Side-Chain Chromophore Orientation and Excitation Energy Transport in Films Prepared from Poly[N^5-(*R*)- and N^5-(*S*)-1-(1-naphthyl)ethyl-L-glutamines]

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ABSTRACT: The side-chain chromophore orientation and singlet excitation energy transport in films prepared from poly[N^5-(*R*)- and N^5-(*S*)-1-(1-naphthyl)ethyl-L-glutamines] (**1** and **2**) were examined by circular dichroic (CD) and fluorescence spectroscopy. A CD spectrum similar to that in solution was observed with **1**, affording large CD signals suggestive of exciton coupling in the ^1B_b band of the naphthalene chromophore. **2**, on the other hand, gave a CD spectrum much different from that in solution, suggesting that intermolecular interactions brought about by molecular packing give rise to significant changes in polymer conformation and thus in side-chain orientation. These films showed pseudo-second-order transitions at ca. 130 °C, which apparently relate to the onset of collective motion of the side chains. While the IR spectra initially show that the side-chain amide groups are extensively hydrogen-bonded, their changes upon annealing suggest that **2**, unlike **1**, undergoes considerable deformation of the α-helical main chain, causing marked changes in CD. Using the corresponding copolymers having 1.9 and 1.6 mol % of pyrene chromophore (**3** and **4**) and observing total quenching of naphthalene fluorescence by the pyrene chromophore in film, we confirmed efficient singlet excitation energy transport among the naphthalene chromophores. When the copolymers were dispersed in the corresponding homopolymers, we found that the film of 2 wt % of **4** in **2**, particularly after annealing, gives a significantly higher efficiency of excitation energy transport than that of **3** in **1**, evidently reflecting better controlled chromophore orientation of **2** compared with that of **1**.

Introduction

Polymers having chromophores in the side chains can transport excitation energy or charge one-dimensionally along the polymer chain[1,2] and thus can be regarded as potential molecular wires to be used in future microprocessors and other devices. The polymer structures, however, need to be well designed to suppress formation of traps such as excimers and ground-state dimers while facilitating transport of energy and charge.[3] We now know that excimer formation strongly depends on the chromophore structure in the side chains[4,5] and the stereoregularity of the main chain,[5,6] both of which control the total polymer conformation and thus the mutual orientation of the side-chain chromophores.

Chromophores introduced in the side chains of polypeptides are arranged at regular intervals along the helical main chain and can be further oriented with respect to one another and with respect to the main chain by the side-chain/side-chain and side-chain/main-chain interactions.[7−9] In our previous studies, we prepared poly(L-glutamines), i.e., diastereomeric poly[N^5-(*R*)- and N^5-(*S*)-1-(1-naphthyl)ethyl-L-glutamines] (**1** and **2**), where chiral (*R*)- or (*S*)-1-(1-naphthyl)ethyl groups are introduced in the side chains via amide linkage, and examined their fluorescence and CD spectra in dioxane as well as in mixed solvents of dioxane and trifluoroacetic acid (TFA).[10,11] The side-chain naphthalene chromophores in **1** are found to be rather rigidly oriented along the helical main chain in dioxane, suppressing excimer formation and giving rather strong CD signals indicative of exciton coupling in the ^1B_b band of the naphthalene chromophore. The rigid nature of the side-chain amide linkage as well as the steric effects among the bulky side chains evidently plays an important role in orienting the naphthalene chromophores. Addition of TFA up to ca. 40 vol %, while still maintaining the α-helical conformation of the main chain, diminishes CD signals and enhances excimer emission, suggesting disruption of the chromophore orientation in **1**. **2**, on the other hand, shows significant excimer emission and somewhat weak CD signals in dioxane, suggesting less rigid chromophore orientation. Initial addition of TFA, i.e., up to ca. 20 vol %, loosens chromophore orientation still further, but further TFA addition brings about increased chromophore orientation, giving enhanced CD signals and suppressing excimer formation. Increased solvation of the side chains by TFA apparently disrupts hydrogen-bonding interactions among the side chains and leads to significant changes in side-chain conformation and thus in chromophore orientation.

In the present study, we examined the CD spectra of **1** and **2** in film and their changes upon annealing to see, together with changes in IR spectra, how intermolecular interactions in film affect the hydrogen-bonding interactions among the side-chain amide groups and the orientation of the side-chain chromophores. Excitation energy transport in **1** and **2** was also examined using copolymers having small amounts of pyrene chro-

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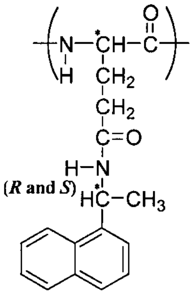
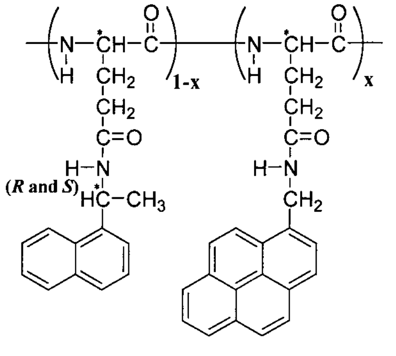
mophore as an energy acceptor to see how the chromophore orientation and its changes upon annealing affect the energy transport efficiency in these polymers.



1: ***R***
2: ***S***



3: ***R*** **(x=0.019)**
4: ***S*** **(x=0.016)**

Experimental Section

Materials. The side-chain methyl esters of poly(γ-methyl-L-glutamate) (DP 700), obtained from Ajinomoto Co., Ltd., Tokyo, were first converted to 2-chloroethyl esters, hydrolyzed, and then reacted with (*R*)- and (*S*)-1-(1-naphthyl)ethylamines (Tokyo Kasei Co., Ltd., Tokyo) to obtain **1** and **2** using *N*,*N*′-dicyclohexylcarbodiimide and 1-hydroxybenzotriazole as condensing agents as previously described.[10] Elemental analysis and ^{1}H NMR spectroscopy in trifluoroacetic acid-*d* confirmed full derivatization of the side-chain carboxyl groups. The monomeric model compounds, i.e., (*R*)- and (*S*)-1-(1-naphthyl)-ethylacetamides, were prepared from the corresponding amines and acetyl chloride.

Poly[N^5-(*R*)- and N^5-(*S*)-1-(1-naphthyl)ethyl-L-glutamine-*co*-N^5-1-pyrenylmethyl-L-glutamines] (**3** and **4**) were prepared by treating the poly(L-glutamic acid) first with 1-pyrenylmethylamine (Aldrich Co., Ltd., New York) and then with (*R*)- and (*S*)-1-(1-naphthyl)ethylamines. Using the molar extinction coefficient of 1-methylpyrene, i.e., $\epsilon_{344} = 38\,000$ L mol^{-1} cm^{-1}, the contents of the pyrenyl moiety in **3** and **4** were determined as 1.9 and 1.6 mol %, respectively.

Measurements. UV absorption and fluorescence spectra were recorded on a Hitachi U-3210 spectrophotometer and on a Hitachi F-4010 fluorescence spectrophotometer, respectively. CD spectra were recorded on a JASCO J-500A circular dichrograph. Films were prepared by casting 50 μL of DMAc solutions onto 2.5 cm^2 quartz plates. The solvent was removed in vacuo at room temperature. Film thickness in terms of naphthalene mol cm^{-2} was determined by rotating the sample with 45° intervals, averaging observed absorptions, and applying the molar extinction coefficient of the homopolymer, i.e., $\epsilon_{283} = 6700$ L mol^{-1} cm^{-1} or 6.7×10^6 cm^2 mol^{-1}. Macroscopic anisotropy in the film, i.e., excessive alignment of polymer chains or, to be more exact, that of transition moments therein, in any one direction, was checked by measuring the absorption spectra using vertically and horizontally plane-polarized light and observing differences in spectral shape and intensity, i.e., linear dichroism (LD). This was repeated by rotating the film by 45°. When the film was thin, e.g., $<1 \times 10^{-8}$ dmol cm^{-2}, significant LD was often observed, suggesting that the plate surface can cause macroscopic anisotropy in the film. Such a film gave, in addition to the CD of the thicker film, spurious CD due to LD and linear birefringence (LB), which resembles the absorption spectrum in spectral shape and changes its magnitude and sign upon film rotation.[12] When the film was ca. 5×10^{-8} mol cm^{-2} in thickness, it gave no detectable LD. The observed CD spectrum did not change significantly upon film rotation, showing split signals indicative of exciton coupling unlike spurious CD due to LD and LB. The CD intensities measured by rotating the film were then averaged to obtain the molar ellipticity using the average film thickness.

IR spectra were recorded on a JASCO JIR-7000 FT-IR spectrophotometer by using the KBr pellet method. Wide-angle X-ray diffraction (XRD) measurements were performed on films cast on glass plates using a MacScience MXP X-ray diffractometer with Cu Kα radiation. Differential scanning calorimetry (DSC) was conducted on a MacScience 3100S differential scanning calorimeter. The heating rate was 10 deg min^{-1}. ^{1}H NMR spectra were measured using a JEOL LA-500 MHz spectrometer. Elemental analysis was carried out on a CHN Perkin-Elmer 2400 elemental analyzer. Annealing was performed by heating each film in vacuo for 1 h.

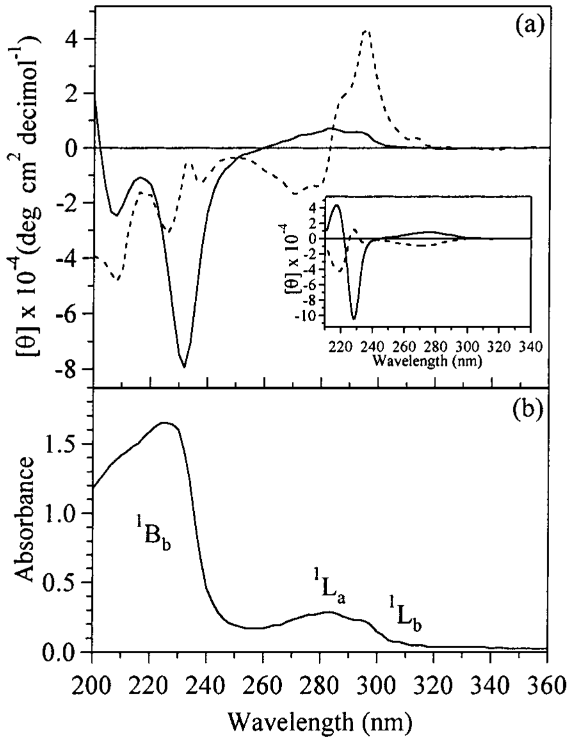


Figure 1. (a) CD spectra of films prepared from **1** (—) and **2** (- - -) at room temperature. (b) UV absorption spectrum of film prepared from **1**. [Naph] = 4×10^{-8} mol cm^{-2}. Inset is the CD spectra of **1** (DP 70) (—) and **2** (- - -) in dioxane. [Naph] = 1.0×10^{-4} M, cell length = 2 mm. CD intensities are expressed in terms of naphthalene concentration.

Results and Discussion

CD Spectra of Poly(L-glutamines). The CD spectra of films prepared from **1** and **2** by casting from DMAc are shown in Figure 1. **1** gives a CD spectrum, similar to that in dioxane (inset in Figure 1), showing rather strong CD signals suggestive of exciton coupling of negative exciton chirality, i.e., negative first and positive second Cotton effects, in the ^{1}B$_b$ band of the naphthalene chromophore.[13] (However, in addition to CD due to α-helical main chain,[14] that due to exciton interaction between the naphthalene ^{1}B$_b$ transition and the amide transitions in the main chain and side chains may also appear in the same wavelength region as has been pointed out for closely placed transitions with comparable transition energies.[13]) **2**, on the other hand, affords a CD spectrum much different from that in dioxane, giving exciton coupling of positive exciton chirality in the ^{1}L$_a$ band. It is thus suggested that intermolecular interactions in the film bring about significant changes in polymer conformation and in side-chain orientation. (In dioxane, both **1** and **2** afforded CD signals in the ^{1}L$_a$ band similar to those of the corresponding monomeric model compounds, evidently reflecting only the local chirality of the side chains.)

XRD of films prepared from **1** and **2** shows rather high crystallinity and gives, in addition to a broad peak due

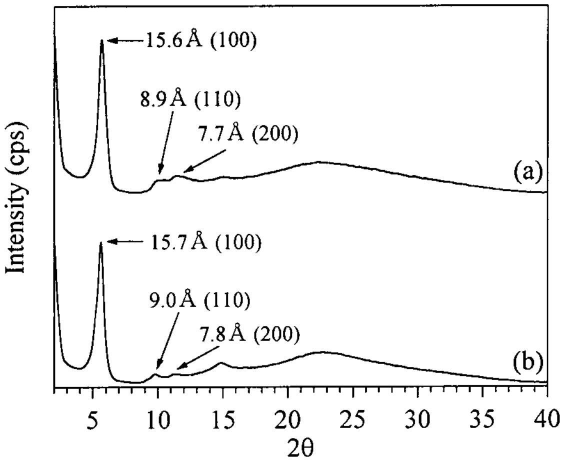


Figure 2. X-ray diffraction of films prepared from **1** (a) and **2** (b).

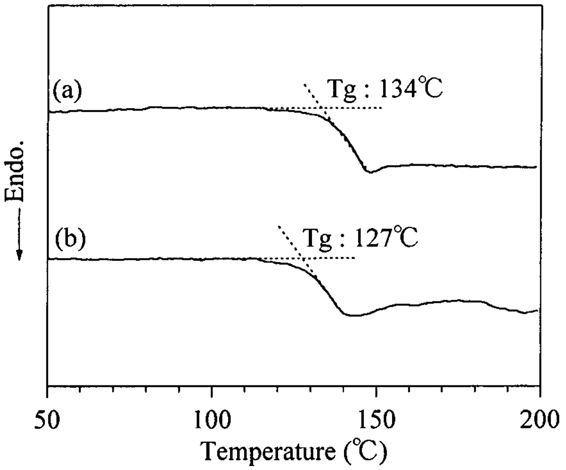


Figure 3. DSC traces of films prepared from **1** (a) and **2** (b).

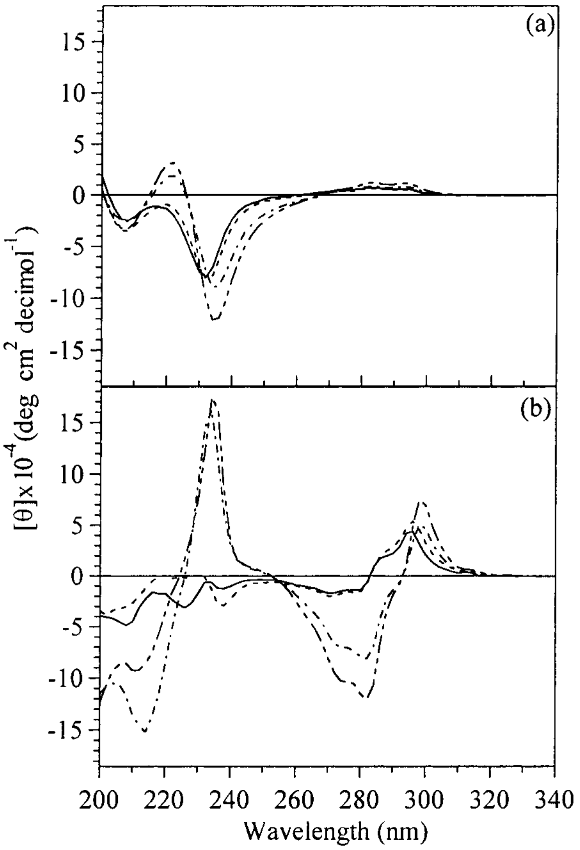


Figure 4. (a) CD spectra of film prepared from **1**: as cast (—) and annealed at 110 °C (- - -), at 180 °C (- • -), and at 200 °C (- • • -). (b) CD spectra of film prepared from **2**: as cast (—) and annealed at 110 °C (- - -), at 170 °C (- • -), and at 200 °C (- • • -). CD intensities are expressed in terms of naphthalene concentration.

to amorphous region, peaks corresponding to hexagonal lattices (Figure 2). As with other polypeptides cast from particular solvents,[15] cholesteric liquid crystal structures formed in concentrated DMAc solutions apparently collapse to form hexagonal lattices as the solvent evaporates.

DSC, on the other hand, shows pseudo-second-order transitions similar to glass transitions of amorphous polymers (Figure 3). These apparently correspond to the onset of collective motion of the side chains.[16] The observed transition temperatures, i.e., 134 and 127 °C for **1** and **2**, suggest that the side chains of **1** are slightly more rigid compared with those of **2**.

The CD spectra of **1** and **2** do not change appreciably upon annealing at temperatures below the above transition temperatures (Figure 4). When annealed at temperatures higher than the transition temperature, **1** undergoes monotonic changes in CD, eventually giving a spectrum very much similar to that in dioxane (Figure 4a). **2**, on the other hand, undergoes more distinct changes upon annealing above the transition temperature (Figure 4b): a rather strong positive peak appears in the ^1B_b band, i.e., at ca. 235 nm, and the splitting at the ^1L_a band becomes increasingly less symmetric with the negative peak at ca. 280 nm growing much faster than the positive one at ca. 300 nm.

IR Spectra of Poly(L-glutamines). The IR spectra are shown in Figures 5 and 6. Initially, these films show virtually no free amide N−H absorption, normally observed at ca. 3440 cm^{-1}, suggesting that the side-chain amide groups are extensively hydrogen-bonded with one another or, though less likely, with the main-chain amide groups. Upon annealing at 110 °C, i.e., a temperature below the transition temperatures, both **1** and **2** show significant decrease in hydrogen-bonded amide carbonyl absorption at ca. 1625 cm^{-1} and slight increase in free amide carbonyl absorption at ca. 1680 cm^{-1} with concurrent broadening of the amide N−H absorption to the higher wavenumber (Figure 5). Taken together, these changes suggest that full hydrogen bonds apparently formed among the side-chain amide groups are broken and converted to partial hydrogen bonds. This, however, does not lead to significant changes in chromophore orientation of either **1** or **2** as no significant CD changes are observed after annealing at 110 °C (Figure 4). When the annealing temperature is raised above the transition temperatures, **1** shows only small changes in IR, suggesting that most of breakable hydrogen bonds have already been broken at 110 °C. **2,** on the other hand, shows further decrease of 1625 cm^{-1} absorption and emergence of free amide N−H absorption at ca. 3415 cm^{-1}, which is accompanied by a marked shift, i.e., ca. 20 cm^{-1}, of the amide N−H absorption peak to the higher wavenumber. The observed peak shift suggests a major reorganization of hydrogen bonds among the side-chain and main-chain amide groups and a considerable deformation of the α-helical main chain, which must lead to a marked change of chromophore orientation as revealed by the large CD changes (Figure 4b).

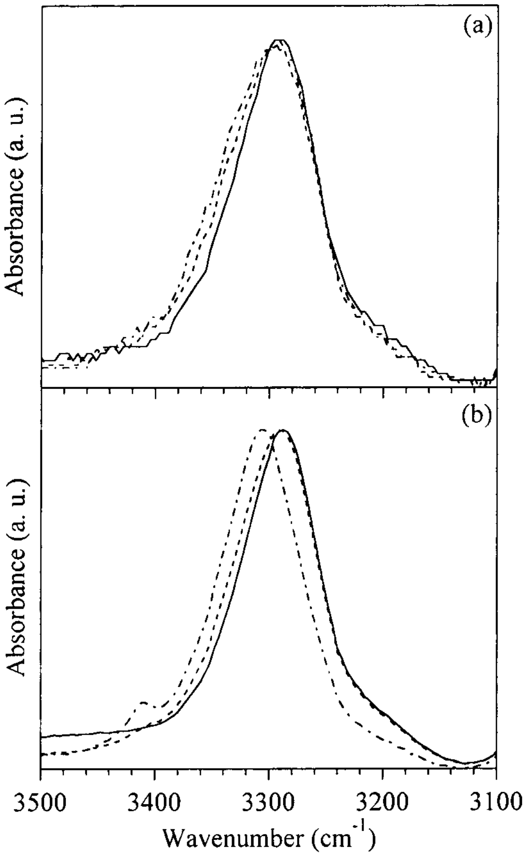


Figure 5. Amide N−H absorption of films prepared from **1** (a) and **2** (b), normalized at the peak top: as cast (—) and annealed at 110 °C (- - -) and at 200 °C (- • -).

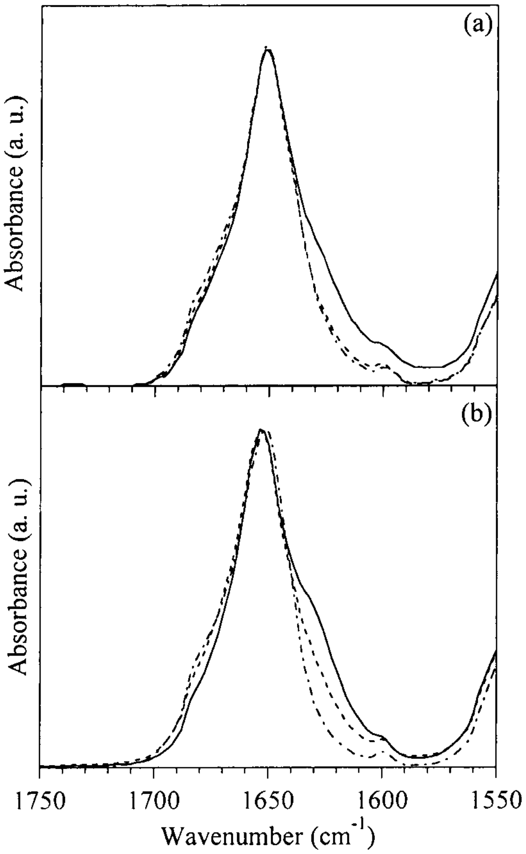
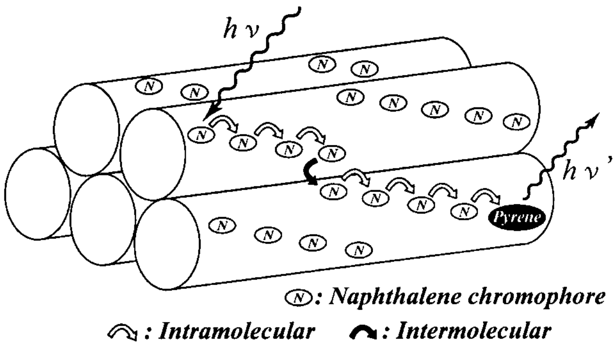


Figure 6. Amide carbonyl absorption of films prepared from **1** (a) and **2** (b), normalized at the peak top: as cast (—) and annealed at 110 °C (- - -) and at 200 °C (- • -).

Fluorescence and Excitation Energy Transport of Poly(L-glutamines). In Figure 7 are shown the fluorescence spectra of **1** and **2** in DMAc together with those of the corresponding copolymers having pyrenyl moieties, i.e., **3** and **4**. As reported previously, **1** gives very little excimer emission while **2** affords appreciable excimer emission around ca. 400 nm in accord with the weaker CD of the latter, suggesting the less rigid chromophore orientation of **2** in solution. When excited at 292 nm, where absorption by pyrene chromophore is negligible, **3** and **4** give significant pyrene fluorescence with decreased naphthalene fluorescence, indicating transfer of naphthalene excitation energy to the pyrene chromophore. The extent of transfer is notable when one considers the small pyrene contents in the copolymers, i.e., 1.9 and 1.6 mol %. No remarkable difference, however, is noted between **3** and **4**. In film, **3** and **4** give no naphthalene fluorescence, and only pyrene fluorescence is observed as shown for **4** in Figure 8. (As also shown in Figure 8, the corresponding homopolymer gives rather strong excimer emission around 400 nm, indicating extensive trapping of migrating energy at excimer-forming sites.) In film, efficient intermolecular as well as intramolecular energy migration thus leads to total transport of the naphthalene excitation energy, via migration and transfer, to the pyrene sites. Again, no difference between **3** and **4** is observed: energy transport is so efficient in both films that we do not see a difference reflecting the side-chain orientations.

Scheme 1. Schematic Illustration of Energy Transport in Copolymer-in-Homopolymer Film



While no appreciable differences in CD in the naphthalene absorption region are noted between the homopolymers and the copolymers, induced CD signals of opposite signs are observed in the ^1L_a band of the pyrene chromophore (Figure 9), suggesting that the pyrene chromophores in **3** and **4** are in the unique chiral environments provided by the main chain and the respective 1-(1-naphthyl)ethyl side groups. (In solution, neither **3** nor **4** gives corresponding CD signals in the pyrene absorption region. Apparently, the side chains, whose orientation fluctuates in solution, do not provide a chiral environment rigid enough to induce pyrene CD.) In accord with better controlled side-chain orientation of **2** suggested by CD, **4** gives more intense induced pyrene CD than **3** despite its lower pyrene content. As we did not see the expected difference in energy transport efficiency in film, we prepared mixed films of the copolymers (2 wt %) with the corresponding homopolymers, designated as **3**-in-**1** and **4**-in-**2** films, respectively, and examined their energy transport efficiencies (see Scheme 1). We now observed a significant difference in sensitization of pyrene fluorescence be-

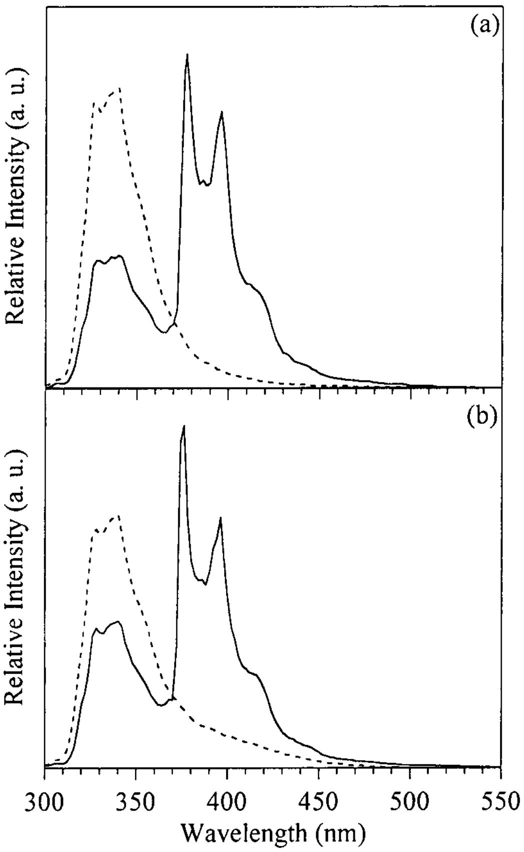


Figure 7. Fluorescence spectra of (a) **1** (- - -) and **3** (—) and those of (b) **2** (- - -) and **4** (—) in DMAc at 20 °C. [Nap] = 1 × 10^{-5} M, λ_{ex} = 292 nm.

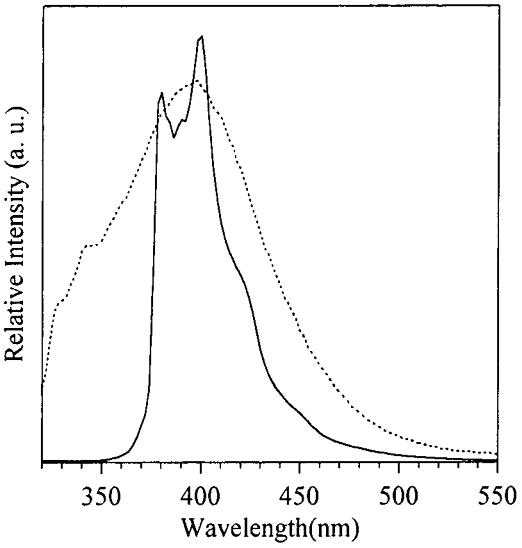


Figure 8. Fluorescence spectra of films prepared from **2** (···) and **4** (—). λ_{ex} = 292 nm.

tween the two films as shown in Figure 10a. The more enhanced orientation of side-chain naphthalene chromophores in the **4**-in-**2** film apparently leads to more efficient energy transport to the pyrene chromophores. Intermolecular energy transport between the naphthalene chromophores on the adjacent polymer chains either within the crystal domain or across the neighboring crystal domains no doubt plays an important role in film. Even though we cannot completely rule out that the intermolecular energy transport efficiency differs significantly between **1** and **2**, we may attribute the observed difference mostly to that in intramolecular energy transport. When these films are annealed at 200 °C, one observes improvement of sensitization of pyrene fluorescence in both films (Figure 10b). The improvement, however, is much larger for the **4**-in-**2** film, apparently reflecting much improved chromophore orientation of **2** upon annealing.

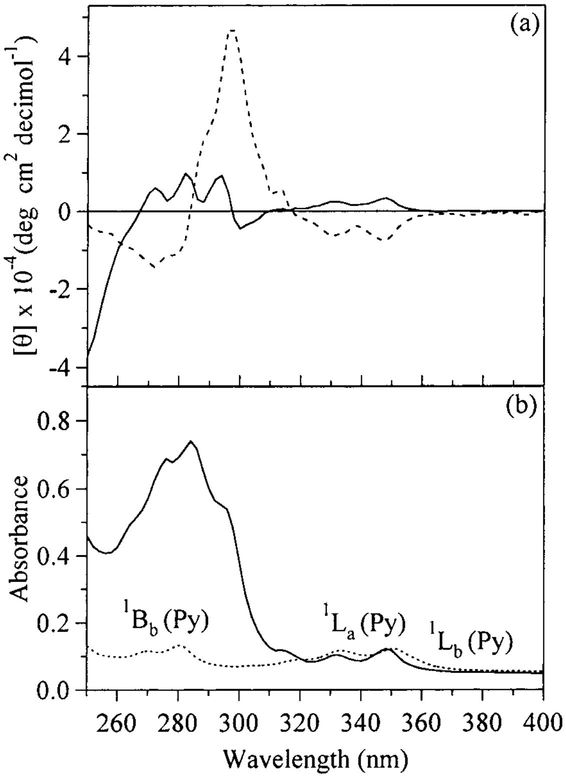


Figure 9. (a) CD spectra of films prepared from **3** (—) and **4** (- - -). [Naph] = 1 × 10^{-7} mol cm^{-2}. (b) UV absorption spectra of films prepared from **3** (—) and that of poly[N^5-1-pyrenylmethyl-L-glutamine] (• • •). The absorption spectrum of poly[N^5-1-pyrenylmethyl-L-glutamine] film is adjusted so as to have an intensity at ca. 350 nm comparable to that of **3**. CD intensities are expressed in terms of naphthalene concentration.

We are yet to know the exact structures of **1** and **2** in film. Structural analysis by molecular mechanics calculations and evaluation of theoretical CD of the low-energy structures obtained thereby will afford, in conjunction with the IR and CD data, an insight into the actual structures of **1** and **2** in solution as well as in film. In the present study, we focused our attention on the mutual orientation of the naphthalene chromophores as revealed by CD. As mentioned in the Experimental Section, these films show negligible macroscopic anisotropy, indicating undirectional distribution of crystal domains, which enabled us to examine the chromophore orientation of each polymer by CD in the present study. Alignment of the crystal domains in one direction, e.g., by drawing a concentrated solution, however, is important in bringing anisotropy to excitation energy transport in films. Work along this line is in progress and will be reported in a future publication.

Conclusion

While in solution the side-chain orientation of **1** is apparently better controlled than that of **2**, intermolecular interactions in film bring about better side-chain orientation of **2** compared with that of **1**. The breaking

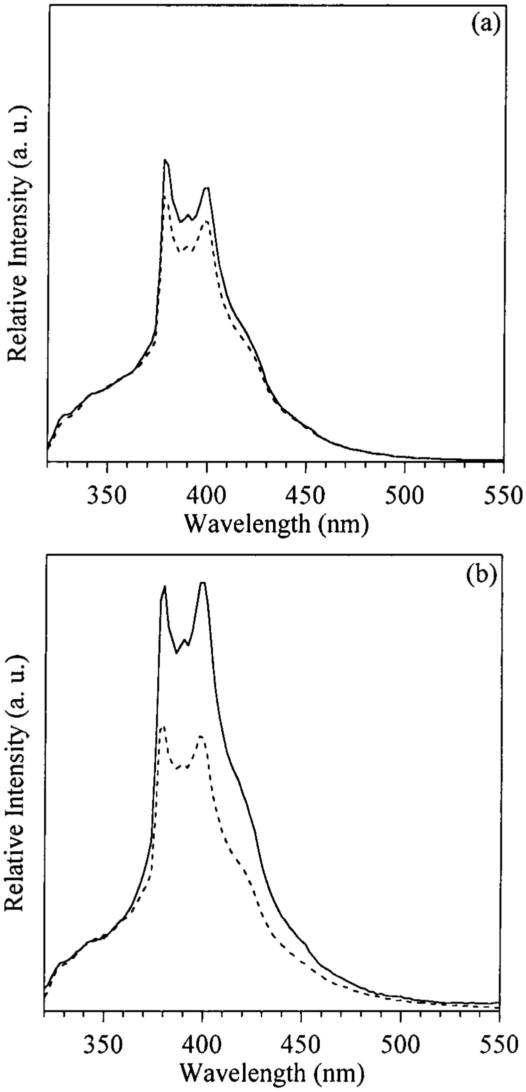


Figure 10. Fluorescence spectra, normalized at 340 nm, of **3**-in-**1** film (- - -) and **4**-in-**2** film (—): as cast (a) and annealed at 200 °C (b). $\lambda_{ex} = 292$ nm.

of the full hydrogen bonds formed among the side-chain amide groups, which occurs upon annealing below the pseudo-second-order transition temperatures, does not significantly affect the side-chain orientation of either **1** or **2**. Upon annealing above the transition temperature, considerable deformation of the α-helical main chain occurs with **2**, which leads to a marked change in its CD. Efficient transport of excitation energy leading to sensitized pyrene fluorescence observed with the film of **4** dispersed in **2**, particularly after annealing, evidently reflects the better controlled chromophore orientation of **2** as compared with that of **1**.

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