Secondary Structure and Side-Chain Chromophore Orientation in Poly(L-glutamines) Having Pyrene Chromophores in the Side Chains

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ABSTRACT: Poly(L-glutamines) with pyrene groups in the side chains (PPyMLGln) having different degrees of polymerization, i.e., DP 700, 360, and 70, and those with 45 and 25 mol % in pyrene content (PPy(45)MLGln (DP 360) and PPy(25)MLGln (DP 360)) were prepared, and their side-chain chromophore orientation was examined in solution and in film. In DMAc, these polymers, except PPy(25)MLGln, showed circular dichroism (CD) indicative of exciton coupling among the pyrene chromophores, suggesting that despite the long side chains the pyrene chromophores are oriented with respect to the main chain and with respect to one another owing to the rigid side-chain amide linkage and the bulkiness of the pyrene chromophores. In film, PPyMLGln (DP 700) showed CD signals remarkably different from those of the other polymers, suggesting that intermolecular interactions lead to a change in side-chain as well as main-chain conformation and thus to a change in chromophore orientation. Molecular mechanics calculations gave two regulated conformations with theoretical CD in accord with those observed with PPyMLGln (DP 700) in solution and in film, respectively. In DMAc, these polymers gave excimer emission whose intensity decreased with decreasing DP and decreasing pyrene content. Diminished excimer emission and rather strong exciton coupling found with PPy(45)MLGln suggest that many of its pyrene groups are situated in proximity and orientation, allowing exciton interaction but not allowing excimeric interaction.

Introduction

Over the past few decades a considerable number of studies have been carried out on the photoexcitation energy and charge transport in polymers having aromatic and other chromophores in the side chains. [1−6] If excitation energy and charge are transported efficiently through the side-chain chromophores, we would have "molecular wires" capable of transporting excitation energy and charge one-dimensionally along the polymer chain. However, the chromophores need to be highly oriented to bring about efficient energy and charge transport through the pendant chromophores. Sisido et al. reported the side-chain orientation of polyalanine having naphthalene and other aromatic chromophores in the side chains.[2] They observed strong CD signals indicative of exciton coupling at the absorption bands of the chromophores and suggested that the short side chains are required for chromophore orientation along the helical main chain. In fact, poly(L-glutamates) with naphthalene chromophores introduced in the side chains via ester linkage did not show evidence for exciton coupling,[7,8] indicating that the orientation of chromophores placed at the ends of the relatively long and flexible side chains is not well controlled.

In our previous studies, we prepared poly(L-glutamines) where naphthyl groups are introduced in the side chains via amide linkage, i.e., poly[N^5-(1-naphthyl)methyl-L-glutamine] (PNMLGln) and poly[N^5-(*R* or *S*)-1-(1-naphthyl)ethyl-L-glutamine] (P(*R* or *S*)NELGln) and examined how the amide linkage and the side-chain structure affect the chromophore orientation.[9,10] P(*R* or *S*)NELGln gave, in solution, strong CD signals indicative of exciton coupling at the ^1B_b band of naphthalene chromophore. We concluded that the bulkiness of the 1-(1-naphthyl)-ethyl groups, together with the rigid side-chain amide linkage, plays a critical role in orienting the naphthalene chromophores.

In the present work, we prepared poly(L-glutamines) having pyrene chromophores in the side chains, i.e., poly[N^5-1-(1-pyrenyl)methyl-L-glutamine] (PPyMLGln of DP 700, 360, and 70), and the corresponding copolymers with 45 and 25 mol % in pyrene content, i.e., PPy(45)-MLGln (DP 360) and PPy(25)MLGln (DP 360). The secondary structure and side-chain orientation of these polymers were explored by molecular mechanics calculations and theoretical CD of the low-energy structures obtained thereby. We are particularly interested in how differences in degree of polymerization and those in pyrene content affect side-chain orientation in solution and in film.

Experimental Section

Polymer Synthesis. PPyMLGln samples were prepared from poly(L-glutamic acid) and 1-pyrenylmethylamine using *N*,*N*-dicyclohexylcarbodiimide and 1-hydroxybenzotriazole as condensing agents as described previously.[9,10] Poly(L-glutamic acid) (DP 700) were obtained by hydrolyzing poly(γ-methyl-L-glutamate) supplied by Ajinomoto Co., Ltd. Poly(L-glutamic acid) (DP 360 and 70) and 1-pyrenylmethylamine hydrochloride were obtained from Aldrich Co. Elemental analysis and ^{1}H NMR confirmed full derivatization of the side-chain carboxyl groups. Two samples of poly[N^5-1-(1-pyrenyl)methyl-L-glutamine-*co*-L-glutamic acid], i.e., PPy(45)MLGln (DP 360) and PPy(25)MLGln (DP 360), were prepared likewise using

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Scheme 1

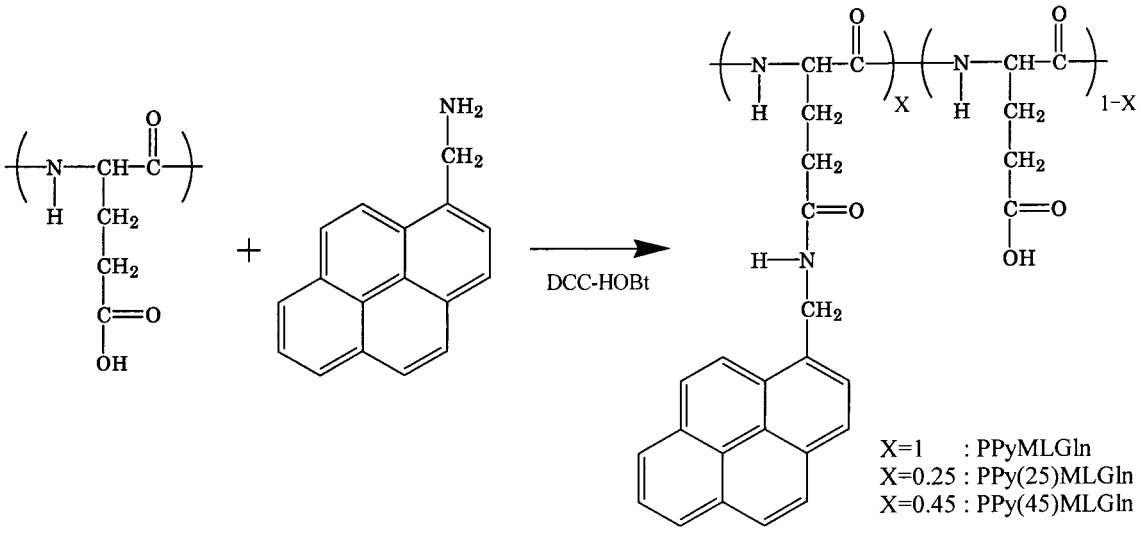


Table 1. Search for Low-Energy Conformations

conformation	conformational energy (kcal/monomer unit mol)	dihedral angles (deg)					
		$\chi1$	$\chi2$	$\chi3$	$\chi4$	$\chi5$	$\chi6$
1	−4.56	180.0	60.0	60.0	180.0	150.0	90.0
2	−4.43	180.0	150.0	90.0	180.0	120.0	270.0
3	−3.64	180.0	150.0	90.0	180.0	180.0	90.0
4	−3.24	180.0	180.0	90.0	180.0	90.0	330.0
5	−3.14	180.0	210.0	90.0	180.0	210.0	90.0
6	−3.11	180.0	180.0	150.0	180.0	180.0	120.0
7	−3.03	180.0	180.0	120.0	180.0	180.0	120.0
8	−3.02	180.0	150.0	270.0	180.0	180.0	240.0
9	−3.01	180.0	180.0	180.0	180.0	150.0	120.0
10	−2.95	180.0	60.0	90.0	180.0	120.0	90.0
11	−2.92	180.0	180.0	90.0	180.0	210.0	240.0
12	−2.86	180.0	180.0	150.0	180.0	150.0	120.0
13	−2.55	180.0	210.0	90.0	180.0	180.0	270.0
14	−2.49	180.0	210.0	120.0	180.0	180.0	240.0
15	−2.49	180.0	60.0	90.0	180.0	90.0	270.0
16	−2.46	180.0	180.0	90.0	180.0	210.0	120.0

one-half and one-quarter the amount of 1-pyrenylmethylamine used in full derivation, respectively. ^{1}H NMR in DMSO-d_6 at 100 °C showed signals for main-chain α-methyne protons at ca. 4.2 ppm, indicating that α-helical conformation is essentially maintained in these polymers[11] (Scheme 1).

Sample Preparation. Films for CD and UV measurements were prepared by casting 50 μL of DMAc solutions onto 2.5 cm^2 quartz plates. The solvent was removed under vacuum at room temperature. Samples for XRD measurement were prepared by casting the DMAc solutions onto glass plates repeatedly until they have appropriate thickness.

Measurements. UV and CD spectra were recorded on a Hitachi U-3210 spectrophotometer and on a Jasco J-500A circular dichrograph, respectively. The CD measurements of the films were performed by rotating the sample by 45° eight times. No CD signals indicative of macroscopic anisotropy were found with any of the films examined. Crystalline domains, if any, are thus distributed uniformly in the films. Steady-state fluorescence spectra were recorded on a Hitachi F-4010 fluorescence spectrophotometer. X-ray diffraction (XRD) was recorded on a MacScience M18XHF X-ray diffractometer with Cu Kα radiation. ^{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.

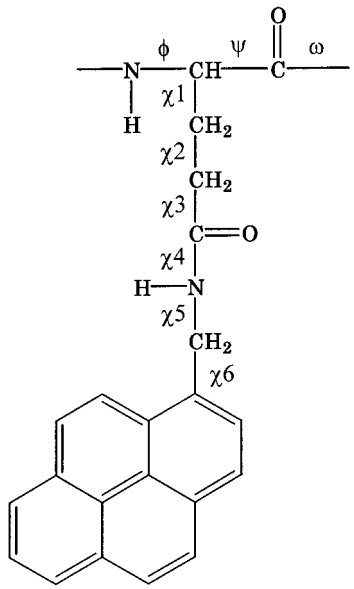
Calculations. Partial charges on the monomer unit were estimated by MOPAC semiempirical molecular orbital calculations.[12] Molecular mechanics calculations were carried out stepwise. Initial energy minimization was performed, by the PEPCON program developed by Sisido,[13] on the 20-mer assuming all the monomer units have a common conformation. Empirical potential functions reported by Scheraga et al. were employed, which include electrostatic, nonbonded van der Waals, hydrogen-bonding, and torsional energies.[14] All the bond lengths and bond angles were fixed at the standard values. Calculation was started by fixing the dihedral angles of the main chain at those of right-handed α-helix ($\phi = -62.5°$, $\psi = -42.3°$, and $\omega = 180°$)[15] and $\chi4$ of the side chain at 180° and varying all the other side-chain dihedral angles, $\chi1$, $\chi2$, $\chi3$, $\chi5$, and $\chi6$, with 30° intervals. Making of this multidimensional "energy contour map" was time-consuming but afforded 16 low-energy spots (Table 1), which led to eight low-energy conformations when optimized simultaneously with respect to $\chi1$, $\chi2$, $\chi3$, $\chi5$, and $\chi6$ (Table 2). Finally, the 40-mer in each of the first five low-energy conformations obtained above was subjected to total optimization by simultaneously varying all the bond lengths, bond angles, and dihedral angles of the main chain as well as those of the side chains using the CAChe MM2 program.[16]

Theoretical CD was evaluated using the exciton chirality method.[17] The directions of transition moments of pyrene have been reported: the first, the second, and the third transitions, located at 360−380, 290−360, and 250−290 nm, are polarized in the directions of short axis, long axis, and short axis and assigned as ^1L_b, ^1L_a, and ^1B_b, respectively, according to Platt's notations.[18−20] The magnitudes of the transition moments were determined from UV absorption as described in ref 17. Each pyrene transition moment vector was placed in the center of the pyrene ring. The mutual orientation of the transition moments of the neighboring pyrene groups and their positions were estimated from the geometries of neighboring pyrene groups in the conformations obtained by the molecular mechanics calculations. Only the interactions between the like transition moments were taken into consideration. Exciton interaction in the ^1L_b transition was not considered due to its

Table 2. Conformations Optimized with Respect to $\chi1$, $\chi2$, $\chi3$, $\chi5$, and $\chi6$

conformation		conformational energy (kcal/monomer unit mol)	dihedral angles (deg)					
			$\chi1$	$\chi2$	$\chi3$	$\chi4$	$\chi5$	$\chi6$
5	A							
7	A							
12	A	−9.28	195.6	204.6	89.7	180.0	186.6	108.0
16	A							
9	A							
6	A							
10	B	−7.20	178.8	62.5	72.4	180.0	136.8	97.2
1	B							
2	C	−7.03	177.7	152.6	64.7	180.0	163.1	257.2
3	D	−6.20	179.0	146.5	90.2	180.0	177.2	106.5
11	E							
14	E	−6.19	188.9	185.6	79.2	180.0	177.7	252.5
13	E							
4	F	−4.36	188.8	185.1	79.0	180.0	89.8	332.6
8	G	−4.16	179.9	161.1	270.5	180.0	176.6	241.9
15	H	−3.16	177.6	60.4	77.5	180.0	107.1	264.0

Chart 1. Definition of Dihedral Angles



small transition moment. The interactions between the amide transitions and the pyrene transitions were not considered as they differ considerably in transition energy. Polymeric electronic states were not considered in the present work, and the overall CD was estimated as a sum of exciton interactions between various pairs of pyrene groups. UV absorption was simply fitted with a Gaussian function to represent the CD profile (Figure 7).

Results and Discussion

CD Spectra of PPyMLGln. No appreciable differences in absorption spectrum are noted on going from the monomeric model compound, i.e., 1-methylpyrene, to PPyMLGln, indicating no significant ground-state interactions are present among the pyrene chromophores in PPyMLGln. The CD spectra of PPyMLGln of DP 700, 360, and 70 measured in DMAc are shown in Figure 1.[21] Even though the side-chain 1-pyrenylmethyl groups are not optically active, PPyMLGln showed CD signals indicative of exciton coupling of positive exciton chirality, i.e., positive first and negative second Cotton effects,[17] in both ^1L_a and ^1B_b bands of pyrene chromophore. Thus, despite the relatively long side chains, exciton chirality is induced in the side chains by the right-handed main-chain α-helix apparently due to the rigidity of the side-chain amide linkage and the steric effects among the bulky pyrene chromophores. (When 1-pyrenylmethyl groups were replaced with 1-naphthylmethyl groups, no appreciable CD except that of the main chain was observed in solution as previously shown.[9] As seen later, PPy(25)MLGln shows no appreciable CD signals in the pyrene absorption region (>250 nm) in DMAc, indicating that the pyrenyl groups, being virtually isolated from one another, apparently have little conformational restriction and therefore do not reflect the main-chain chirality.) The CD spectra were virtually identical except for signal intensities. PPyMLGln of DP 700 showed the most intense CD signals of the three, and that of DP 70 showed the least intense ones. The disturbance at the polymer ends alone does not appear to explain the observed intensity differences. They may reflect differences in exciton band length. A similar observation has been made for poly[L-(1-pyrenyl)alanine]: a shorter polymer showed smaller CD signals.[22]

In film, PPyMLGln (DP 360) showed exciton coupling more or less similar to that in solution except for the intensity (Figure 2). The intensity will depend on the degree of conformational fluctuation in the side chains. PPyMLGln (DP 700), on the other hand, showed strong exciton coupling whose chirality is opposite to that in solution at both ^1L_a and ^1B_b absorption bands. Such a difference in exciton chirality must reflect a difference in intermolecular interactions. The X-ray diffraction of PPyMLGln (DP 700) film gave, in addition to a broad peak due to amorphous region, sharp and intense XRD peaks corresponding to a hexagonal lattice,[23] indicating a relatively high crystallinity (Figure 3). The intermolecular interactions must force the side chains to come near the main chain, which may lead to chromophore orientation different from that in solution or in lower DP film and result in overall exciton coupling of negative exciton chirality. As PPyMLGln (DP 360) has a shorter helical chain and thus weaker intermolecular interactions in film than PPyMLGln (DP 700), the orientations of many of its chromophores are likely to remain as in solution. The weaker CD signals observed with the DP 360 film are consistent with the presence of the two opposing CD signals canceling each other.

In the above argument for films, possible exciton interactions among the pyrene groups of neighboring polymer chains were not taken into account. In studying the arrangement of two α-helical segments in a polypeptide, Nishino et al. introduced a pyrene group to each segment and observed "intermolecular" exciton coupling between the two pyrene groups.[24] In the present case,

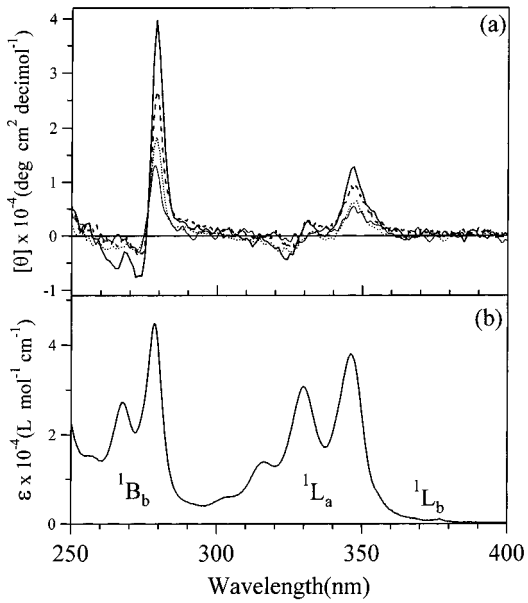


Figure 1. (a) CD spectra of PPyMLGln of DP 700 (thick solid line), DP 360 (- - -), and DP 70 (···) and PPy(45)MLGln(DP 360) (thin solid line) in DMAc at room temperature. [Py] = 2×10^{-3} M; cell length = 0.1 mm. (b) Absorption spectrum of PPyMLGln of DP 360. The CD intensities are expressed in terms of pyrene concentration.

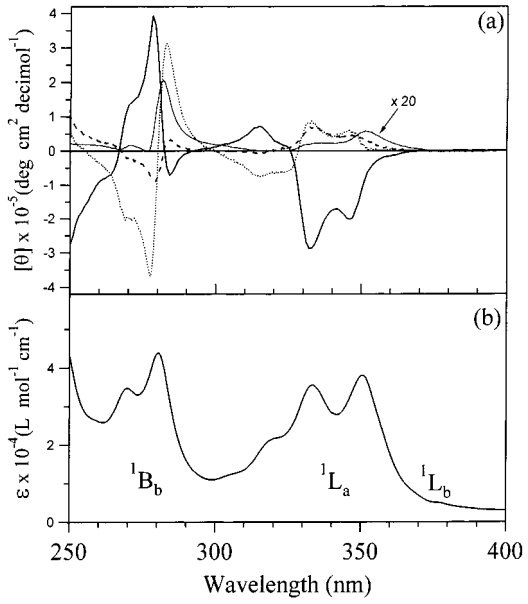


Figure 2. (a) CD spectra of PPyMLGln of DP 700 (thick solid line) and DP 360 (- - -), PPy(45)MLGln (DP 360) (···) and PPy(25)MLGln (DP 360) (thin solid line) in film at room temperature. (b) Absorption spectrum of PPyMLGln (DP 360) in film. The CD intensities are expressed in terms of pyrene concentration. The CD intensity of PPy(25)MLGln (DP 360) is 1/20 that shown.

the bulkiness of pyrene groups and their dense population along the helical main chain likely prevent intermolecular stacking or face-to-face arrangement of the pyrene groups of the neighboring polymer chains. The polymer diameter (ca. 22 Å) obtained for PPyMLGln (DP 700) from the spacings by assuming a hexagonal lattice agrees with ca. 23 Å obtained by molecular mechanics calculation (see below). We, however, cannot completely rule out a contribution of intermolecular exciton coupling in the CD profile.

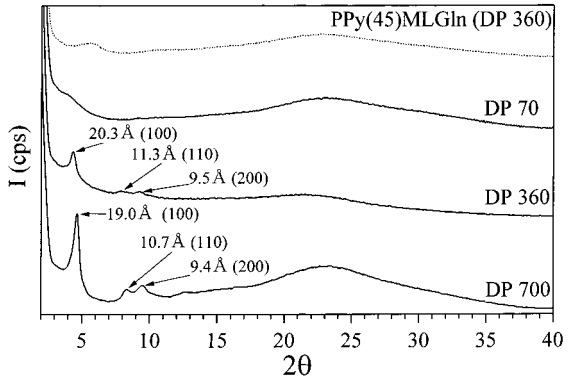


Figure 3. X-ray diffraction of films prepared from PPyMLGln of DP 700, DP 360, and DP 70. X-ray diffraction of film prepared from PPy(45)MLGln (DP 360) is also shown.

Conformational Analysis and Theoretical CD of PPyMLGln. In Table 1 are listed the initial 16 low-energy conformations obtained by fixing ϕ, ψ, and ω at those of the right-handed α-helix[15] and χ4 at 180° and varying χ1, χ2, χ3, χ5, and χ6 with 30° intervals (see Chart 1). They converged to eight conformations A−H when optimized simultaneously with respect to χ1, χ2, χ3, χ5, and χ6 (Table 2). When the first five of these low-energy conformations, A−E, were subjected to full optimization with respect to all structural parameters using the CAChe MM2 program, we obtained the respective conformations, A′−E′, listed in Table 3. Essentially, α-helix is maintained in these structures. However, one notes significant shifts of side-chain dihedral angles, particularly those of χ3 and χ5, on going from A−E to A′−E′. One also notes that while B′ and D′ have rather uniform side-chain conformations, A′, C′, and E′ have large deviations of dihedral angles from the average among the monomer units. Closer examination reveals that A′ has a periodicity composed of five monomer units (Figure 4a) while C′ and E′ have more or less random side-chain conformations. In addition, hydrogen bonds are noted in A′ between the side-chain amide NH and main-chain amide carbonyl groups in two of the five monomer units, e.g., 21st and 22nd monomer units, as indicated in the top view of A′ shown in Figure 5. The dihedral angles vs monomer unit number as well as the side view and top view of one of the more uniform conformations, D′, are shown in Figures 4b and 6.

Even though C′ and E′, or any parts of them, may exist in PPyMLGln in solution or in film, we assume that their overall CD cancels out due to likely random orientation of their pyrene groups. We therefore examined only the theoretical CD of the three regulated conformations A′, B′, and D′ by the exciton chirality method (Figure 7a).[17] In the case of A′, CD varies depending upon which pair of chromophores undergo exciton interaction in the periodic structure. We thus evaluated its CD as a sum of various interactions. CD in the ^1B_b band is found to be dominated by $i/i+2$ and $i/i+3$ exciton interactions of negative exciton chirality, i being any of the five monomer units in the periodic structure. In the ^1L_a band, dominant $i/i+1$ and $i/i+3$ interactions give exciton coupling of negative and positive exciton chirality, respectively, giving an overall CD of negative exciton chirality. Conformation A′ thus gives calculated CD matching that observed with PPyMLGln (DP 700) in film, suggesting that it is the major regulated conformation in well-packed film. Conformation B′, which has a more or less uniform conformation

Table 3. Optimized Conformations of PPyMLGln

conformation	conformational energy (kcal/monomer unit mole)	dihedral angles (deg)								
		ϕ	ψ	ω	$\chi1$	$\chi2$	$\chi3$	$\chi4$	$\chi5$	$\chi6$
A′	−65.8	−66.0[a]	−40.1	174.1	184.4	210.2	129.5	186.4	142.0	114.4
		± 26.0[b]	± 32.8	± 11.3	± 21.7	± 34.6	± 64.4	± 10.4	± 27.2	± 23.0
B′	−64.8	−69.1	−35.9	175.7	185.8	63.2	54.2	175.8	153.9	100.3
		± 14.1	± 12.8	± 8.4	± 2.8	± 4.1	± 4.2	± 2.6	± 7.1	± 6.1
C′	−64.4	−63.8	−42.9	180.1	185.6	185.4	353.6	181.5	216.2	275.3
		± 9.7	± 15.9	± 5.5	± 9.0	± 24.4	± 78.6	± 13.1	± 66.9	± 41.9
D′	−62.5	−58.7	−44.4	181.1	179.3	171.3	51.6	174.7	192.5	110.4
		± 4.2	± 5.6	± 2.0	± 3.9	± 2.8	± 2.9	± 0.9	± 5.1	± 2.9
E′	−64.5	−66.6	−40.1	176.7	183.3	184.2	106.8	181.8	159.9	248.6
		± 21.9	± 16.0	± 22.9	± 29.5	± 10.4	± 89.6	± 6.3	± 64.4	± 7.8

[a] The average of 10 monomer units in the middle of 40-mer. [b] Maximum deviation from the average.

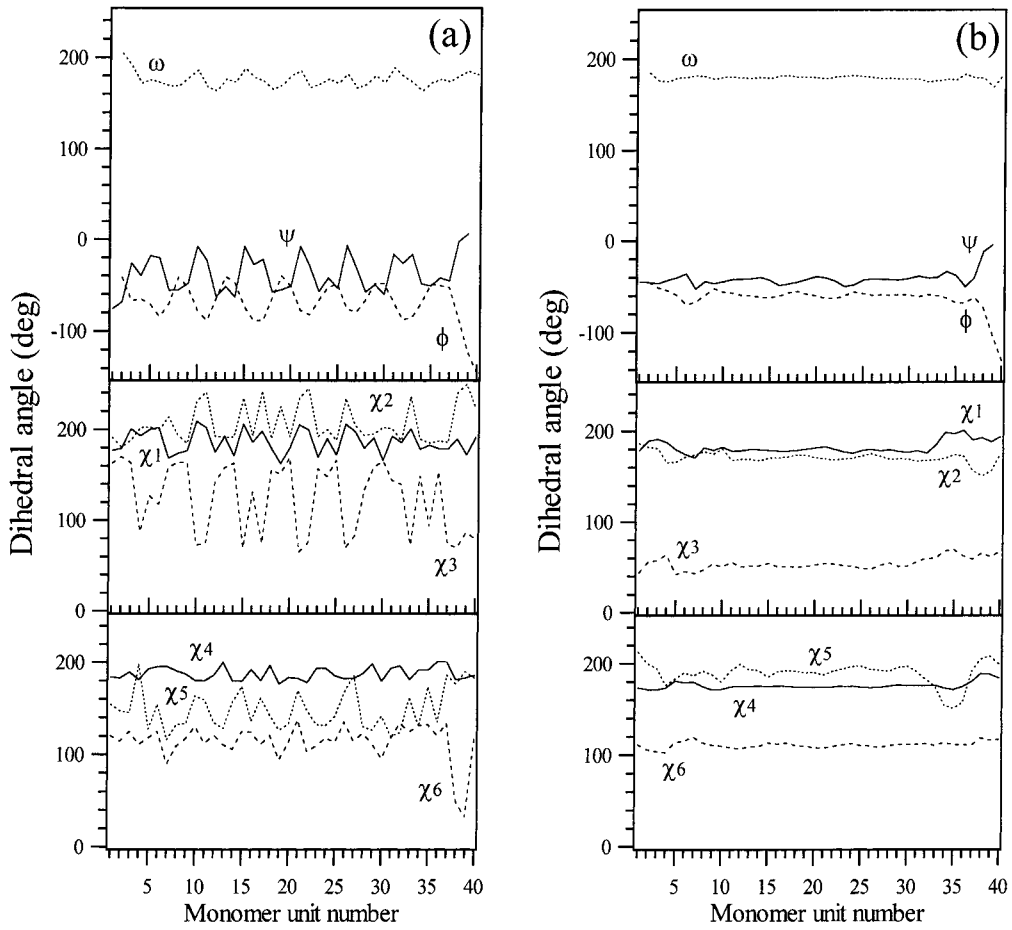


Figure 4. Dihedral angles of (a) conformation A′ and (b) conformation D′ of PPyMLGln vs monomer unit number. Monomer units are numbered from the N-end to the C-end of the polypeptide.

as D′, gives dominant *i*/*i*+3 and *i*/*i*+4 interactions of opposing exciton chiralities both in the ^1L_a band and in the ^1B_b band, affording exciton interactions of opposite exciton chiralities in the two absorption bands. The calculated CD of D′ in the ^1L_a band is dominated by *i*/*i*+1 and *i*/*i*+2 interactions of positive exciton chirality and that in the ^1B_b band by *i*/*i*+3 and *i*/*i*+4 interactions also of positive exciton chirality, which matches that observed with PPyMLGln in solution, suggesting that it is the major regulated conformation in solution. While A′ and D′ are thus likely to be the major regulated conformation in film and that in solution, that does not exclude that other conformations including B′, C′, and E′ are also present in part in solution as well as in film. We may also have to take the results of CD calculation with some reservation because of the limitations of the exciton chirality method being applied to the polymeric systems. Nonetheless, we believe the regular arrangements of the pyrenyl groups in A′ and D′ are good candidates for those giving the exciton interactions in film and in solution.

CD Spectra of PPy(45)MLGln and PPy(25)-MLGln. PPy(45)MLGln (DP 360) in DMAc showed exciton coupling of positive chirality resembling that of PPyMLGln (DP 70) in signal intensity as shown in Figure 1. PPy(45)MLGln must thus have many of its pyrene groups in proximity and orientation similar to those in PPyMLGln (DP 70). In theory, a partial block copolymer may be formed. Its extensive formation, however, is unlikely considering the steric effects of the pyrene groups in their introduction to the polymer side chains. We might assume that PPy(45)MLGln has some characteristic of an alternating copolymer and that many of its pyrene chromophores are situated in every

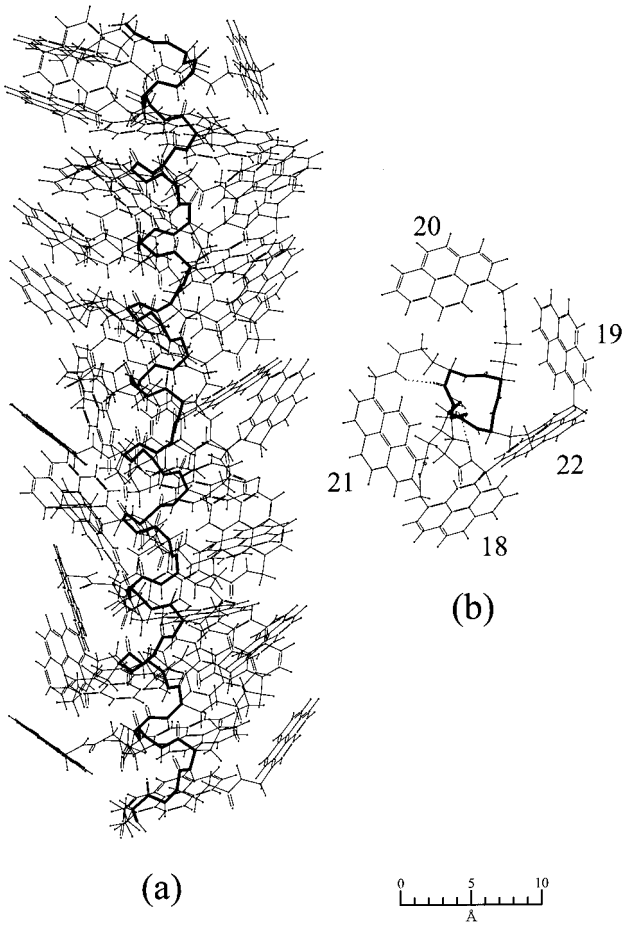


Figure 5. (a) Side view and (b) top view (five monomer units in the middle of 40-mer) of PPyMLGln in conformation A′. Dotted lines in (b) indicate side-chain/main-chain hydrogen bonding.

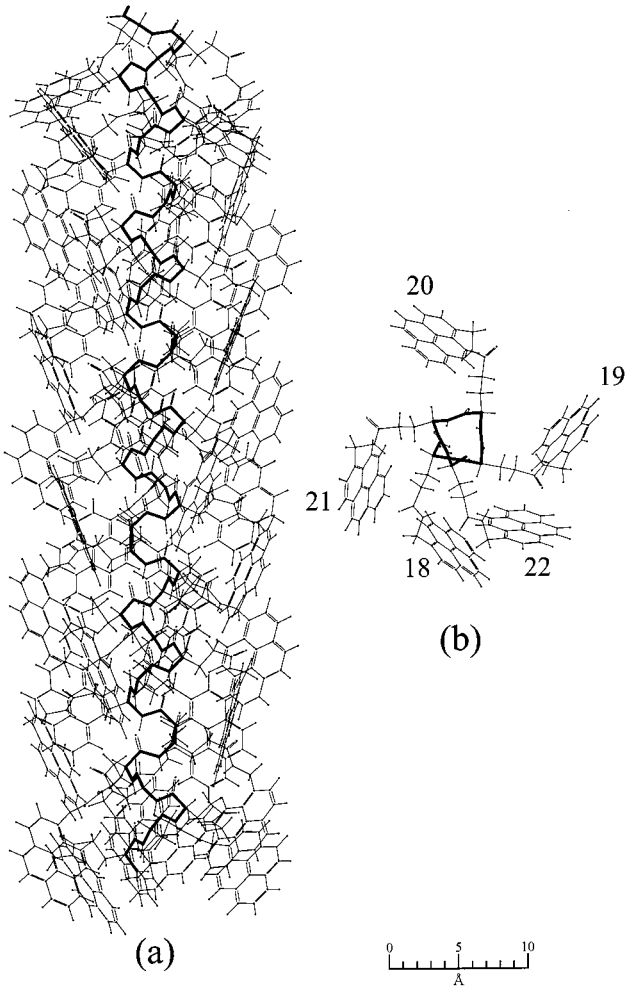


Figure 6. (a) Side view and (b) top view (five monomer units in the middle of 40-mer) of PPyMLGln in conformation D′.

other monomer unit. We, however, reserve any conclusion on its structure until we separately prepare the perfectly alternating copolymer and compare its CD with that of PPy(45)MLGln. PPy(25)MLGln (DP 360), on the other hand, showed virtually no CD signals attributable to pyrene groups in DMAc and showed only weak localized CD in film (Figure 2).

PPy(45)MLGln (DP 360) film showed CD somewhat similar to that of PPyMLGln (DP 360) film (Figure 2). It, however, gave significantly larger and more distinct CD signals indicative of exciton coupling interactions of positive chirality in both ^1L_a and ^1B_b bands. XRD showed a low crystallinity for PPy(45)MLGln (Figure 3). Thus, intermolecular interactions that would lead to the conformational change are apparently much weaker with PPy(45)MLGln (DP 360). However, we cannot exclude significant intermolecular exciton interaction in the case of the copolymers.

Excimer Formation in PPyMLGln, PPy(45)-MLGln, and PPy(25)MLGln. The fluorescence spectra of these polymers in DMAc show intense excimer emission around 480 nm. The higher the DP of the polymer, the larger the excimer emission relative to the monomer emission (Figure 8). 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, or to efficient energy 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. Compared with those in the inner sections of the polymer, the pyrene groups near the polymer ends may form excimers more easily as they have more conformational freedom. Since the higher DP polymer exhibits stronger excimer emission, however, most of excimers appear to be formed in the inner sections of the polymer. We suspect that energy migration is so efficient that excitation energy travels a long distance, e.g., over 100 pyrene chromophores or so, before being trapped as excimers. The probability of pairs of chromophores undergoing excimeric interaction assumed to be equal, PPyMLGln of the lower DP apparently has a smaller number of excimer forming sites in a single polymer and thus forms excimers less extensively.

Extensive excimer formation is definitely disadvantageous for efficient energy and charge (hole) transport. PPy(45)MLGln (DP 360), which showed a marked decrease of pyrene excimer emission, must still have pyrene groups in close proximity to give the CD signals as strong as those of PPyMLGln (DP 70). Apparently, in PPy(45)MLGln, excimers are formed where the pyrene groups are densely populated, as in PPyMLGln, by the irregularity of pyrene introduction. PPy(25)-MLGln gave much reduced excimer emission but scarcely showed pyrene CD signals in DMAc. Most of the pyrene groups are apparently so separated that they can undergo neither exciton coupling nor excimer forming interaction.

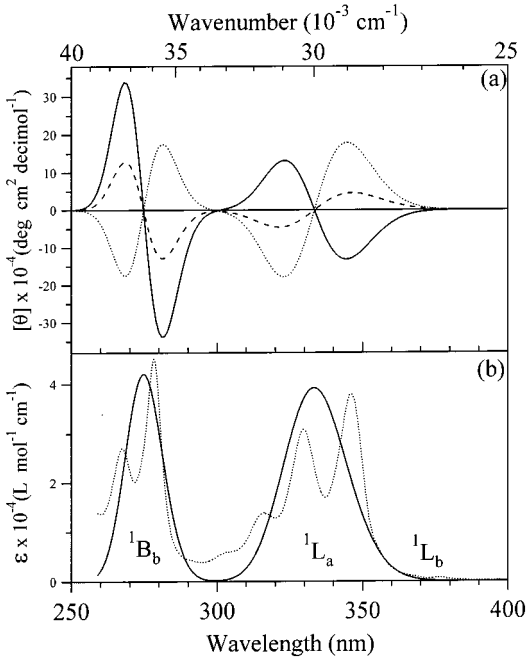


Figure 7. (a) Theoretical CD spectra of PPyMLGln in conformation A′ (—), conformation B′ (- - -), and conformation D′ (···). (b) UV absorption spectrum of PPyMLGln of DP 360 in DMAc (···) fitted with Gaussian functions (—).

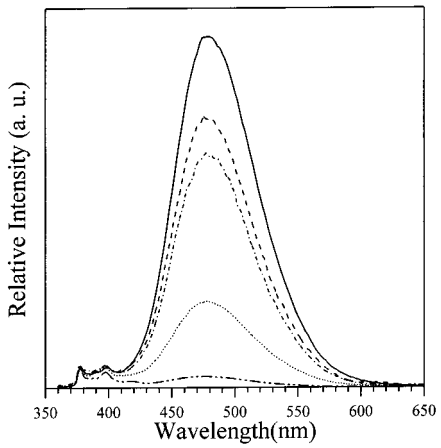


Figure 8. Fluorescence spectra, normalized at 377 nm, of PPyMLGln of DP 700 (—), DP 360 (- - -), and DP 70 (- • -) in DMAc at 20 °C. Those of PPy(45)MLGln (DP 360) (···) and PPy-(25)MLGln (DP 360) (- •• -) are also shown. $\lambda_{ex} = 350$ nm; [Py] $= 1 \times 10^{-5}$ M.

Conclusions

Rather strong CD signals at the pyrene absorption bands exhibited in solution by the PPyMLGln samples and the corresponding copolymer PPy(45)MLGln indicate that despite the long side chains the pyrene groups in these polymers are oriented with respect to the helical main chain and with respect to one another due to the rigid side-chain amide linkage and the bulkiness of the pyrene groups. A remarkable difference in CD observed in film between PPyMLGln (DP 700) and the other polymers suggests that the increased intermolecular interactions of the former lead to a change in side-chain and main-chain conformation and to that in chromophore orientation. Conformational analysis and theoretical CD calculations led to two probable conformations for PPyMLGln, A′ and D′, which appear to correspond to the major regulated conformation in well-packed film and that in solution, respectively. PPy(45)-MLGln, while giving CD similar to that of PPyMLGln (DP 70), showed much reduced excimer emission in solution compared with PPyMLGln (DP 70), suggesting that many of the pyrene groups in PPy(45)MLGln are situated along the main chain in proximity and orientation that allow exciton interaction but prevent excimeric interaction.

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(21) We examined the CD spectra of PPyMLGln (DP 360) in DMAc by changing the polymer concentration from 1.0×10^{-3} to 4.0×10^{-3} M and found no change in CD profile or intensity. We presume that association among the polymers does not lead to formation of a cholesteric liquid crystal phase in the concentration range examined. In film, as the solvent evaporates, cholesteric structures formed in concentrated solutions apparently collapse to form hexagonal lattices as so indicated by X-ray diffraction measurement. Watanabe et al. reported similar observation on poly(γ-methyl D-glutamate) film cast from solvents such as chloroform.[23]
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