The liquid crystalline luminescent amylose-based helical polymer exhibited remarkable chiral recognition ability for many racemates as a chiral stationary phase for HPLC whose resolving capability was comparable to that of a commercially available amylose-based CSP (ADMPC). The APPV–PC retains its inclusion structure after chemical modification of the hydroxy groups of the exterior amylose, and therefore, its helical structure may be changed from that of

ADMPC, amylose tris(3,5-dimethylphenylcarbamate), which results in different chiral recognition abilities for several racemates. The APPV–PC specifically resolved cyclic dibenzamide and dibenzanilide racemates more efficiently than ADMPC. These findings will be useful for developing novel amylose-based CSPs with much higher resolving ability for specific enantiomers.

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