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Tuning of Fluorescence by Controlling the Secondary Structure of Amino Acid-Based Poly(*N*-propargylamides) Having Pendant Pyrene Groups

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ABSTRACT: Copolymerizations of 1-pyrenebutyric acid *N*-propargylamide (PY) with chiral amino acid-based *N*-propargylamides, *N*-(*tert*-butoxycarbonyl)-L-valine-*N*-propargylamide (LV) and *N*-(*tert*-butoxycarbonyl)-D-alanine-*N*-propargylamide (DA) were conducted with (nbd)$Rh^+[\eta^6\text{-}C_6H_5B^-(C_6H_5)_3]$ as a catalyst to obtain novel pyrene-functionalized helical poly(*N*-propargylamides). The controllable secondary structure of the copolymers by various compositions of the chiral amino acid units or solvent environment led to a controlled orientation of the side-chain pyrene. For instance, poly(PY_{30}-*co*-LV_{70}) exhibited a large specific rotation and a CD signal, while it emitted very weak fluorescence. On the other hand, poly(PY_{30}-*co*-LV_{35}-*co*-DA_{35}) exhibited a small specific rotation and a CD signal, while it emitted fluorescence eight times larger than poly(PY_{30}-*co*-LV_{70}) did. The CD signal disappeared by the addition of MeOH to a THF solution of poly(PY_{30}-*co*-LV_{70}), while the fluorescence intensity increased.

Introduction

In recent years, considerable effort is devoted to chromophore-functionalized polymer systems, because chromophores linked to polymers show different behavior from free ones and show unique photophysical as well as photochemical properties.[1] The polymer structures much influence the performance of chromophores, when the chromophores are regularly arranged along the polymer chain. In particular, in the case of helical polymers, they can efficiently transport excitation energy and charge one-dimensionally along the polymer backbone, and thus they can be regarded as potential molecular wires, which are applicable to microprocessors and other devices.[2] For this purpose, most studies have focused on polypeptides as candidates because they can form secondary structures such as α-helices and β-sheets, where the side chains are arranged at regular intervals along the main chains.[3]

Meanwhile, amino acid- and peptide-based synthetic polymers exhibit biocompatibility, biodegradability, and unique optical properties.[4] We have recently reported that amino acid-based poly(*N*-propargylamides) form a helix stabilized by intramolecular hydrogen bonding between the amide groups,[5] and the helical structure can be controlled by competition between structurally different chiral amino acids.[6] In the present study, we report a new helical array of pyrene chromophores on helical poly(*N*-propargylamides) derived from chiral amino acids (Scheme 1). We anticipate that the structurally different chiral amino acids at the pendent compete each other and the chiral information is transmitted to the polymer backbone, leading to controlled helical array of pyrene by varying the composition of the chiral units or changing solvent environment. It is also expected that the change of the secondary structure of the copolymers affects the formation of excimers at the side chain chromophores and thus influences the fluorescence properties.

Experimental Section

Measurements. ^1H and ^{13}C NMR spectra were recorded in chloroform-*d* ($CDCl_3$) on a JEOL EX-400 spectrometer. IR spectra were measured on a Shimadzu FTIR-8100 spectrophotometer. Elemental analysis was carried out at the Kyoto University Elemental Analysis Center. The number- and weight-average molecular weights (M_n and M_w) of polymers were determined by gel permeation chromatography (GPC) on a Jasco Gulliver system (PU-980, CO-965, RI-930, and UV-1570) equipped with polystyrene gel columns (Shodex columns K804, K805, and J806), using THF as an eluent at a flow rate of 1.0 mL/min, calibrated by polystyrene standards at 40 °C. Melting points (mp) were measured on a Yanaco micro melting point apparatus. Specific rotations ($[\alpha]_D$) were measured on a Jasco DIP-1000 digital polarimeter with a sodium lamp as a light source. CD and UV spectra were recorded in a quartz cell (thickness: 1 cm) using a Jasco J-820 spectropolarimeter. Fluorescence measurements were carried out at room temperature using Jasco FP-750 sepctrofluorometer.

Materials. THF was distilled over CaH_2 prior to use. 4-[4,6-Dimethoxy-1,3,5-triazine-2-yl]-4-methylmorpholinium chloride (TRIAZIMOCH) was supplied by Tokuyama Co. (nbd)$Rh^+[\eta^6\text{-}C_6H_5B^-(C_6H_5)_3]$ was prepared as reported.[7] *N*-(*tert*-Butoxycarbonyl)-L-valine-*N*-propargylamide (LV) and *N*-(*tert*-butoxycarbonyl)-D-alanine-*N*-propargylamide (DA) were synthesized according to our previous methods.[6] All other regents were used as received without purification.

Monomer Synthesis. 1-Pyrenebutyric Acid *N*-Propargylamide (PY). 1-Pyrenebutyric acid (2.02 g, 7 mmol) and propargylamine (0.56 g, 10 mmol) were dissolved in AcOEt (100 mL), and the resulting solution was stirred at room temperature for 10 min. TRIAZIMOCH (2.6 g, 10 mmol) was added to the solution, and the resulting mixture was stirred at room temperature overnight. The mixture was subsequently washed with 1 N HCl, saturated $NaHCO_3$(aq), and saturated NaCl(aq), and then dried over anhydrous $MgSO_4$ and concentrated by rotary evaporation. The residue was purified by recrystallization from *n*-hexane and AcOEt to obtain solid PY in 61% yield. Mp: 157 °C.^1H NMR (400 MHz, $CDCl_3$): δ 2.23 (s, 1H, C≡C*H*), 2.32 (m, 2H, CH_2CH_2CO), 2.45 (m, 2H, CH_2CH_2CO), 3.58 (m, 2H, CH_2 attached to pyrenyl), 4.23 (m,

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Scheme 1

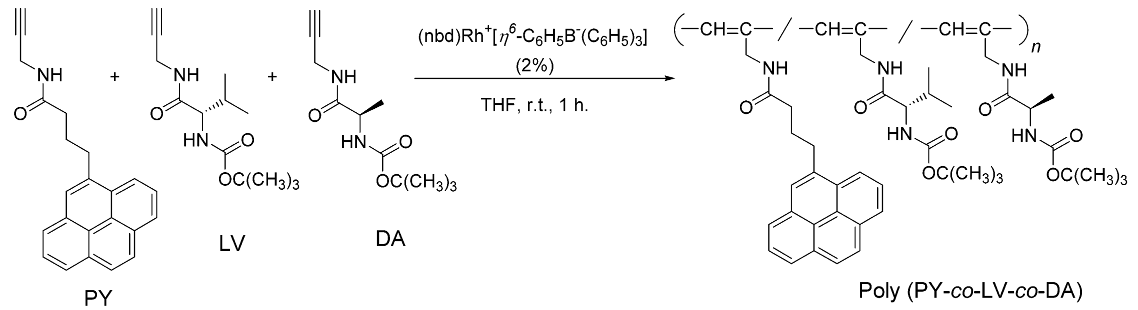

Table 1. Copolymerization of PY, LV, and DA[a]

run	PY:LV:DA	yield[b] (%)	M_n[c]	M_w/M_n[c]	$[\alpha]_D$[d] (deg)
1	30:70:0	93	20500	2.07	−1057
2	30:55:15	91	16000	2.03	−747
3	30:45:25	94	11900	2.09	−81
4	30:35:35	71	9900	2.16	+14
5	30:25:45	100	8714	1.96	+98
6	30:15:55	100	17200	1.33	+150
7	30:0:70	93	21100	2.03	+771

[a] Conditions: $[M]_{0,\ total}$ = 1.0 M in THF; $[M]_{0,\ total}/[M]_{cat}$ = 50, catalyst, (nbd)Rh$^+$[η^6−$C_6H_5B^-(C_6H_5)_3$], nbd = norbornadiene; 30 °C; 1 h. [b] *n*-Hexane-insoluble part. [c] Estimated by GPC (THF, PSt standards). [d] *c* = 0.10−0.11 g/dL in THF.

2H, C*H*$_2$NH), 5.77 (s, 1H, N*H*CO), 7.41−8.50, (m, pyrenyl). ^{13}C NMR (100 MHz, CDCl$_3$): δ 27.16(*C*H$_2$CH$_2$CO), 29.17 (*C*H$_2$NH), 32.61(C*H*$_2$CO), 35.59, (*C*H$_2$ attached to pyrenyl), 71.56 (HC≡), 79.47 (HC≡*C*), 123.27−135.58 (pyrenyl), 172.08 (*C*ONH). IR (cm^{-1}, KBr): 3266 (H−C≡), 3038, 1686 (C=O), 1561, 1509, 1261, 841, 760, 725, 668. Anal. Calcd for $C_{23}H_{19}NO$: C, 84.89; H, 5.89; N, 4.30. Found: C, 84.72; H, 5.74; N, 4.18.

(Co)polymerization Procedures. All the polymerizations were carried out in a glass tube equipped with a three-way stopcock under nitrogen. (nbd)Rh$^+$[η^6-$C_6H_5B^-(C_6H_5)_3$] was added to a THF solution of monomers under dry nitrogen, and the resulting solution ($[M]_{total}$ = 1.0 M, $[M]_{0\ total}/[M]_{cat}$ = 50) was kept at 30 °C for 1 h. The resulting solution was poured into a large amount of *n*-hexane to precipitate a polymer. It was separated by filtration using a membrane filter (ADVANTEC H100A047A) and dried under reduced pressure.

Results and Discussion

Synthesis of the Copolymers. The copolymes of 1-pyrenebutyric acid *N*-propargylamide (PY), *N*-(*tert*-butoxycarbonyl)-L-valine-*N*-propargylamide (LV), and *N*-(*tert*-butoxycarbonyl)-D-alanine-*N*-propargylamide (DA) with various compositions were prepared by the polymerization with (nbd)Rh$^+$[η^6-$C_6H_5B^-(C_6H_5)_3$] as a catalyst in THF at 30 °C for 1 h. The monomers satisfactorily underwent copolymerization to afford the corresponding copolymers with moderate molecular weights in good yields, which were soluble in THF, CH_2Cl_2, and $CHCl_3$ but insoluble in *n*-hexane (Table 1). The monomer conversions were quantitative, which were determined by ^{1}H NMR spectroscopy, and hence the compositions of the copolymers should be the same as the monomer feed ratios.

Fluorescence Dependence on the Secondary Structure of Poly(*N*-propargylamides) with Various Compositions of Chiral Amino Acids. The secondary structure of polymers was examined by polarimetric, CD and UV−vis spectroscopic methods. The specific rotation of the copolymers measured in THF ranged from −1057 to +771° at room temperature as displayed in Table 1, which depended on the composition of chiral amino acids. Poly(PY$_{30}$-*co*-LV$_{70}$) exhibited a large specific rotation, indicating that the polymer adopts a helical conformation with an excess of one-handed screw sense. The specific rotation gradually shifted from negative to positive with decreasing LV and increasing DA contents. Figure 1 shows the CD and UV−vis spectra of the copolymers measured in THF at room temperature. The copolymers having large specific rotations exhibited intense Cotton effects in the CD spectra and strong UV−vis absorption at 400 nm attributable to the polymer main chain, which confirms that the copolymers take helix structures. The difference in the sign of the Cotton effects indicates that the helical sense of the copolymer having an opposite specific rotation is opposite to each other. The copolymers having small specific rotations showed almost no CD signal and UV−vis aborption at 400 nm, which confirms that they take a random coil according to our previous studies.[5] The copolymers showed absorption peaks attributable to the pyrene units in the range of 300−370 nm in the UV−vis spectra. All the data mentioned above revealed that the helical senses of the polymers could be successfully tuned by the composition of chiral units and thus lead to a controlled array of chromophores.

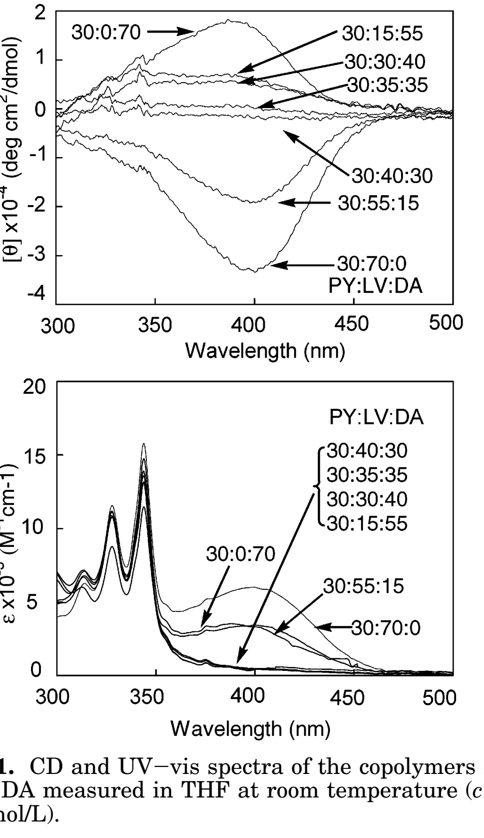

Figure 1. CD and UV−vis spectra of the copolymers of PY, LV, and DA measured in THF at room temperature (*c* = 1.0 × 10^{-4} mol/L).

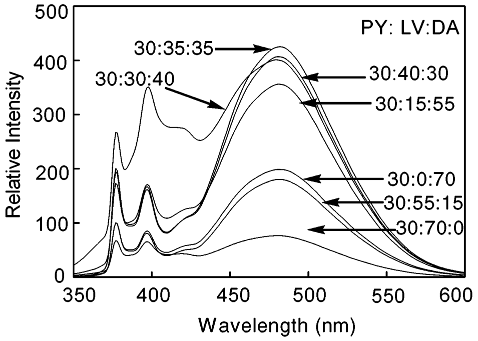

Figure 2. Fluorescence spectra of the poly(PY-*co*-LV-*co*-DA) (measured in THF atroom temperature, excited at 345 nm, [pyrene] = 10^{-5} mol/L).

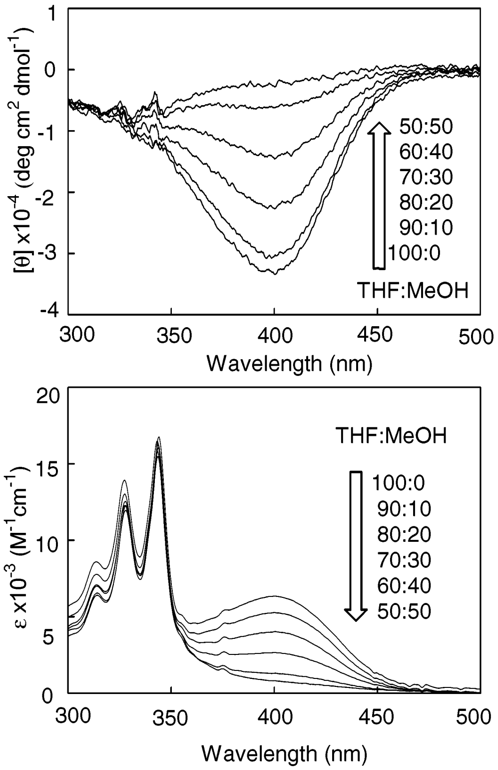

Figure 3. CD and UV−vis spectra of poly(PY_{30}-*co*-DA_{70}) by variation of solvent composition (measured at room temperature ($c = 1.0 \times 10^{-4}$ mol/L)).

The variation of polymer compositions not only resulted in the difference of secondary structure of the copolymers but also the fluorescence property of the side chain chromophore. The pyrene unit exhibited three emission bands at 380, 395, and 480 nm on excitation at 345 nm as shown in Figure 2. The former two bands originate from the isolated pyrene units, and the latter one is due to the excimer fluorescence.[8] The emission at 480 nm largely changed according to the secondary structure of the copolymer. Namely, the intensity of the excimer-based fluorescene of poly(PY_{30}-*co*-LV_{35}-*co*-DA_{35}) was approximately eight times larger than that of poly(PY_{30}-*co*-LV_{70}). The larger the specific rotation and the CD signal at 400 nm of copolymer (i.e., helicity) were, the smaller the fluorescence was. This means that a random coil structure is favorable to formation of the excimer.

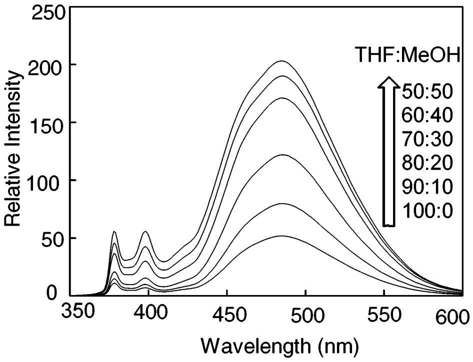

Figure 4. Variation of fluorescence spectra of poly(PY_{30}-LV_{70}) with solvent compositions (measured at room temperature, excited at 345 nm, [pyrene] = 10^{-5} mol/L).

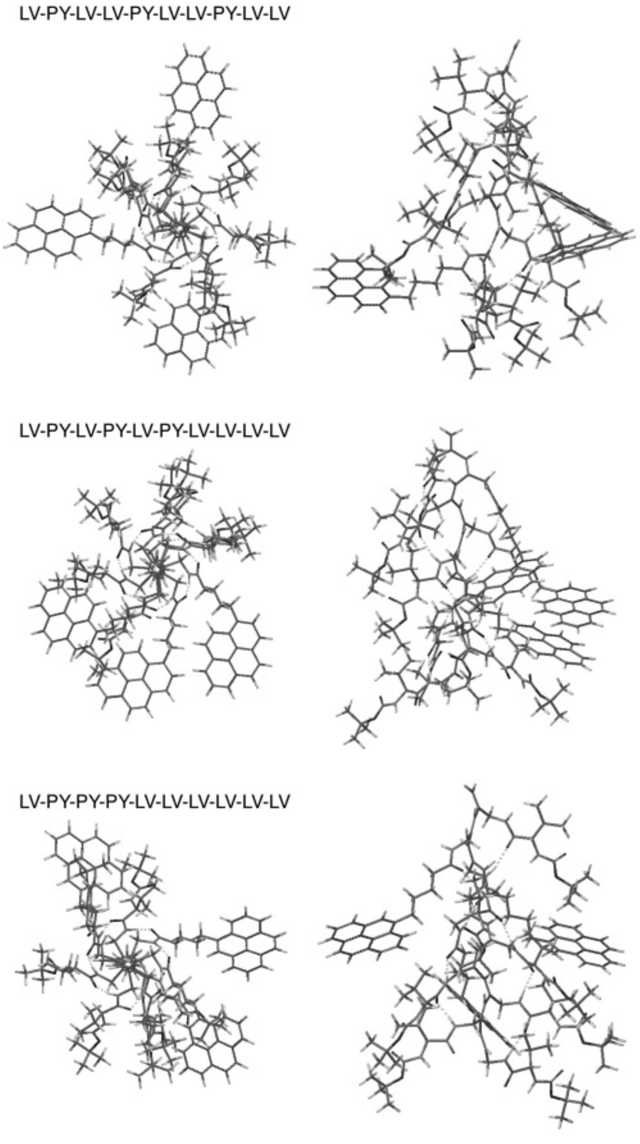

Figure 5. Possible structures of PY_{30}-*co*-LV_{70} 10-mers, whose unit sequences are LV−PY−LV−LV−PY−LV−LV−PY−LV−LV (top), LV−PY−LV−PY−LV−PY−LV−LV−LV−LV (middle), and LV−PY−PY−PY−LV−LV−LV−LV−LV−LV (bottom). Left: View from the top of the main chain. Right: View from the side of the main chain.

Fluorescence Dependence on the Solvent-Induced Change of Secondary Structure of Poly(*N*-propargylamides). The helical structure of poly(*N*-propargylamides) is stabilized by intramolecular hydrogen bonding between the amide groups of the side chains.[9] It is predictable that the helical conformation of the polymer transforms into a random one, when the intramolecular hydrogen bond is cleaved by adding polar additives.[10] We examined the solvent-induced conformational change of the poly(PY_{30}-*co*-LV_{70}) and the fluorescence properties. As shown in Figure 3, the CD and UV−vis signals at 400 nm due to a helix structure gradually decreased by raising the MeOH content, and completely disappeared when it reached 50%. This means that the helical structure of the copolymer transformed into random coil by the addition of MeOH. As shown in Figure 4, the emission based on excimers at 480 nm increased the intensity as MeOH content increased. The intensity of the fluorescene in the presence of 50% MeOH was approximately four times larger than that in the absence of MeOH. It was confirmed that the solvent-induced random coil structure is favorable for excimer formation in a fashion similar to the case tuned by the composition of the structurally different enantiomers as depicted in Figure 2.

Conformation Analysis with Molecular Models. Figure 5 shows the models of PY_{30}-*co*-LV_{70} 10-mers. The comonomer sequences include LV−PY−LV−LV−PY−LV−LV−PY−LV−LV, LV−PY−LV−PY−LV−PY−LV−LV−LV−LV, and LV−PY−PY−PY−LV−LV−LV−LV−LV−LV, whose both chain ends are capped with hydrogen. The dihedral angles at the double and single bonds of the main chain are set at 0 and 140° in the present models, respectively, according to our previous study concerning the analysis of helical structure of poly(*N*-propargylamides) by MM and MO methods, along with the wormlike touched-bead model theory.[11] The main chain forms a right-handed helix, and the amide groups of the side chains form hydrogen bonds (indicated as dotted lines) along the helix axis between *n*th and (n+2)th repeating units. In every sequence, the pyrene groups locate apart from each other, due to the restriction of the mobility by the helical structure of the main chain. It is therefore considered that the helical structure is unfavorable for the formation of excimers of pyrenes. On the other hand, when the main chain takes a random coil structure, it is likely that the pyrene groups can locate at the positions capable to form excimers, because the mobility of the main chain should be larger than the helix form.

Conclusions

In conclusion, we have successfully synthesized pyrene-functionalized poly(*N*-propargylamides) based on amino acids, and controlled the secondary sturecture by varying the composition of structurally different amino acids, and by solvent composition. We could tune the excimer fluorescene of the pyrene moiety at the side chain according to the secondary structure of the copolymers.

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