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Highly controlled side-chain chromophore orientation in poly[N^5-1-(1-pyrenyl)ethyl-L-glutamines]

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Abstract

Poly[N^5-(*R* and *S*)-1-(1-pyrenyl)ethyl-L-glutamines] (**1** and **2**) were prepared by condensation of poly(L-glutamic acid) with optically resolved amines. In solution, these polymers, **2** in particular, gave large circular dichroism (CD) indicative of exciton coupling among the side-chain pyrene chromophores. When compared with the corresponding polymer with achiral side groups, i.e. poly(1-pyrenylmethyl-L-glutamine) (**3**), **1** and **2** not only gave much stronger CD, but also gave much reduced excimer emission with a significant hypsochromic shift of emission maximum. The highly controlled orientation of the side-chain chromophores is apparently brought about by the specific steric interactions among the bulky chiral side chains along the helical main chain.

Keywords: Poly-L-glutamine; Side-chain orientation; Pyrene chromophore

1. Introduction

Polymers having aromatic chromophores in the side chains are of interest because their chromophore arrays can allow them to become 'molecular wires' capable of transporting excitation energy and charge one-dimensionally along the polymer backbone [1–6]. The secondary structure of the polymer, including that of the side chain, however, is of critical importance in controlling the chromophore orientation to bring about efficient transport of energy and charge while suppressing formation of traps such as excimers and ground-state dimers [1–4]. Polypeptides are promising candidates for such polymers as their side chains are arranged at regular intervals along the helical main chains. Short spacer chains between the chromophore and the main chain, however, have been suggested to be required for high control of side-chain chromophore orientation [5,6].

Previously, we prepared poly(L-glutamines), known α-helical polypeptides, having naphthalene chromophores in the side chains, i.e. poly[N^5-(*R* and *S*)-1-(1-naphthyl)-ethyl-L-glutamines], and examined their circular dichroism (CD) in solution [7,9]. Despite the relatively long spacer chains, these polymers, particularly that having (*R*)-1-(1-naphthyl)ethyl side groups, gave CD signals indicative of exciton coupling at the naphthalene ^1B_b band. The corresponding polymer without chirality-inducing methyl substituents in the side chains, i.e. poly(N^5-1-naphthylmethyl-L-glutamine), showed no appreciable CD at the naphthalene absorption bands. Poly(N^5-1-pyrenylmethyl-L-glutamine) (**3**), where naphthyl groups are replaced with pyrenyl groups, on the other hand, shows CD signals indicative of exciton coupling at the ^1L_a and ^1B_b bands of pyrene chromophore, indicating that the bulkiness of the chromophore itself plays an important role in orienting the side-chain chromophores [10]. These results led us to prepare poly[N^5-(*R* and *S*)-1-(1-pyrenyl)ethyl-L-glutamine] (**1** and **2**) and examine their CD to confirm that the specific steric interactions among the bulky chiral side chains along the helical main chain lead to highly controlled side-chain chromophore orientation (Scheme 1).

2. Experimental

2.1. Sample preparation

Racemic 1-(1-pyrenyl)ethylamine was synthesized from 1-acetylpyrene (Aldrich) using the Leuckart reaction [11]. Optical resolution was accomplished by repeated

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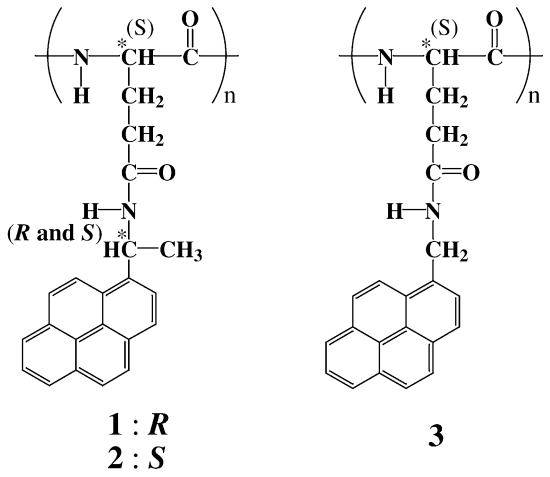

Scheme 1.

crystallization of salts formed in the presence of either L- or D-tartaric acid [12]. The optical purity was confirmed by ^{1}H NMR in chloroform-*d* in the presence of two equivalents of (*R*)-1,1′-bi-2-naphthol [13]. The absolute configuration of (*R*)-1-(1-pyrenyl)ethylamine was established by X-ray structural analysis of its ammonium salt formed with (1*S*)-10-camphorsulfonic acid. The optical rotation ($[\alpha]_D^{25}$) of (*R*)-1-(1-pyrenyl)ethylamine and that of (*S*)-1-(1-pyrenyl)-ethylamine were $+82.1°$ ($c = 0.84$ g dL^{-1}) and $-81.8°$ ($c = 0.90$ g dL^{-1}) in THF, respectively. **1** and **2** were prepared from poly(L-glutamic acid) (DP 385, Aldrich) and the above amines with an amine–carboxylic acid molar ratio of 2 using DMAc as a solvent and *N*,*N*-dicyclohexylcarbodiimide and 1-hydroxybenzotriazole as condensing agents as reported previously for **3** (DP 360) [10]. Full derivatization of the side-chain carboxyl groups was confirmed by ^{1}H NMR in DMSO-d_6 at 120–140 °C, the peak area of the side-chain methyne proton at ca. 5.85 ppm, relative to that of the main-chain α-methyne proton at ca. 4.25 ppm, being 1.02 ± 0.03. Monomeric model compounds, i.e. (*R* and *S*)-1-(1-pyrenyl)ethylacetamides, were prepared from the corresponding amines and acetyl chloride.

2.2. Measurements

X-ray crystallographic analysis was carried out on a Rigaku RAXIS-II diffractometer with graphite monochromated Mo Kα radiation. Optical rotations were recorded on a JASCO DIP-370 polarimeter. ^{1}H NMR spectra were measured using a JEOL LA-500 MHz and a JEOL LA-400 MHz spectrometer. UV and CD spectra were recorded on a HITACHI U-3210 spectrophotometer and on a JASCO J-820 circular dichrograph, respectively. Steady-state fluorescence spectra were recorded on a HITACHI F-4010 fluorescence spectrophotometer.

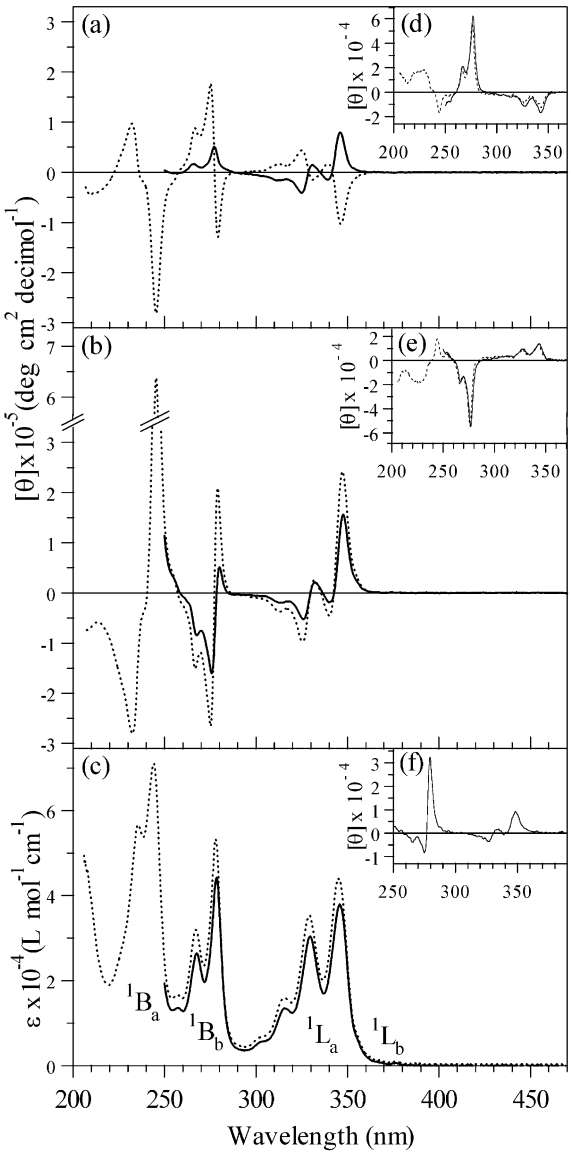

Fig. 1. CD spectra of **1** (a) and those of **2** (b) in DMAc (solid line) and in THF (dotted line) at room temperature. [Py] = 1.5×10^{-4} M (in THF), 2.0×10^{-3} M (in DMAc); cell length = 1 mm (in THF), 0.1 mm (in DMAc). Insets are the CD spectra of (*R*)-1-(1-pyrenyl)ethylacetamide (d), (*S*)-1-(1-pyrenyl)ethylacetamide (e), and **3** (f), measured under the same conditions. The CD intensities are expressed in terms of pyrene concentration. The absorption spectra of **2** in DMAc (solid line) and in THF (dotted line) are shown in (c).

3. Results and discussion

No significant differences in absorption spectrum are noted on going from the monomeric model compounds to the polymers, indicating no significant ground-state interactions among the side-chain pyrene chromophores either in DMAc or in THF. **1** and **2** show CD signals indicative of exciton coupling in most of the pyrene absorption bands (Fig. 1). (CD did not change in the pyrene concentration range of 1.0×10^{-4}–1.0×10^{-3} M. Presumably, association among the polymers, e.g. formation of cholesteric liquid

crystals often observed in concentrated polypeptide solutions [14,15], does not occur in the concentration range used.)

The observed CD signals, except that in the ^1B_b band of **1** in DMAc, are much larger than those of the corresponding monomeric model compounds (Fig. 1(d) and (e)) and those of **3** previously reported (Fig. 1(f)) [10], suggesting that the methyl groups placed near the pyrene chromophores, together with the bulkiness of the pyrene chromophores themselves, bring about highly controlled chromophore orientation. The molar ellipticities observed with **2** in THF are as large as 6.4×10^5, -2.7×10^5, and 2.4×10^5 deg cm^{-1}decimol^{-1} at 245, 275, and 347 nm, respectively. The former two values are several times as large as the corresponding values, i.e. -1.8×10^5 and -0.3×10^5 deg cm^{-1}decimol^{-1}, for poly(L-1-pyrenylalanine) in trimethyl phosphate, reported by Sisido et al., where pyrene chromophores are introduced to the polypeptide backbone via a very short methylene linkage [6]. It is also noted that while **2** gives similar spectra, albeit with different intensities, in both solvents, **1** in THF gives a CD spectrum markedly different from that in DMAc. The mirror image relationship in the ^1L_a band is remarkable as it suggests the reversal of exciton chirality on going from DMAc to THF. In addition, the CD signal in the ^1B_b band in DMAc is very much similar, in spectral shape and intensity, to that of the monomeric model compound, evidently reflecting only the local chirality of the side chain. The dependence of the CD spectra on the solvent was examined further by changing the solvent composition as shown in Fig. 2. On addition of DMAc to THF, the CD spectrum of **1** undergoes continuous changes with 'isoelliptic' points at both ^1L_a and ^1B_b bands (Fig. 2(a)). These changes were found to be reversible. **2**, on the other hand, shows monotonous decrease of CD signals at both ^1L_a and ^1B_b bands without changing the exciton chirality. In principle, a reversal of the main-chain helical sense may occur upon changing the solvent. The continuous nature of the CD changes of Fig. 2(a), however, suggest that such conformational transition does not occur. The observed dependence of CD on the solvent and the relatively weak CD signals thus suggest that the pyrene chromophore orientation of **1** is not as firmly controlled as that of **2**, indicating that the chirality of the side chains in relation to that of the main chain is important in controlling chromophore orientation along the helical main chain.

When compared with that from **3**, excimer emission (I_D) from **1** and **2**, relative to monomer emission (I_M), decrease significantly as shown in Fig. 3. This is accompanied by a ca. 6 nm hypsochromic shift of emission maximum. Even so, rather strong excimer emission is observed with both **1** and **2**. Efficient excimer formation is attributed either to a large number of excimer forming sites in the polymer, i.e. pairs of chromophores in distances and geometries that allow excimeric interactions, and/or to efficient energy

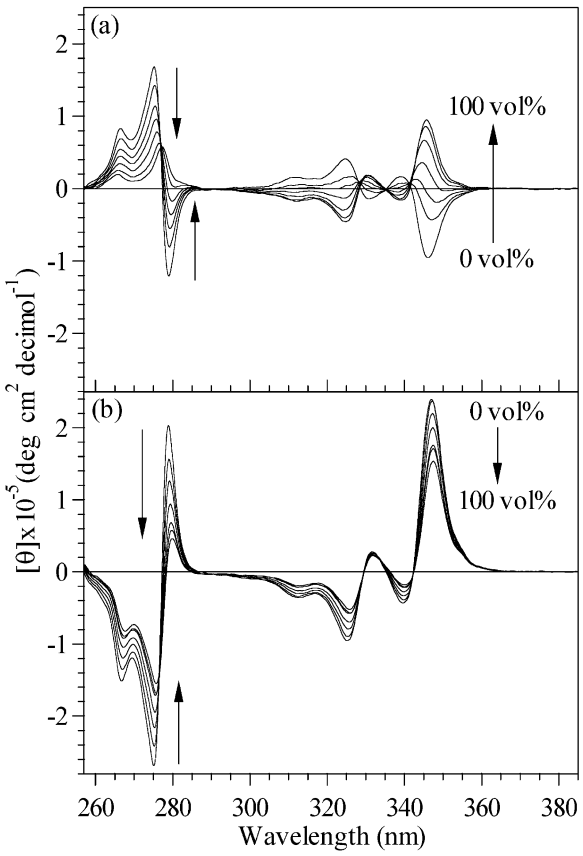

Fig. 2. CD spectra of **1** (a) and those of **2** (b) in mixed solvents of THF and DMAc at room temperature. Solvent compositions are shown in terms of increasing DMAc vol%: 0, 5, 10, 20, 40, 80, and 100 vol%. [Py] = 2.0×10^{-4} M; cell length = 1 mm. The CD intensities are expressed in terms of pyrene concentration.

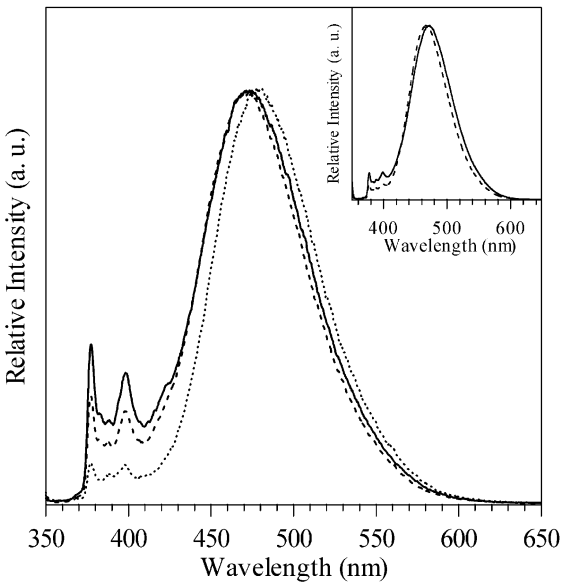

Fig. 3. Fluorescence spectra, normalized at emission maxima of: **1** (solid line), **2** (broken line), and **3** (dotted line) in DMAc at 20 °C. λ_{ex} = 345 nm; [Py] = 1.0×10^{-5} M. Those of **1** (solid line) and **2** (broken line) in THF are shown in the inset.

migration among the chromophores to those sites. In solution, excimer-forming sites are apparently formed by thermal fluctuations of main-chain and side-chain conformations. The probability of a pair of chromophores undergoing excimeric interaction in **1** and **2** appears to be much smaller than that in **3** as their chromophore orientation is better controlled. It is, however, somewhat intriguing that **2**, which has better-controlled chromophore orientation than **1**, affords larger I_D/I_M. We suspect that the energy migration in **2** is so efficient that excitation energy is trapped efficiently at less populated excimer-forming sites. A support for this assumption is given by the observation that in THF, where chromophore orientation is suggested to be better controlled, both **1** and **2** show I_D/I_M significantly larger than that in DMAc (inset in Fig. 3). **2** shows a further hypsochromic shift, i.e. ca. 10 nm, of excimer emission maximum. Formation of stable excimers is prevented even further in **2** apparently due to the better-controlled chromophore orientation in THF.

Thus, the present study gives conclusive evidence for the importance of the specific steric interactions among the bulky chiral side chains along the helical main chain in controlling the side-chain chromophore orientation. A study on the efficiency of singlet energy transport along the polymer chain and its dependence on the pyrene chromophore orientation is currently underway and will be reported in a future publication.

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