A Polypeptide Carrying *p*-(Dimethylamino)phenyl and 1-Naphthyl Chromophores Periodically Arranged To Induce Efficient Electron Transfer and Exciplex Formation

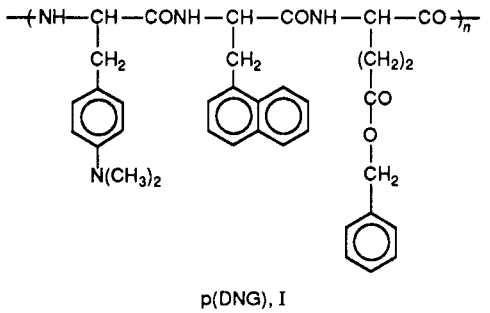
Masahiko Sisido,*,† Yoshihito Inai,‡ and Yukio Imanishi‡

Research Center for Medical Polymers and Biomaterials and Department of Polymer Chemistry, Kyoto University, Sakyo, Kyoto 606, Japan. *Received June 2, 1989; Revised Manuscript Received September 12, 1989*

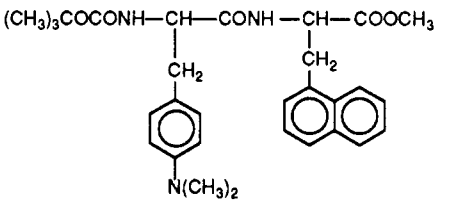
ABSTRACT: A sequential polypeptide, poly[dmaPhe-napAla-Glu(OBzl)] [dmaPhe = L-*p*-(dimethylamino)phenylalanine, napAla = L-1-naphthylalanine, Glu(OBzl) = γ-benzyl L-glutamate], was synthesized. The main-chain conformation of the polypeptide in trimethyl phosphate solution was a right-handed α-helix. The orientation of the side-chain chromophores was predicted from a conformational energy calculation. The interchromophore distance between the nearest pair of the dimethylanilino group and the naphthyl group was estimated to be 6.1 Å. The fluorescence of the naphthyl group is largely quenched and a small exciplex emission was observed. This indicates that the major photophysical processes on the chromophoric system are the electron-transfer quenching and the exciplex formation. The exciplex formation in the polypeptide required a very small thermal activation. It is concluded that the chromophore arrangement along the polypeptide chain is particularly suited for efficient electron transfer and exciplex formation.

Molecular electronic devices have attracted the interest of a number of researchers in the fields of chemistry, physics, and biology, not only for their fascinating name but also for their timeliness.[1] Molecular electronic devices should be based on the construction of molecular assemblies in which electrons or excited-state energy can move along a specified route. However, there are currently only a limited number of techniques available for arranging different types of chromophores in a specific sequence with a designed spatial orientation.

We have employed helical polypeptide as a rigid molecular framework and synthesized one-dimensional aromatic arrays of naphthyl,[2,3] pyrenyl,[4,5] and anthryl[6] chromophores along the helix. For the extension of this line of work, we attempted to synthesize polypeptides carrying different types of chromophores in a specific sequence. This paper describes the first attempt to arrange two types of chromophores alternatively along a polypeptide chain. The polypeptide prepared has the repeating unit dmaPhe-napAla-Glu(OBzl) [dmaPhe = L-*p*-(dimethylamino)phenylalanine, napAla = L-1-naphthylalanine, Glu(OBzl) = γ-benzyl L-glutamate] [p(DNG), I]. The orientations of the side-chain chromophores (*N*,*N*-dimethylanilino group = D, 1-naphthyl group = N) are determined and photophysical processes along the chromophoric array are discussed. As the model compound having the same dmaPhe-napAla sequence, but with a flexible chain, compound II [Boc-dmaPhe-napAla-OMe, BDNM] was also synthesized. Boc-Glu(OMe)-dmaPhe-Glu(OMe)$_3$-OMe (BGDGM) and Boc-Glu(OMe)-napAla-Glu(OMe)$_2$-OBzl (BGNGBz) were used as model compounds for isolated D and N group.



p(DNG), I



BDNM, II

Experimental Section

Materials. The sequential polypeptide contains two optically active artificial amino acids, dmaPhe and napAla. The Boc ((*tert*-butyloxy)carbonyl) derivative of dmaPhe was prepared by a reductive methylation of Boc-L-*p*-nitrophenylalanine (Boc-nitroPhe), under the same conditions reported for the synthesis of *N*-phthaloyl-L-*p*-(dimethylamino)phenylalanine methyl ester.[7] Synthesis and optical resolution of napAla have been reported.[2] The polypeptide was prepared by a polymerization of the corresponding tripeptide active ester, H-dmaPhe-napAla-Glu(OBzl)-OSu (OSu = *N*-hydroxysuccinimide ester). The synthetic route of the tripeptide was chosen so as to maximize the yield and to minimize the racemization. All the intermediates and the final products were checked for their purity by thin-layer chromatography, ^{1}H NMR, and elemental analysis.

NapAla-OBzl·TosOH. L-1-Naphthylalanine (0.5 g) was suspended in benzene (15 mL) and benzyl alcohol (15 mL) and *p*-toluenesulfonic acid monohydrate (1.8 g) was added. Water and benzene were distilled off by refluxing the mixture at 93–95 °C for 5 h. Addition of diethyl ether to the resulting solution gave the product. Yield, 1.0 g (92%); mp 172.5–175.0 °C. Anal. Calcd

* Correspondence should be addressed to this author at Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan.
† Research Center for Medical Polymers and Biomaterials.
‡ Department of Polymer Chemistry.

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for $C_{27}H_{27}NO_5S$: C, 67.91; H, 5.70; N, 2.93. Found: C, 68.01; H, 5.67; N, 3.00.

Boc-dmaPhe-napAla-OBzl. Boc-dmaPhe (0.50 g) and napAla-OBzl·TosOH (0.77 g) were dissolved in dimethylformamide (DMF). Triethylamine (0.21 mL), hydroxybenzotriazole hydrate (HOBT) (0.23 g), and 1-ethyl-3-[3-(dimethylamino)propyl]carbodiimide hydrochloride (water-soluble carbodiimide) (0.33 g) were added to the solution under cooling with ice. The mixture was stirred at 0 °C for 3 h and the stirring was continued overnight at room temperature. The solvent was evaporated and the residue was redissolved in ethyl acetate. The solution was washed with 10% citric acid, 10% NaCl, 3% $NaHCO_3$, and 10% NaCl solutions and dried over $MgSO_4$. Evaporation of the solvent and recrystallization from ethyl acetate/hexane gave white crystals, which were further purified on a silica gel/ethyl acetate column. Yield, 0.63 g (66%); mp 104–106 °C. Anal. Calcd for $C_{36}H_{41}N_3O_5$: C, 72.58; H, 6.94; N, 7.05. Found: C, 72.55; H, 6.89; N, 7.07.

Boc-dmaPhe-napAla-OH. Boc-dmaPhe-napAla-OBzl (0.15 g) was dissolved in ethanol (10 mL) containing water (1%) and 5% palladium carbon (0.07 g) was added. The mixture was stirred at room temperature for 3.5 h under atmospheric hydrogen. The catalyst was removed and the solvent was evaporated. The residual oil was solidified by the addition of hexane. The solid product was used for the next step without further purification. Yield, 63 mg (49%); mp 124–126 °C.

Boc-dmaPhe-napAla-Glu(OBzl)-OSu. Boc-dmaPhe-napAla-OH (63 mg) was dissolved in anhydrous tetrahydrofuran (1 mL) and *N*-methylmorpholine (14 μL) and isobutylchloroformate (17 μL) were added at −10 °C. The mixture was stirred at −10 °C for 5 min and Glu(OBzl)-OSu·HCl (γ-benzyl L-glutamate *N*-hydroxysuccinimide ester hydrochloride) (48 mg) in DMF (1 mL) and *N*-methylmorpholine (15 μL) were added. The mixture was stirred at −10 °C for 1 h and then under ice temperature overnight, and the solvent was evaporated. The residue was redissolved in ethyl acetate and the solution was washed with 5% aqueous NaCl solution and dried over $MgSO_4$. Evaporation of the solvent and recrystallization from ethyl acetate/hexane gave white crystals. Yield, 70 mg (71%); mp 129–131 °C. Anal. Calcd for $C_{45}H_{51}N_5O_{10}$: C, 65.76; H, 6.25; N, 8.52. Found: C, 65.50; H, 6.15; N, 8.32.

Poly[dmaPhe-napAla-Glu(OBzl)] [p(DNG)]. Boc-dmaPhe-napAla-Glu(OBzl)-OSu (60 mg) was dissolved in 4 N HCl/dioxane (20 mL) and left to stand at room temperature for 50 min. The solvent was evaporated and the residue was solidified by adding ethyl ether. The precipitate was washed with ether and dried under vacuum. The deprotected tripeptide was dissolved in DMF (0.5 mL) and 1.5-fold excess of triethylamine (15 μL) was added. After 2 days, further triethylamine (10 μL) was added and the mixture was stored at room temperature for 1 week. Excess methanol was then added to the mixture and the precipitate was washed with 3% $NaHCO_3$, water, methanol, and ether. The polypeptide was subjected to gel chromatography (Sephadex LH-60 in DMF), and the component eluted at the limit of high molecular weight (MW > 10^4) was collected.[21]

Boc-dmaPhe-napAla-OMe (BDNM). The dipeptide was synthesized by a similar method as for Boc-dmaPhe-napAla-OBzl; mp 153–155.5 °C. Anal. Calcd for $C_{30}H_{37}N_3O_5$: C, 69.34; H, 7.18; N, 8.09. Found: C, 69.28; H, 7.09; N, 8.07.

Preparation of poly[Lys(Z)-Lys(Z)-napAla] [p(L_2N)] has been reported previously.[3] Boc-Glu(OMe)-dmaPhe-Glu(OMe)$_3$-OMe (BGDGM) and Boc-Glu(OMe)-napAla-Glu(OMe)$_2$-OBzl (BGNGBz) were synthesized by the liquid-phase technique. The details will be described elsewhere.[8]

Measurements. Spectroscopic measurement was made in trimethyl phosphate (TMP), which is transparent down to 190 nm. TMP was distilled twice under vacuum. For fluorescence and fluorescence lifetime measurement, the TMP solution was bubbled with nitrogen gas for 20 min. The following spectrometers were used: UV, Hitachi 200-20; fluorescence, Hitachi MPF-4; CD, Jasco J-20. Fluorescence rise and decay curves were measured on a home-built single-photon counting apparatus equipped with Ortec electronics. The exciting wavelength was 295–320 nm and the monitor wavelength was >440 nm. The rise curve of the exciplex was measured on the single-photon counting apparatus with a picosecond laser as the light source (314 nm).

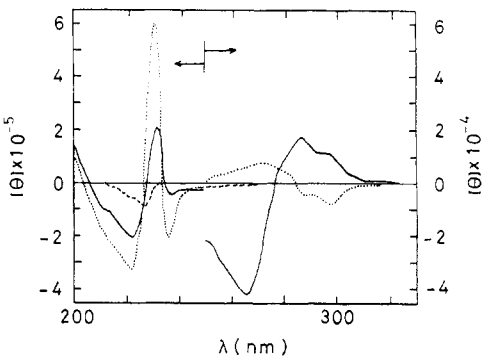
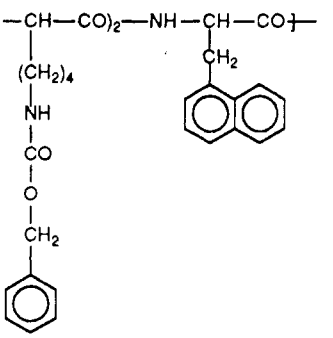


Figure 1. CD spectra of p(DNG) (—), p(L_2N) (· · ·), and BDNM (- - -) in TMP at room temperature. The ordinate is the molar ellipticity with respect to the concentration of naphthyl groups: [naphthyl group] = 1.0 × 10^{-4} M, cell length = 1 mm (200–250 nm), 10 mm (250–330 nm).

Results and Discussion

CD Spectra and the Ground-State Conformation. CD spectra of p(DNG) and BDNM in TMP are shown in Figure 1. The ordinate of Figure 1 is the molar ellipticity with respect to the concentration of N group. The ellipticity with respect to the amide group is one-third of the value in the figure. Poly(DNG) exhibits a moderately strong exciton splitting at the ^{1}Bb absorption band of N group. The shape of the exciton splitting resembles that observed with poly[Lys(Z)$_2$-napAla] [p(L_2N), III], whose conformation has been concluded to be a right-handed α-helix on the basis of the theoretical analysis of the CD spectrum in the UV region[3] and the experimental CD in the vibrational region (VCD).[9] Since both



p(L_2N), III

p(DNG) and p(L_2N) have N groups in every three amino acid units along the polypeptide chain, the resemblance is not accidental. The similarity of CD spectra indicates that the main chain of p(DNG) also takes an α-helical conformation and the arrangement of N groups along the helix is similar to that in p(L_2N). The α-helical conformation of the main chain of p(DNG) is supported also by the characteristic infrared absorptions observed in the TMP solution: amide I, 1658 cm^{-1}; amide II, 1547 cm^{-1}.[10] However, the regularity of the helical arrangement of N groups of p(DNG) should be lower than that of p(L_2N), in view of the smaller CD intensity of p(DNG). Since the amide CD band around 200–220 nm is hidden by the strong naphthyl CD band, one cannot estimate the helix content of the main chain directly from the CD spectrum. Therefore, it is not clear whether the small naphthyl CD band is due to the instability of the main-chain helix or to the fluctuation in the side-chain orientation of the N group.

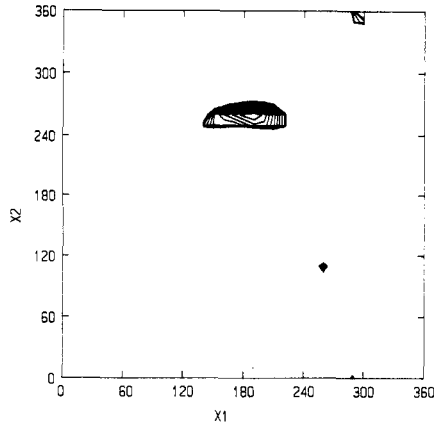


Figure 2. Side-chain energy contour map of the napAla unit in Ac-Ala$_4$-napAla-Ala$_4$-NMA. The interval of the contour lines is 0.5 kcal mol^{-1}. The minimum-energy point appears at χ_1 = 190°, χ_2 = 260°.

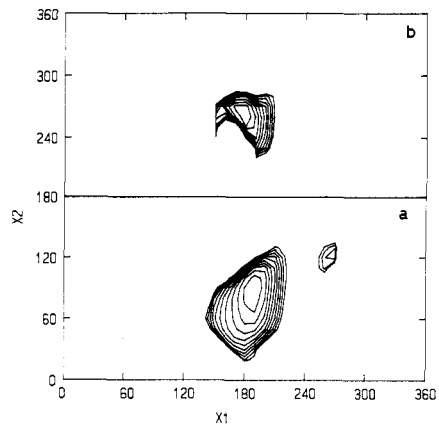


Figure 3. Side-chain energy contour map of the dmaPhe unit in (a) Ac-Ala$_4$-dmaPhe-Ala$_4$-NMA and in (b) (damPhe-napAla-Ala)$_8$. Since the rotation around C^β–C^γ has C_2 symmetry, the upper half and the lower half of the map are identical. Only the lower half is shown for (a) and upper half is shown for (b). The minimum-energy point appears at χ_1 = 190°, χ_2 = 90° for (a) and χ_1 = 180°, χ_2 = 80° for (b).

The orientation of the D group is not clear from the CD spectrum. The broad negative peak around 266 nm, which is not observed in p(L$_2$N), may be assigned to a coupled band of D and N groups. The theoretical CD spectrum of poly(L-*p*-aminophenylalanine) has been calculated by assuming that the polypeptide chain takes a regular helix and the aminophenyl groups are arranged regularly along the helix.[11] The calculation predicted the absence of larger CD intensity than $[\theta] = 1 \times 10^4$ above 210 nm. Indeed, the weak CD has been experimentally observed over the wavelength range of 210–310 nm by Goodman and Peggion.[12] Therefore, the small contribution of D group to the CD spectrum of p(DNG) does not necessarily indicate a random orientation of the chromophore. Conversely, the fairly large CD at 266 nm indicates that D groups are arranged in a definite orientation along the polypeptide chain.

The CD spectrum of BDNM showed no large signal, indicating the importance of the regular and dense arrangement of the chromophores in showing strong CD.

Empirical Potential Energy Calculation. Empirical energy calculation was carried out to predict the average orientation of side chains of p(DNG). The structure and the energy parameters employed in the calculation are based on the ECEPP,[13] which was modified to include parameters for the two artificial amino acids. The details are described in the Appendix.

The energy calculation was carried out by assuming an α-helical main-chain conformation ($\phi = -57°, \psi = -47°$). For simplicity, the calculation was made by replacing the alanine (Ala) unit for the Glu(OBzl) unit. The side-chain orientations (χ_1 and χ_2) of dmaPhe and napAla units were varied from 0° to 360° at an interval of 10°. The methyl group of the Ala unit was fixed to a staggered position (χ_1 = 60°). First, the stable orientation of an isolated 1-naphthylmethyl group and that of a *p*-(dimethylamino)benzyl group in an α-helical polypeptide chain were searched for in the side-chain energy contour maps for Ac-(Ala)$_4$-Xyz-(Ala)$_4$-NMA (NMA = *N*-methylamide group, Xyz = dmaPhe or napAla). The energy contour map for the side-chain orientation (χ_1 and χ_2) of the napAla unit in the α-helical nonapeptide is shown in Figure 2. The contour map shows that the orientation of an isolated N group is restricted in a very narrow range ($\chi_1 = 190 \pm 15°$, $\chi_2 = 260 \pm 5°$) near room temperature (thermal energy = 1 kcal/mol). Figure 3 (bottom) shows the side-chain energy contour map for an isolated D group in the nonapeptide in an α-helical conformation. Only one potential minimum is found near room temperature, but the range of thermal fluctuation is larger than that for the napAla unit; $\chi_1 = 190 \pm 15°$ and $\chi_2 = 270 \pm 30°$.

Starting from the stable side-chain orientations found for the isolated side-chain chromophores, energy minimization was carried out to search for the most stable side-chain orientation of p(DNG). In this calculation, an α-helical structure of the main chain ($\phi = -57°$ and $\psi = -47°$) was retained. Furthermore, a helical symmetry for the side chains was assumed; i.e., the side-chain rotational angles in the dmaPhe-napAla-Ala unit are assumed to be the same for all the tripeptide units. The number of the tripeptide units was 8. The minimum-energy side-chain orientations obtained are as follows: (χ_1, χ_2) = (176.3°, 263.9°) for D and (189.6°, 256.8°) for N. The stable orientation of N group is not shifted from that of the isolated N group in an α-helix, whereas that of the D group is considerably shifted from the most stable orientation for an isolated D group (190°, 270°). The shift of the stable orientation indicates the presence of steric constraints by neighboring N groups along the helix. Indeed, a comparison of the energy contour map for an isolated D group (Figure 2, bottom) and that for a D group in poly(dmaPhe-napAla-Ala) (n = 8) (top) shows that the orientation of the latter D group is considerably restricted in a narrower range.

It is concluded from the energy calculation that only one side-chain orientation is allowed for D and N group in p(DNG), and their thermal fluctuation is not so large as to induce a rotation of the chromophores. However, as suggested from the CD spectrum, the chromophore arrangement may not be so stable as in the case of p(L$_2$N).

The ball-and-stick atomic model for the minimum-energy conformation is illustrated in Figure 4.[11] The center-to-center and the edge-to-edge distances between the nearest N–N pair are 7.6 and 5.5 Å, respectively. Those for the nearest D–D pair are 7.1 and 5.4 Å. The nearest-neighbor D–N pair is the 1–5 pair (the numbers indicate the amino acid unit). The center-to-center D–N distance is 6.1 Å and the nearest edge-to-edge distance is 4.3 Å. The center-to-center distance of the 1–2 D–N pair is 7.8 Å and the corresponding edge-to-edge distance is 4.9 Å. The interchromophore distances are schematically shown in Figure 5.

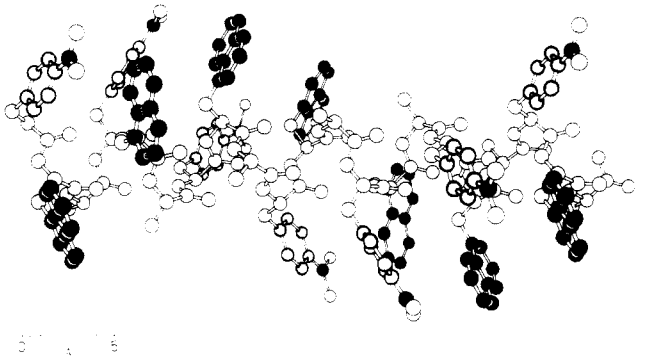


Figure 4. Minimum-energy conformation of poly(dmaPhenapAla-Ala). The hydrogen atoms are omitted, although they are considered in the energy calculation.

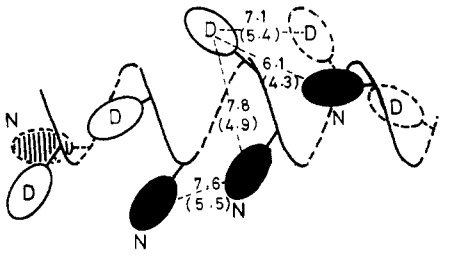


Figure 5. Center-to-center (edge-to-edge) interchromophore distance for the minimum-energy conformation of p(DNG).

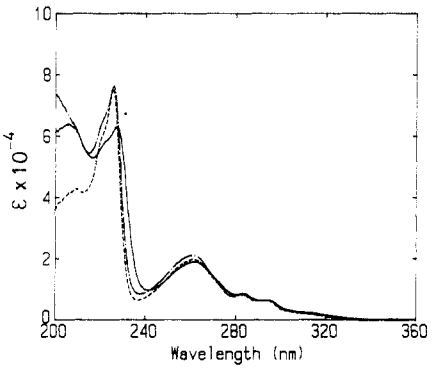


Figure 6. Absorption spectra of p(DNG) (—), BDNM (- - -), and the sum of the spectra of BGDGM and BGNGBz (- · -) in TMP at room temperature.

Absorption Spectra and the Interaction in the Ground State. Figure 6 shows absorption spectra of p(DNG), BDNM, and an equimolar mixture of BGDGM and BGNGBz in TMP. The sharp peak at 225 nm and weak peaks at 283 and 295 nm are assigned to the N group. The broad peak around 260 nm and the shoulder around 300–330 nm are assigned to the D group. At longer wavelengths than 240 nm, the three spectra in Figure 6 agree with each other within experimental error, indicating that N and D groups are correctly incorporated in p(DNG) and that no ground-state interaction occurs between N–N, N–D, and D–D pairs in the polypeptide. The absence of ground-state interaction between the N–D pair is especially noteworthy, since intra- and intermolecular charge-transfer interactions have been reported in polymeric systems carrying pyrenyl and (dimethylamino)phenyl groups.[15] However, the absence of D–N interactions cannot be interpreted by an inconvenient arrangement of the two chromophores along the polypeptide chain, since the D–N interaction was not observed in the BDNM molecule, either.

The absence of the ground-state interaction was further confirmed by the coincidence of the patterns of

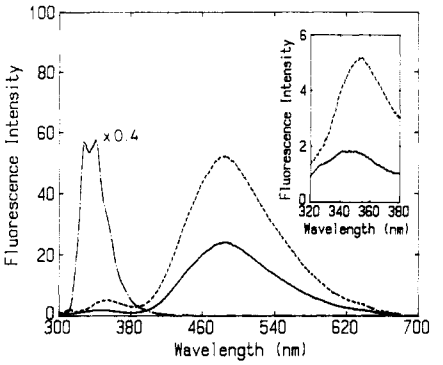


Figure 7. Fluorescence spectra of p(DNG) (λ_{ex} = 285 nm (—), 265 nm (- - -)) and those of p(L_2N) (285 nm (- · -)). The fluorescence spectra of p(L_2N) are multiplied by 0.4. The insert is the enlarged spectra of p(DNG) at the monomer emission region. Solvent, TMP; [naphthyl group], 1.7×10^{-5} M; room temperature.

absorption spectrum and excitation spectrum monitored at the exciplex emission (480 nm).

A small hypochromic effect and a small red shift were observed at the ^{1}Bb absorption band of p(DNG) (227 nm), as compared with the spectrum of the mixture of BGDGM and BGNGBz (224.5 nm). On the other hand, the absorption spectrum of BDNM is virtually the same as that of the mixture. The hypochromic effect of p(DNG) is related to the splitting observed in the CD spectrum around 230 nm and suggests the exciton-type interchromophoric interaction in the high-energy excited state of N groups, due to strong dipole–dipole interactions.

Distribution of the Photoenergy in p(DNG). Since absorption spectra of N and D groups are largely overlapped, neither the N nor the D group can be photoexcited selectively. For example, 54% of photoenergy is absorbed by the N group at 300 nm, 79% at 285 nm, and 19% at 265 nm.

The photoenergy absorbed by an N or D group may redistribute among the chromophores by energy transfer. The critical distances r_0 (in Å) for the energy transfer are calculated to be 8.8 for N* → N, 13.8 for N* → D, 5.6 for D* → N, and 8.7 for D* → D. The r_0 values were determined spectroscopically by using BGDGM and BGNGBz as the model compounds.[16] As is found from the comparison of the r_0 values and the interchromophore distances listed in Figure 5, the energy transfer can occur in all four directions. According to Förster's theory, the rate of energy transfer is given by the equation, $k_{et} = \tau_0^{-1}(r_0/r)^6$, where τ_0 is the lifetime of the energy donor (ca. 3.8 ns for BGDGM and 59 ns for BGNGBz).[17] Using the interchromophore center-to-center distance shown in Figure 5 and the r_0 values, the rate constants k_{et} were estimated as follows: 9.2×10^8 s^{-1} for D* → D, 1.5×10^9 s^{-1} for D* → N, 4.1×10^7 for N* → N, and 2.2×10^9 s^{-1} for N* → D. The four rate constants are smaller than or comparable to 10^9 s^{-1}. As will be described later, exciplex is formed within about 100 ps in the present system. Therefore, the energy-transfer processes may not affect much the fluorescence spectrum of p(DNG).

Fluorescence Spectra and Their Temperature Dependence. Fluorescence spectra of p(DNG) and p(L_2N) excited at 265 nm and at 285 nm are shown in Figure 7. The monomer fluorescence of N group is markedly quenched in p(DNG) and the exciplex emission appeared. The exciplex of p(DNG) is intramolecular in nature, since the spectrum profile is virtually identical in a more dilute solution ([N] = 1×10^{-6} M). The peak

position of the exciplex is independent of the excitation wavelength. The quantum yield of the exciplex is 0.024 for λ_{ex} = 265 nm and 0.025 for 285 nm. These results indicate that the excitation of either N or D group leads to the same exciplex with similar quantum yields. Contribution from the monomer emissions of D and N groups was only marginal.

The fluorescence quantum yield of the exciplex of p(DNG) is much smaller than that of the monomer emission of N group of p(L_2N) (0.12). This indicates either that the exciplex has a very small fluorescence quantum yield or that the electron-transfer quenching of the excited N group is predominant. The latter explanation seems more likely, since the fluorescence lifetime of the exciplex (>40 ns) is comparable to that of the N group in p(L_2N) (about 50 ns). Therefore, it is suggested that the major photophysical process in the polypeptide is a fluorescence quenching by an electron-transfer mechanism. The electron transfer to form a $D^{\bullet+}$–$N^{\bullet-}$ ion pair has been reported for the naphthalene–diethylaniline mixture in solution.[18]

It has been discussed whether the exciplex is formed before the electron transfer or after the electron transfer.[19] It is also possible that the two processes take place competitively at different sites in the polypeptides, depending on the interchromophore distance between D and N groups. The first possibility that the exciplex formation precedes the electron transfer may be excluded, since the lifetime of the exciplex is relatively long (>40 ns) but the quenching occurs with a high quantum yield. The adequacy of the remaining two possibilities is judged by whether the process is accompanied by molecular motion. If the exciplex is formed after the electron transfer, the D–N pair should approach each other after the electron transfer. The conformational change may require some thermal activation energy. The alternative mechanism is that the exciplex is formed when the D–N pair is close and the electron-transfer quenching occurs when they are separated. In the former case, exciplex formation may be accelerated with increasing temperature, but in the latter case, it will be insensitive to the temperature.

Figure 8 shows the temperature dependence of the quantum yield of the exciplex in p(DNG) and BDNM. As the temperature was raised from −60 to 20 °C, the quantum yield of exciplex in p(DNG) decreased, whereas that in BDNM increased. The quantum yield ratio of the exciplex to the monomer fluorescence of D of p(DNG) increased with temperature, but the temperature dependence is less marked than for BDNM. This contrasting behavior clearly indicates that the exciplex formation in p(DNG) needs only small thermal activation, whereas that in BDNM requires thermally activated conformational changes. A similar tendency was observed when the polymer or the dipeptide was excited at 285 nm.

Therefore, the most probable mechanism of the photophysical process in p(DNG) is that the photoenergy absorbed by either the D or the N group induces electron transfer when the D–N pair is separated by, say, 7.8 Å and the exciplex formation results when the pair is closer than the average interchromophore distance. Energy transfer between chromophores of the same kind and between D and N groups may play some role in finding the most convenient pathway for the electron transfer and/or the exciplex formation. However, since the whole processes is completed within 100 ps, their effect on the spectral profile may not be important.

A small amount of monomer fluorescence (310–390 nm) is observed in the fluorescence spectra in Figure 7 (insert).

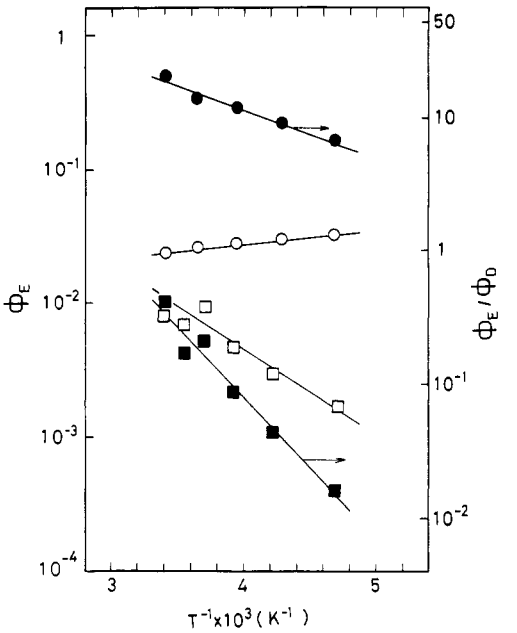


Figure 8. Temperature dependence of fluorescence quantum yield of the exciplex emission from p(DNG) (○) and BDNM (□). The ratio of the fluorescence quantum yields of the exciplex to the monomer emission of the D group is also plotted for p(DNG) (●) and for BDNM (■). Excitation wavelength is 265 nm.

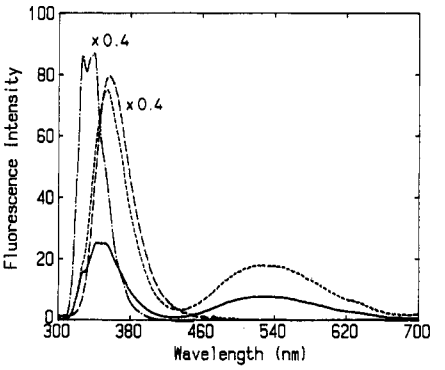


Figure 9. Fluorescence spectra of BDNM (λ_{ex} = 285 nm (—), 265 nm (- - -)). Spectra of BGNGBz (λ_{ex} = 285 nm (- · -)) and BGDGM (λ_{ex} = 265 nm (- · -)) are also shown with a multiplication factor of 0.4. Solvent = TMP; [naphthyl group] = [dimethylanilino group] = 1.7 × 10^{-5} M; room temperature.

The monomer fluorescence consists of those of D and N groups and the relative contribution varies with the excitation wavelength or with the initial distribution of the photoenergy between N and D groups. The monomer fluorescence is minor and may appear when an excited D or N group is located at a position where electron transfer or exciplex formation is difficult. The unfavorable position may be the ends of the polypeptide chain or partially unfolded parts of the helix.

Fluorescence Spectra of the Model Compound and Their Temperature Dependence. Figure 9 shows fluorescence spectra of the bichromophoric dipeptide (BDNM) and the model compounds containing D (BGDGM) and N (BGNGBz) groups. The naphthyl fluorescence of BDNM is again largely quenched and an exciplex emission appears at 520 nm, which is shifted about 40 nm to longer wavelength than that of p(DNG). The exciplex/monomer ratio of the quantum yield of BDNM is smaller than that of p(DNG). The temperature dependence of the exciplex quantum yield and that of the exciplex/monomer ratio is shown in Figure 8. The exciplex formation of BDNM is markedly suppressed at

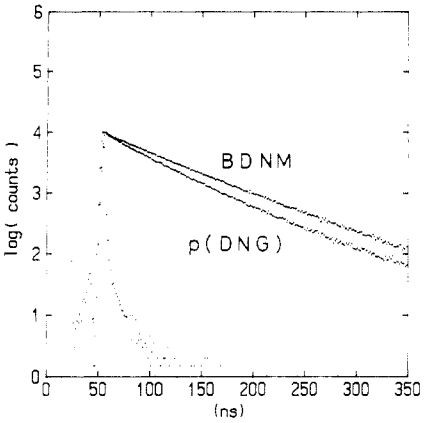


Figure 10. Decay curves of the exciplex emission from p(DNG) or BDNM. The former curve can be fitted to $I(t) = 0.49 \exp(-t/30$ ns) + 0.51 exp($-t/65$ nm) ($\chi^2 = 1.9$) and the latter to 0.45 exp($-t/45$ ns) + 0.55 exp($-t/76$ ns) ($\chi^2 = 1.4$).

low temperatures. As described above, the different results for BDNM and p(DNG) can be explained in terms of different mechanisms of exciplex formation. In the dipeptide, no specific conformation exists in TMP solution as deduced from the CD spectrum, and the exciplex formation may require thermally activated molecular motions, which bring the two chromophores close to each other during the lifetime of the excited state.

Fluorescence Decay Analysis. To evaluate the rate of exciplex formation directly, the fluorescence rise curves of exciplex in p(DNG) and BDNM were measured by using a picosecond laser as the exciting light source (314 nm). However, a rise time longer than the instrumental limit of time resolution (ca. 50 ps) was detected neither in the polypeptide nor in the model dipeptide at room temperature, indicating that the exciplex formation is a very fast process in both systems. The reason for the fast exciplex formation may be different in the two systems. In the polypeptide, a close proximity of the D–N pair may explain the fast exciplex formation, but in the model dipeptide, the molecular motion may be very fast at room temperature.

The decay curves of the exciplex of p(DNG) and BDNM are shown in Figure 10. Both of the decay curves deviated from a single-exponential decay law. However, the curvature of the logarithmic plot is more marked with p(DNG). The distribution of decay time suggests that several types of exciplexes coexist in the polypeptide. Presumably, exciplexes between the 1–2 D–N pair and the 1–5 D–N pair may be possible. A preliminary experiment showed that a polypeptide carrying a single 1–2 D–N pair in the midway of a helical chain formed an exciplex with the lifetime of 33 nm at room temperature (solvent, THF). The polypeptide carrying a single 1–4 D–N pair formed an exciplex with a longer lifetime (51 ns).[8] These results suggest that both the 1–2 and 1–5 types of exciplexes are occurring in p(DNG) and the two exciplexes have different lifetimes.

The decay curve of BDNM also deviated from the single-exponential law, but the deviation is less marked than that of p(DNG). The nonlinear decay curve of BDNM also indicates the presence several types of exciplexes.

Conclusions

A chromophoric assembly consisting of two different types of aromatic groups that are arranged alternatively along a helical polypeptide chain was synthesized. Photophysical processes in the chromophoric system were examined. The major photophysical process was an electron transfer accompanied by the exciplex formation. The exciplex is formed without large conformational change in the polypeptide, in contrast to the case of the bichromophoric dipeptide. It is concluded that the molecular arrangement shown in Figures 4 and 5 is favorable for efficient electron transfer accompanied by some exciplex formation.

Acknowledgment. We thank Dr. Yoshio Taniguichi and Masashi Kiguchi, Advanced Research Laboratory, Hitachi, Ltd., for measuring the decay curves in the picosecond region. We also appreciate professor H. A. Scheraga of Cornell University for sending us the CNDO(ON) program. This study is supported by a Grant-in-Aid for Scientific Research on Priority Areas, New Functionality Materials—Design, Preparation and Control, The Ministry of Education, Science and Culture, Japan.

Supplementary Material Available: Figures with structure parameters and partial charges of the L-*p*-(dimethylamino)phenylalanine and L-1-naphthylalanine residues (4 pages). Ordering information is given on any current masthead page.

Appendix. Structural Parameters and Partial Charges of L-1-Naphthylalanine (napAla) and L-*p*-(Dimethylamino)phenylalanine (dmaPhe)

In order to include the two artificial amino acids in the ECEPP system,[13] structural parameters and partial atomic charges of the two units were determined. The structural parameters for naphthyl moiety of napAla were the same as reported before and those of dmaPhe were taken from tyrosine and *N*,*N*-dimethyl-*p*-toluidine.

The partial charges of the two amino acids were determined from the CNDO(ON) molecular orbital calculations[20] on *N*-acetyl-L-1-naphthylalanine *N*-methylamide and *N*-acetyl-*p*-(dimethylamino)phenylalanine *N*-methylamide. The partial charges for two different main-chain conformations corresponding to a right-handed α-helix and the extended structure were averaged to obtain the effective partial charges. The parameters are available as Supplementary Material.

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(21) It is known that some racemization is unavoidable during polypeptide synthesis by the activated ester method. No direct evaluation for the extent of racemization in the present polypeptide was made. However, poly[Lys(Z)-Lys(Z)-napAla] obtained by the activated ester method (number of repeating units > 10) showed similar but stronger CD ($\Delta\epsilon_{230} = 6 \times 10^5$ in TMP) than Boc-(Ala-napAla-Aib)$_6$-OBzl obtained by stepwise condensation ($\Delta\epsilon_{228} = 4.8 \times 10^5$ in TMP: Nishino, N., Private communication). Therefore, the racemization is not so serious under the condition employed in this series of study.

Iodine-127 and Potassium-39 NMR Study of the Interaction of Ions with Water-Soluble Polymers

Seok Heon Oh,† Ryong Ryoo,‡ and Mu Shik Jhon*,†

Department of Chemistry, Korea Advanced Institute of Science and Technology, P.O. Box 150, Cheongryang, Seoul, Korea, and Department of Chemistry, Korea Institute of Technology, Taeduk Science Town, Taejon, 305-701 Korea.
Received March 8, 1989; Revised Manuscript Received August 18, 1989

ABSTRACT: Thermodynamic parameters including the equilibrium constant for the binding of iodide anion with polymers in aqueous solutions have been determined from the excess line widths of the ^{127}I NMR. Comparison of these parameters with the NMR line widths suggests that a specific binding exists to cause severe line broading of the ^{127}I NMR in solutions of poly(vinylpyrrolidone) (PVP), isotactic poly(2-hydroxyethyl methacrylate), and poly(acrylamide). Even in the absence of significant polymer–iodide binding, the asymmetric hydration of iodide anions in the solutions of poly(ethylene oxide) and poly(vinyl alcohol) seems to cause moderate line broadening. The magnitude of the binding constant of iodide anions can be related to the dipole moment of the polymer segment, which suggests that an electrostatic interaction is responsible for the specific iodide binding with PVP. The ^{127}I NMR line widths obtained with different alkali ions and the ^{39}K NMR data indicate no effects of countercation on the ^{127}I NMR.

Introduction

The recently developed multinuclear NMR technique[1-3] can be expected to give detailed information on polymer salt solutions. The information obtained can be discussed at the microscopic level and should provide direct information about the behavior of ions. Furthermore, by selecting the nucleus to observe, one can obtain information about individual ions in the presence of water-soluble polymers. These characteristics give the technique a great potentiality for investigating a complex mixture of ionic species in polymer salt solutions. ^{127}I NMR has only rarely been utilized for studies of macromolecular systems because of its poor detection limits caused by extreme line broadening. The NMR of iodide ion has been used in some cases to study ionic interaction[4,5] in aqueous salt solutions. But, there are only a few reports[6-8] on studies for macromolecular systems using ^{127}I NMR as a chemical probe.

The purpose of this study is to examine the origin of the line broadening of ^{127}I NMR in a macromolecular system, the binding of iodide anions with water-soluble polymers, and the behavior of countercation ^{39}K during the iodide binding. We have studied the polymer–iodide interactions in aqueous solution by measuring ^{127}I and ^{39}K NMR line widths for seven water-soluble polymers.

† Korea Advanced Institute of Science and Technology.
‡ Korea Institute of Technology.

Table I
Physical Properties of Water-Soluble Polymers Used in This Study

polymer	10^{-4} MW[a]	$[\eta]$[b]	M[c]	V[d]	ρ_a[e]	μ[f]
PEO	1.85	0.348	44.1	39.2	1.125	0.418
PVAL	2.50	0.392	49.1	39.5	1.243	0.447
PAAM	1.00	0.036	71.1	54.6	1.302	1.051
PAAMA	20.00	3.433[h]	73.4			
PAAMB	20.00	26.280[h]	87.1			
iso-PHEMA	5.40[g]	0.040	130	102.0	1.274[i]	0.769
PVP	4.00	0.235	111.1	88.9	1.25	4.07[j]

[a] Nominal molecular weights stated by Polysciences Co. [b] Intrinsic viscosity measured at 298 K in water and expressed in dL/g. [c] Molar weight (g/mol). [d] Molar volume (cm^3/mol). [e] Density (g/cm^3). [f] Average dipole moment calculated according to the Debye equation (D). [g] Measured by using the Mark–Houwink equation reported in ref 9. [h] Reduced viscosity measured at a concentration of 0.5 g/dL. [i] Reference 28. [j] Reference 23.

Experimental Section

Materials. Poly(vinylpyrrolidone) (PVP), poly(ethylene oxide) (PEO), poly(vinyl alcohol-*co*-vinyl acetate) (PVAL) containing 12 mol % acetate, poly(acrylamide) (PAAM), poly(acrylamide-*co*-acrylic acid) sodium salt containing 10 mol % carboxyl (PAAMA), and poly(acrylamide-*co*-acrylic acid) sodium salt containing 70 mol % carboxyl (PAAMB) received from Polysciences Co. were dried under vacuum over P_2O_5. Isotactic poly(2-hydroxyethyl methacrylate) (iso-PHEMA) was prepared by the same procedure as reported earlier.[9] In Table I the physical properties[10] of the polymers such as molecular weight, intrinsic viscosity in water at 298 K, molar volume, molar weight,

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