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Synthesis and properties of pyrene-functionalized polyacetylene. A stable helical polymer emitting fluorescence

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Abstract

Pyrene-functionalized chiral *N*-propargylamide, (R)-HC≡CCH$_2$NHCOCH(CH$_3$)O-1,4-C$_6$H$_4$-OCO(CH$_2$)$_3$-1-pyrenyl (**1**) was polymerized with (nbd)Rh$^+$[η^6-C$_6$H$_5$B$^-$(C$_6$H$_5$)$_3$] as a catalyst to obtain the corresponding polymer with a moderate weight in a good yield. Poly(**1**) was soluble in CHCl$_3$, CH$_2$Cl$_2$, and THF. The polarimetric and CD spectroscopic data indicated that poly(**1**) existed in a helical structure with predominantly one-handed screw sense in these solvents. The helical structure was stable upon heating and addition of MeOH. Poly(**1**) showed very large excimer-based fluorescence compared with **1**.

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Keywords: Polyacetylene; Pyrene; Helix

1. Introduction

Chromophores linked to polymers show different behavior from non-linked ones, and exhibit unique photophysical and photochemical properties [1]. Especially in the case of helical polymers having chromophores in the side chains, excitation energy or charge is possibly transported one-dimensionally along the polymer chain. Thus chromophore-carrying polymers are regarded as molecular wires, which are applicable to microprocessors and other devices [2]. Polypeptides functionalized with chromophores have been widely studied for these purposes, because they can form regulated secondary structures such as α-helix and β-sheet, where the side chains are arranged at regular intervals along the main chains [3–7].

Polyacetylene derivatives exhibit unique properties such as semiconductivity, high gas permeability, nonlinear optical properties, and the ability to form helical structures [8,9]. We have previously reported the copolymerization of a pyrene-containing achiral *N*-propargylamide with chiral *N*-progargylamides [10,11]. The copolymers with certain compositions take a helical structure with predominately one-handed screw sense, which is tunable by the composition of the chiral units. This enables the control of orientation of pyrene moieties along the helical polymer backbone. The copolymers emit weak fluorescence when they form a helix. On the other hand, they emit strong fluorescence when they take a randomly coiled structure. The fluorescence properties of the pyrene-carrying copolymers greatly depend on the secondary structure. In this paper, we report the synthesis of a novel optically active polyacetylene with pendent pyrene groups (Scheme 1), secondary structure of the polymer, and the fluorescence property.

2. Experimental

2.1. Measurements

^{1}H 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 the polymer were determined by gel permeation chromatography (GPC) eluted with THF 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–vis spectra were recorded in a quartz cell (thickness: 1 cm) using a JASCO J-820

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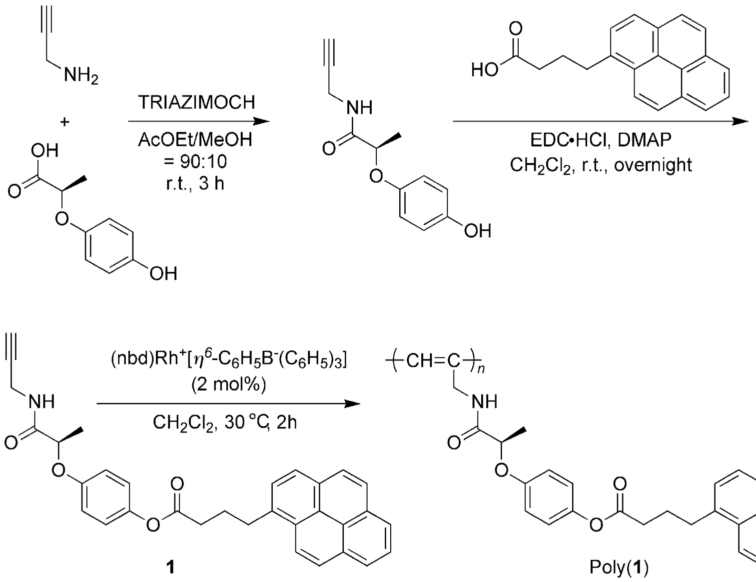

Scheme 1. Synthesis of poly(**1**).

spectropolarimeter. Fluorescence spectra were measured using a JASCO FP-750 spectrofluorometer.

2.2. Materials

CH_2Cl_2 was distilled over CaH_2 prior to use. (nbd)$Rh^+[\eta^6$-$C_6H_5B^-(C_6H_5)_3]$ was prepared as reported [12]. All other reagents were used as received without purification.

2.3. Synthesis of (R)-$HC{\equiv}CCH_2NHCOCH(CH_3)O$-1,4-$C_6H_4$-$OCO(CH_2)_3$-1-pyrenyl (**1**)

(R)-2-(4-Hydroxyphenoxy)propionic acid (5.50 g, 30 mmol), propargylamine (1.70 g, 30 mmol), and 4-[4,6-dimethoxy-1,3,5-triazine-2-yl]-4-methylmorpholinium chloride (TRIAZIMOCH, Tokuyama Co., 8.0 g, 30 mmol) were subsequently added to a solution of AcOEt and MeOH (100 mL, 90:10, volume ratio). After the resulting mixture was stirred at room temperature for 3 h, it was subsequently washed with 1 N HCl aqueous solution, saturated $NaHCO_3$ aqueous solution, and water. The organic phase was dried over $MgSO_4$ and concentrated by rotary evaporation. The crude product was purified by silica gel column chromatography eluted with AcOEt to obtain (R)-$HC{\equiv}CCH_2$-$NHCOCH(CH_3)O$-1,4-C_6H_4-OH in 78% yield; mp 112.5–114.0 °C, $[\alpha]_D = +10.0°$ ($c = 1.00$ g/dL, in $CHCl_3$, room temperature). ^1H NMR (400 MHz, $CDCl_3$): δ 1.53 (d, $J = 6.4$ Hz, 3H, CH_3), 2.23 (s, 1H, $HC{\equiv}$), 4.03 (s, 2H, CH_2), 4.56 (s, 1H, $CHCH_3$), 4.57 (s, 1H, OH), 5.94 (s, 1H, NH), 6.78 (s, 4H, C_6H_4). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.56 (CH_3), 28.93 (CH_2), 71.89 ($HC{\equiv}$), 75.97 ($HC{\equiv}C$), 78.87 (CH), 116.28, 117.16 (C_6H_4), 151.15 (COCH), 172.50 (CONH). IR (cm^{-1}, KBr): 3620, 3300, 2125, 1660, 1605, 1508, 1425, 1375, 1346, 1225, 1142, 1093, 1059, 941, 850, 762, 594.

4-(Dimethylamino)pyridine (DMAP, 0.43 g, 3.5 mmol) and 1-(3-(dimethylamino)propyl)-3-ethylcarbodiimde hydrochloride (EDC·HCl, 0.8 g, 3.5 mmol) were subsequently added to a solution of 1-pyrenebutyric acid (1 g, 3.5 mmol) and (R)-$HC{\equiv}CCH_2NHCOCH(CH_3)O$-1,4-$C_6H_4$–OH (0.76 g, 3.5 mmol) in CH_2Cl_2 (50 ml) at 0 °C. The resulting mixture was stirred at room temperature overnight, then CH_2Cl_2 (50 mL) was added to the mixture. It was subsequently washed with 1 N HCl aqueous solution, saturated $NaHCO_3$ aqueous solution, and water. The organic phase was dried over $MgSO_4$ and concentrated by rotary evaporation. The crude product was purified by silica gel column chromatography eluted with AcOEt/n-hexane = 1:2 (volume ratio) to obtain **1** in 71% yield; mp 158–159 °C, $[\alpha]_D = +26.3°$ ($c = 1.00$ g/dL, in $CHCl_3$, room temperature). ^1H NMR (400 MHz, $CDCl_3$): δ 1.57 (s, 3H, CH_3), 2.23 (s, 1H, $HC{\equiv}$), 2.32 (m, 2H, CH_2CH_2COO), 2.69 (m, 2H, CH_2COO), 3.48 (m, 2H, CH_2-pyrene), 4.06 (m, 2H, CH_2NH), 4.65 (s, 1H, $CHCH_2$), 6.64 (s, 1H, NHCO), 6.89–8.17 (m, 13H, aromatic protons). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.37 (CH_3), 27.54 (CH_2CH_2COO), 29.71 (CH_2COO), 33.52 (CH_2NH), 34.61 (CH_2-pyrene), 68.98 ($HC{\equiv}$), 76.33 ($CHCH_3$), 78.13 ($HC{\equiv}C$), 117.13, 117.95, 123.52, 124.01, 125.62, 125.66, 127.58, 128.17, 131.95, 136.16, 146.33, 172.44, 172.97. IR (cm^{-1}, KBr): 3568, 3285, 3045, 2920, 2360, 1753, 1660, 1637, 1561, 1508, 1491, 1458, 1421, 1294, 1240, 1202, 1105, 843, 754, 517. Anal. Calcd for $C_{32}H_{27}NO_4$: C, 78.51; H, 5.56; N, 2.86. Found: C, 78.21, H, 5.56; N, 2.95.

2.4. Polymerization of **1**

The polymerization was carried out in a glass tube equipped with a three-way stopcock under nitrogen. (nbd)$Rh^+[\eta^6$-$C_6H_5B^-(C_6H_5)_3]$ was added to a CH_2Cl_2 solution of **1** under nitrogen, and the resulting solution ($[M]_0 = 1.0$ M, $[M]_0/[Rh] = 50$) was kept at 30 °C for 2 h. Poly(**1**) was isolated by precipitation with a large amount of n-hexane in 98% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 1.55 (s, 3H, CH_3), 2.36 (m, 2H, CH_2CH$_2$COO), 3.06 (br, 4H, CH_2COO, CH_2-pyrene), 4.26 (m, 2H, CH_2NH), 4.66 (s, 1H, C*H*CH$_3$), 5.83 (s, 1H, N*H*CO), 6.81–7.87 (m, 14H, –C*H*=C<, aromatic protons). IR (cm^{-1}, KBr): 3621, 3280, 3040, 2940, 1751, 1736, 1718, 1655, 1649, 1458, 1236, 1192, 1126, 843, 752, 681, 518.

3. Results and discussion

3.1. Synthesis and polymerization of 1

Scheme 1 illustrates the synthetic routes for pyrene-functionalized acetyelene monomer **1**, and the polymerization process. Monomer **1** was synthesized by the condensation of 1-pyrenebutyric acid with (R)-HC≡CCH$_2$NHCOCH(CH$_3$)O-1,4-C$_6$H$_4$-OH, which was prepared by the condensation of (R)-2-(4-hydroxyphenoxy)propionic acid with propargylamine. The structure of **1** was identified by ^{1}H, ^{13}C NMR, and IR spectroscopies besides elemental analysis. The polymerization of **1** was conducted in CH$_2$Cl$_2$ at 30 °C for 2 h catalyzed with (nbd)Rh$^+$[η^6-C$_6$H$_5$B$^-$(C$_6$H$_5$)$_3$]. Poly(**1**) was obtained as yellow powder in 98% yield, whose M_n and M_w/M_n were 13,600 and 2.3, respectively. Poly(**1**) was soluble in CHCl$_3$, CH$_2$Cl$_2$, THF, and partly soluble in DMF, DMSO, and toluene. The structure of poly(**1**) was examined by ^{1}H NMR and IR spectroscopies. It exhibited no proton signal and IR absorption based on ethynyl group, and exhibited reasonable spectroscopic patterns assignable to a polyacetylene structure.

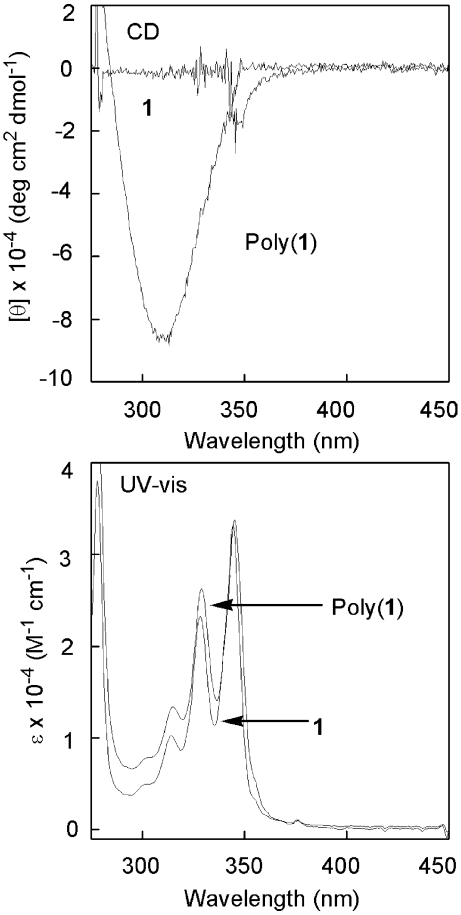

Fig. 1. CD and UV–vis spectra of **1** and poly(**1**) measured in CHCl$_3$ at room temperature, $c=1.0\times10^{-4}$ mol/L.

3.2. Conformation of poly(1) in solution

The secondary structure of poly(**1**) was examined by polarimetric, CD, and UV–vis spectroscopic methods. Compared to the specific rotation of **1** (+26.3° in CHCl$_3$), poly(**1**) displayed very large minus specific rotations, −387° in CHCl$_3$, −429° in CH$_2$Cl$_2$, and −485° in THF, which suggests that it forms a helical structure with predominantly one-handed screw sense in these solvents. Fig. 1 displays the CD and UV–vis spectra of **1** and poly(**1**). Poly(**1**) exhibited an intense CD signal at 310 nm, while **1** exhibited no apparent CD signal. On the contrary, **1** and poly(**1**) showed almost the same UV–vis absorption peaks attributable to the pyrene units at 300–370 nm. It is considered that the CD signal of poly(**1**) arises from the conjugated polyacetylene backbone, which takes a helical structure with predominantly one-handed screw sense. Compared to the ε value of pyrene, that of polyacetylene main chain is one-order small [10,11]. This should be the reason why **1** and poly(**1**) showed almost the same UV–vis spectra, although the CD spectra were largely different.

Helical poly(*N*-propargylamides) stabilize the conformation by intramolecular hydrogen bonding between the amide groups in the side chains as well as steric repulsion. They deform the helical structure upon external stimuli such as heat and polar solvents [13,14]. The solid- and liquid-state IR spectra of **1** and poly(**1**) were measured to confirm the formation of hydrogen bonding in poly(**1**) (Fig. 2). In the solid state, **1** and poly(**1**) exhibited the amide $\nu_{C=O}$ at 1654–1655 cm^{-1}, indicating that the amide groups are hydrogen-bonded. In CHCl$_3$, **1** and poly(**1**) exhibited the amide $\nu_{C=O}$ at 1682 and 1655 cm^{-1}, respectively. Namely, poly(**1**) exhibited the amide absorption

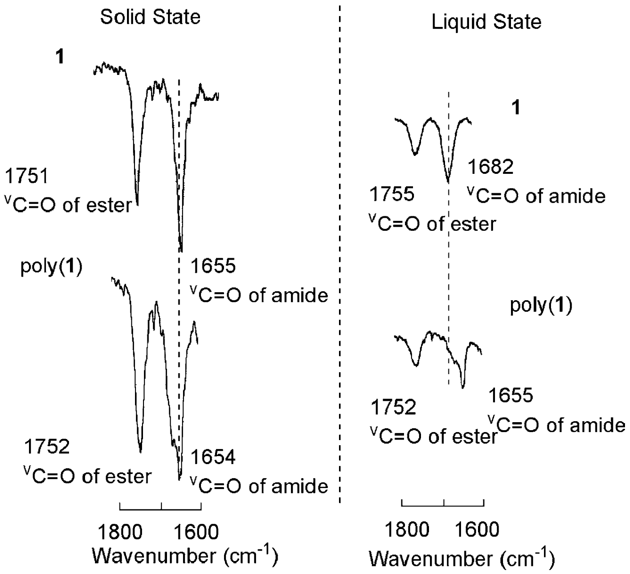

Fig. 2. Solid- and liquid-state IR spectra of **1** and poly(**1**). Solid state: KBr method. Liquid state: in CHCl$_3$ (20 mM).

at the wavenumber 27 cm^{-1} lower than **1** did in $CHCl_3$. It is impossible for poly(**1**) to form hydrogen bonding intermolecularly at this low reagent concentration. It is therefore concluded that poly(**1**) accompanies intramolecular hydrogen bonding, which should promote the main chain to take a helical conformation. We further examined the stability of the helical structure of poly(**1**) to external stimuli. Fig. 3 depicts the temperature dependence of the CD and UV–vis spectra of poly(**1**) measured in $CHCl_3$. Poly(**1**) kept the CD intensity upon raising temperature up to 50 °C. The helical structure was thermally stable. Fig. 4 displays the CD and UV–vis spectra of poly(**1**) measured in mixtures of $CHCl_3$/MeOH with various compositions at room temperature. Poly(**1**) exhibited almost the same CD intensities irrespective of solvent composition. Consequently, we can conclude that the helical structure of poly(**1**) is very stable to heat and MeOH, which is different from the poly(*N*-propargylamides) reported so far [13,14]. This may be due to the tightness of the helical structure. Namely, judging from the wavelength (310 nm) of the Cotton effect of poly(**1**), it is likely that poly(**1**) forms intramolecular hydrogen bonding between the amide groups at *n*th and $n+3$th units [15]. On the other hand, it is considered that helical poly(*N*-propargylamides) showing a CD signal at 400 nm form a helix stabilized by hydrogen bonding between the *n*th and $n+2$th units [13,14]. Poly(**1**) takes the former helical structure, which is tighter than the latter [16]. It is therefore likely that

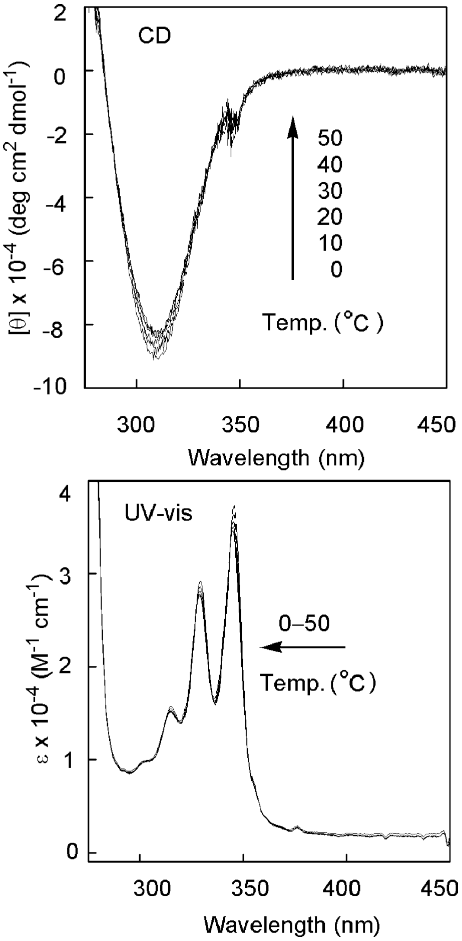

Fig. 3. Temperature dependence of CD spectra of poly(**1**) measured in $CHCl_3$, $c=1.0\times10^{-4}$ mol/L.

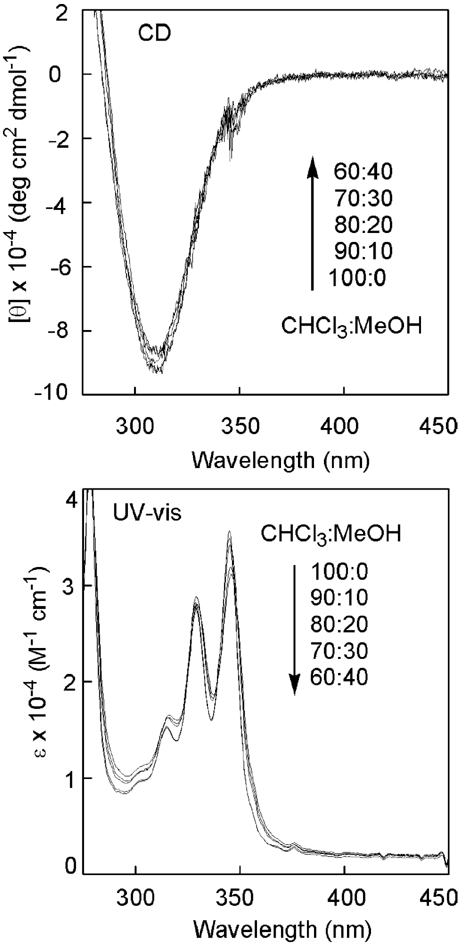

Fig. 4. Effect of $CHCl_3$/MeOH compositions on the CD spectra of poly(**1**) measured at room temperature, $c=1.0\times10^{-4}$ mol/L.

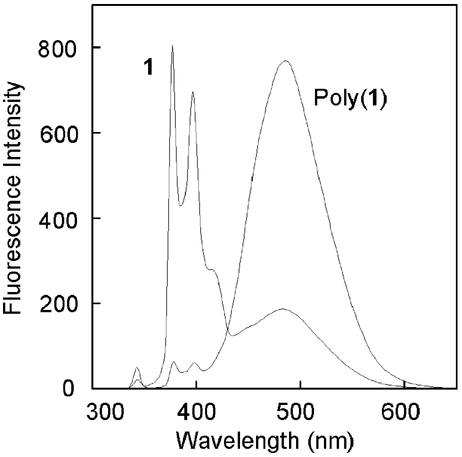

Fig. 5. Fluorescence spectra of **1** and poly(**1**) measured in $CHCl_3$ at room temperature, excited at 345 nm, $c=5.0\times10^{-6}$ M.

poly(**1**) is stable to heat and MeOH compared to the poly(*N*-propargylamides) showing the CD signal at 400 nm.

3.3. Fluorescence properties of the polymers

Fig. 5 depicts the fluorescence spectra of **1** and poly(**1**) measured in $CHCl_3$ at room temperature. Both of them exhibited three emission bands at 380, 395, and 480 nm upon excitation at 345 nm. The former two bands are based on the isolated pyrene units, and the latter one is due to an excimer [10,11]. Poly(**1**) emitted excimer-based fluorescence with four-times larger intensity than **1** did. The excimer-based fluorescence of poly(**1**) was much more stronger than the non-excimer-based one, which was opposite to those of **1**. The pendent pyrene groups of poly(**1**) seem to take positions that are favorable to form the excimer. It is suggested that the helical conformation of poly(**1**) does not disturb the overlap of the pendent pyrene groups each other. This is completely different from the case of the copolymers of *N*-propargylamides carrying pyrene groups, poly($HC{\equiv}CCH_2NHCOCH(CH_3)_3$-1-pyrenyl-*co*-(R)-$HC{\equiv}CCH_2NHCOCH_2CH(CH_3)(CH_2)_3CH(CH_3)_2$) [10] and poly($HC{\equiv}CCH_2NHCOCH(CH_3)_3$-1-pyrenyl-*co*-(*S*)-$HC{=}CCH_2NHCOCH(CH(CH_3)_2)NHCO_2C(CH_3)_3$)-*co*-(R)-$HC{\equiv}CCH_2NHCOCH(CH_3)NHCO_2C(CH_3)_3$)) [11] that we have previously reported. Namely, the previously reported polymers emit strong excimer-based fluorescence when they take a randomly coiled structure. The fluorescence becomes weak when they form a helical structure. Why does poly(**1**) show so different fluorescence behavior from the previously reported poly(*N*-propargylamides)? One possible reason is the difference of the helical structure. As described above, poly(**1**) seems to form a tighter helix accompanying hydrogen-bonding strands between the amide groups at *n*th and $n+3$th units, while the previously reported pyrene-carrying poly(*N*-propargylamides) form a looser helix accompanying hydrogen-bonding strands between the *n*th and $n+2$th amide groups. In the helix based on nth$-n+2$th hydrogen bonding, the population of pyrenes forming excimer is considered to be low [10,11]. On the other hand, in the helix based on nth$-n+3$th hydrogen bonding, the population seems to be high compared to the former case. Another reason may be the difference of density of pyrene groups in the side chain. The previously reported poly(*N*-propargylamides) are copolymers of pyrene-derived *N*-propargylamide with chiral *N*-propargylamides, which are necessary to induce a one-handed helical structure. Since poly(**1**) can form a one-handed helical structure without the assistance of other chiral monomer units, the pyrene density is higher than that of the copolymers. Consequently, poly(**1**) has a higher possibility of excimer formation than the copolymers do. Poly(**1**) has a longer distance between the polyacetylene main chain and pyrene moiety than the previously reported poly(*N*-propargylamides). It is therefore considered that the pyrene moiety of poly(**1**) is more flexible, which results in increase of possibility of excimer formation. As expected from the stability of the helical structure to MeOH, poly(**1**) almost maintained its fluorescence intensity, even though the MeOH content was raised in $CHCl_3$/MeOH (Fig. 6).

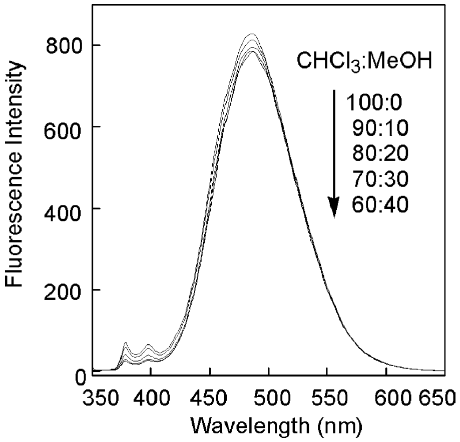

Fig. 6. Effect of $CHCl_3$/MeOH compositions on the fluorescence spectra of poly(**1**), excited at 345 nm, $c=5.0\times10^{-6}$ M.

4. Summary

In this article, we synthesized a pyrene-functionalized novel chiral polyacetylene, poly(**1**). The polarimetric and CD spectroscopic data indicated that poly(**1**) formed a helical structure with predominantly one-handed screw sense, and the helical structure was very stable upon heating and addition of MeOH. Poly(**1**) showed very large excimer-based fluorescence compared to **1**. It was considered that the helical structure was favorable for the pendent pyrene groups to form excimers. Thus, we could obtain a photo-luminescent polymer stable to heat and MeOH. It is expected that the stereo-regular helical main chain of polyacetylenes will endow chromophores with some features such as increasing nonlinear optical response and relaxing the requirement for polar ordering [17].

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