to the gel point. Afterward, it is related to the mole fraction of cross-linked monomer units through eq 35.

Registry No. *p*-DVB, 105-06-6; *m*-DVB, 108-57-6; styrene, 100-42-5; (styrene)·(*p*-DVB) (copolymer), 25086-67-3; (styrene)·(*m*-DVB) (copolymer), 25703-32-6.

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Intramolecular Dimer Radical Cations of α,ω-Di(2-naphthyl)alkanes and Poly(2-vinylnaphthalene)

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ABSTRACT: Dimer radical cation formation in α,ω-di(2-naphthyl)alkanes [(2-naphthyl)–$(CH_2)_n$–(2-naphthyl), (n = 3, 6, 12)] and poly(2-vinylnaphthalene) was measured by the pulse radiolysis method. Two kinds of intramolecular dimer radical cations at 580 and 660 nm were observed for 1,3-di(2-naphthyl)propane and poly(2-vinylnaphthalene), whereas only one dimer radical cation absorption was detected at 580 nm for 1,12-di(2-naphthyl)dodecane. The dimer radical cation with λ_{max} at 580 nm converted to another form with λ_{max} at 660 nm in 20 ns for 1,3-di(2-naphthyl)propane and in 70 and 125 ns for the polymer with the molecular weight of 1950 and 1.2×10^5, respectively. The activation energies of the conversion, 7.4 ± 1.0 and 9.0 ± 1.0 kcal/mol, were obtained for the 1,3-di(2-naphthyl)propane and the polymer (MW = 3.8×10^4), respectively. The conversion process is interpreted as follows. Two kinds of dimer radical cations with different geometrical structures, partial and fully overlapped sandwich structures, are produced through a kinetically controlled process involving the interaction of the monomer radical cation with the ground-state chromophore of the same molecule. Then the unstable partially overlapped state slowly converts in approximately 100 ns to a thermodynamically more stable form, the fully overlapped state, via the double rotation of the chains, unfolding of the chain to the open form, and refolding to the sandwich structure. Solvent effects on the conformational change in the polymer system are also examined.

Introduction

Since the pioneering work of intramolecular excimer formation in diphenylalkanes was carried out by Hirayama,[1] these bichromophoric compounds are recognized as favorable systems for studying the geometrical aspects of the excimer state as well as the dynamics of the conformational changes of vinyl polymer chains.[2-23] Bovey et al.[2] first pointed out the importance of configurational considerations in excimer-forming capacity by using diastereoisomeric 2,4-diphenylpentanes. The difference in the excimer intensity between meso and racemic isomers can be explained by the NMR results concerning the conformational distribution within each isomer in the ground state.

The understanding of the geometrical structures of excimer conformations in bichromophoric systems has been much advanced by the extensive study of De Schryver et al.[4-8] on the transient behavior of the excited state of 2,4-diarylpentanes and 1,1-diaryldiethyl ethers. Two excimers with different geometrical structures have been observed most clearly in meso and racemic 2,4-di(*N*-carbazoyl)pentanes and are related to the two excimers observed in poly(*N*-vinylcarbazole).[9,11,14] The geometrical arguments concerning excimer conformation have been recently extended to the conformation of dimer radical cations in bichromophoric systems and polymers.[10,24]

In a previous paper, we have shown that radical cations of phenyl and naphthyl chromophores in bichromophoric systems and polymer systems have an intramolecular interaction with ground-state chromophores even in a rigid glass matrix at 77 K and have shown that the absorption spectrum varies remarkably with changes in intermolecular distances.[25] The dimer radical cation is a sensitive probe for evaluating weak and rather long distance inter- and intramolecular interactions in comparison with the excimers.[10,25] In addition, because of its long lifetime, the probe gives us information concerning slow conformational changes in polymer chains.

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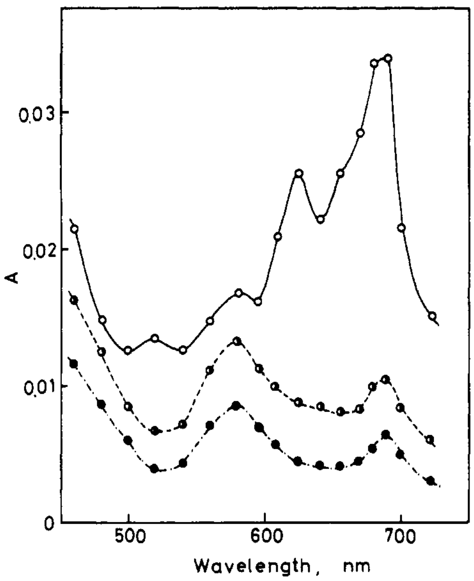

Figure 1. Transient absorption spectra of a methylene chloride solution containing 5 × 10^{-3} M 2-ethylnaphthalene immediately (○), 200 ns (◑), and 750 ns (●) after the pulse.

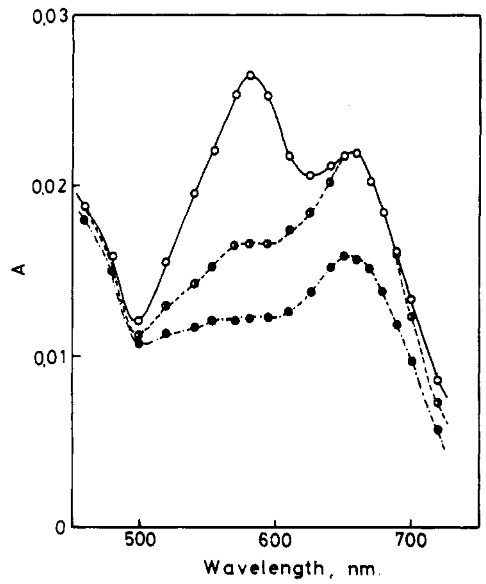

Figure 2. Transient absorption spectra of 5 × 10^{-3} M 1,3-di(2-naphthyl)propane in methylene chloride immediately (○), 200 ns (◑), and 750 ns (●) after the pulse.

In this study, the dynamics of dimer radical cation formation in, α,ω-di(2-naphthyl)alkanes [(2-naphthyl)–$(CH_2)_n$–(2-naphthyl) (n = 3, 6, 12)] and in polymers has been measured by the pulse radiolysis method to reveal the geometrical requirement of the dimer structure and its relation to the conformational changes of polymer chains.

The behavior of radical ions can be detected by pulse radiolysis as well as by laser photolysis. In the latter case, electron-transfer quenching in the fluorescent state of an electron donor (or acceptor) molecule by an acceptor (or donor) leads to the formation of the radical cation and anion pair in polar solvents. The fluorescence state has a conformation different from that of the ground state. The pulse radiolysis method is superior to the photoexcitation method for characterizing the dynamic behavior of ions, because the ions are formed instantaneously by hole or electron transfer to the solute molecules in the ground-state conformations. The solute radical cations, for example, are known to be formed in halogenated alkanes on a picosecond time scale by capturing the rapidly migrating positive holes.[26] This enables us to elucidate the dynamics of the conformational changes, which start from the most stable conformation in the ground state. In the case of fluorescence quenching, only the conformational changes that start from the stable conformation in the fluorescence state can be detected.[10] In the present study, therefore, the pulse radiolysis method has been employed to produce radical ions of solute molecules.

Experimental Section

Materials. α,ω-Di(2-naphthyl)alkanes [(2-naphthyl)–$(CH_2)_n$–(2-naphthyl) (n = 3, 6, 12)] were synthesized according to the method of Chandross[27a] and Szwarc.[27b] Poly(2-vinylnaphthalene) was prepared by anionic polymerization with n-butyllithium initiator. The polymers were purified by repeated precipitation from methylene chloride solutions into methanol. The molecular weight distributions of these polymers measured by GPC are within a value of 1.3 for M_W/M_n. Methylene chloride was carefully purified by fractional distillation and dried over molecular sieves.

Method of Measuring. All sample solutions were degassed by a freeze–thaw cycle under a reduced pressure of less than 10^{-5} mmHg. The solution was irradiated with a single 8-ns electron pulse. Details of the present pulse radiolysis system have been reported previously.[28] Fluorescence decay was detected with a fast response photomultiplier (R843, response time of the measuring system is 350 ps) after excitation with a single 40-ps electron pulse.

Results

I. Absorption Spectra of Dinaphthylalkane Cations. According to Hamill's criterion,[29] radical cations are formed in halogenated alkane solutions. Figure 1 shows the transient absorption spectra of a methylene chloride solution containing 5 × 10^{-3} M 2-ethylnaphthalene, observed immediately after the pulse and at 200 and 750 ns after the pulse. The absorption spectrum is composed of two bands at around 690 and 580 nm. The peak at 690 nm with a subpeak at 620 nm is ascribable to the monomeric radical cation of 2-ethylnaphthalene on the basis of the spectral similarity to the spectrum observed in a rigid butyl chloride matrix containing 2-ethylnaphthalene at low temperature, which is identified as the monomeric radical cation of 2-ethylnaphthalene.[25] The band at 580 nm can be assigned to the absorption of an intermolecular dimer radical cation of 2-ethylnaphthalene by analogy to the dimer radical cation of naphthalene.[30] The absorption band at 690 nm observed immediately after the pulse decayed very rapidly, especially in the initial stage, while the absorption band at 580 nm decayed rather slowly. This spectral change suggests the coexistence of conversion of the monomer radical cations at 690 nm to the dimeric radical cations at 580 nm and neutralization reactions.

A quite different spectral change behavior was observed for the spectrum of 1,3-di(2-naphthyl)propane. Figure 2 shows the transient absorption spectra in methylene chloride after the pulse. Absorption due to monomeric naphthyl radical cations at 690 nm was not observed. The spectrum after the pulse is composed of two absorption bands at 580 and 660 nm. The absorption at 580 nm decayed in a half-time of 20 ns after the pulse and converted to the band at 660 nm.

Although the 580-nm band is similar to the dimer radical cation of 2-ethylnaphthalene, the band is ascribable not to an intermolecular dimer radical cation but mainly to an intramolecular one because the band was clearly observed immediately after the pulse even at very low concentration (less than 10^{-3} M). The conversion of the 580-nm band to the 660-nm band suggests that the absorption at 660 nm is also due to the dimeric radical cation

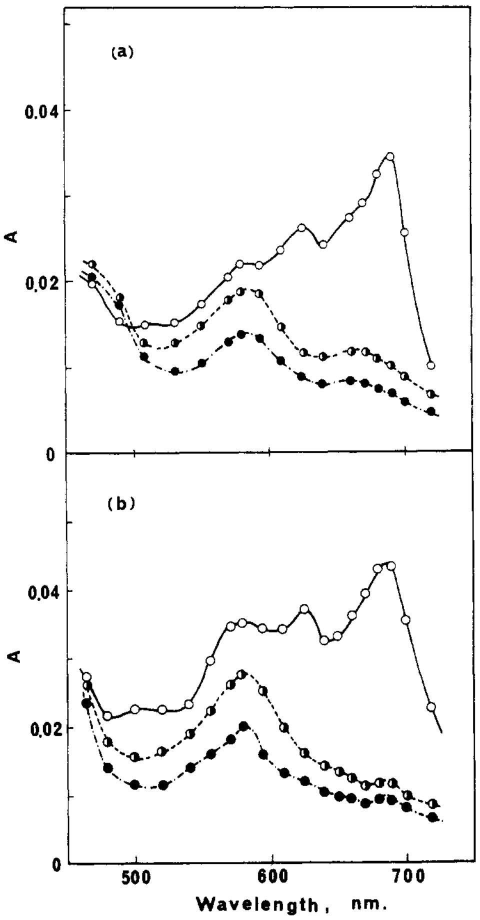

Figure 3. Transient absorption spectra of a methylene chloride solution containing (a) 5 × 10^{-3} M 1,6-di(2-naphthyl)hexane, (b) 5 × 10^{-3} M 1,12-di(2-naphthyl)dodecane immediately (○), 200 ns (◑), and 750 ns (●) after the pulse.

in a different geometrical structure. The possibility of assigning the 660-nm band to a reaction product can be rejected because this band was not observed for 2-ethylnaphthalene.

A monomeric radical cation produced by pulse irradiation reacts quickly with the ground-state naphthalene chromophores in the same molecule and leads to the formation of a dimeric radical cation having a 580-nm band during the pulse in less than 10 ns. The dimer converts to a thermodynamically more stable dimer having a different geometrical structure by a conformational change of the methylene groups. The rate of formation of the stable dimer radical cation was measured to be around 20 ns. It is inferred from the small rate that the relaxation process involves large conformational changes in the connecting methylene chains.

The transient absorption spectra of 1,6-di(2-naphthyl)hexane and 1,12-di(2-naphthyl)dodecane in methylene chloride solution are given in Figure 3. The absorption spectrum of these bichromophoric compounds immediately after the pulse is composed of two bands at 690 and 580 nm. The dynamic behavior of the 690- and 580-nm bands is similar to the behavior of 2-ethylnaphthalene rather than to that of 1,3-di(2-naphthyl)propane. In the spectrum of 1,6-di(2-naphthyl)hexane, a weak absorption was also discerned at around 660 nm, while the band was not observed for 1,12-di(2-naphthyl)dodecane.

In these two bichromophoric molecules, the two naphthyl chromophores are attached to the alkane chains well separated from each other, and the average distance between the chromophores is not close enough to produce the intramolecular dimer radical cations quickly. With decrease in the concentration of these chromophores in methylene chloride, the intensity of 580-nm band decreased to some extent. These results indicate that the 580-nm band involves both intramolecular and intermolecular dimer radical cations.

The appearance of a 660-nm band for 1,6-di(2-naphthyl)hexane suggests a part of the dimer radical cations converts to more stable dimer conformation during the lifetime of the ions. The very small intensity ratio of the 660-nm band to the 580-nm band of 1,6-di(2-naphthyl)hexane in comparison with the intensity ratio of 1,3-di(2-naphthyl)propane provides further evidence that the band at 660 nm observed in 1,3-di(2-naphthyl)propane is due to the dimeric radical cation produced by intramolecular interaction between the two naphthyl chromophores attached to the propane chain.

II. Absorption Spectra of Polymer Cations and Their Dynamic Behavior. Figure 4 shows the transient absorption spectra of poly(2-vinylnaphthalenes) of various molecular weights in methylene chloride after pulse irradiation. The spectral change is similar to that of the 1,3-di(2-naphthyl)propane systems. The spectrum is composed of two absorption bands at 580 and 660 nm. Monomeric radical cation absorption at 690 nm was not observed even immediately after the pulse. The 660-nm band increases with the decay in the 580-nm band absorption. These two bands are ascribable to the dimer radical cations of pendant naphthyl groups of the polymer in different geometrical structures, as discussed for 1,3-di(2-naphthyl)propane.

Although the dimer radical cation spectrum change was similar to the behavior observed for 1,3-di(2-naphthyl)propane, the rate of conversion from the 580- to the 660-nm band was much slower in the polymer. Figure 5 shows the molecular weight dependence of the conversion time. The conversion time was measured from the decay of the 580-nm band. The rate of conversion becomes slower from 70 to 125 ns with an increase in the molecular weight from 1950 to 1.2 × 10^5. The conversion time of 1,3-di(2-naphthyl)propane, 20 ns, was 3–6 times faster than the time of the polymer systems.

Figure 5 also depicts the molecular weight dependence of the formation time of excimer fluorescence for the same polymers produced by a pulse electron irradiation. The time of excimer formation of 1,3-di(2-naphthyl)propane, 2.8 ns, decreased to around 2.0 ns in the polymer systems. The increase in the rate of formation suggests excitation energy migration in the polymer system.

Another interesting feature of the molecular weight dependence of the spectrum is the shape and the intensity of the 660-nm band. The half-width becomes greater and the intensity increases as the molecular weight is increased. This suggests that some fluctuation exists in the dimer structure and that the efficiency of the conversion from the unstable dimer to the stable dimer increases with increase in molecular weight.

The temperature dependence of the rate of stable dimer formation at 660 nm gives us information concerning the activation energy of the conformational change. The activation energy was measured by changing the temperature from −15 to +35 °C, and 7.4 ± 1.0 kcal/mol and 9.0 ± 1.0 kcal/mol were obtained for the 1,3-di(2-naphthyl)propane and poly(2-vinylnaphthalene) (MW = 3.8 × 10^4), respectively. Although the activation energy value had a tendency to increase with increase in molecular weight, the difference was almost within experimental error. The

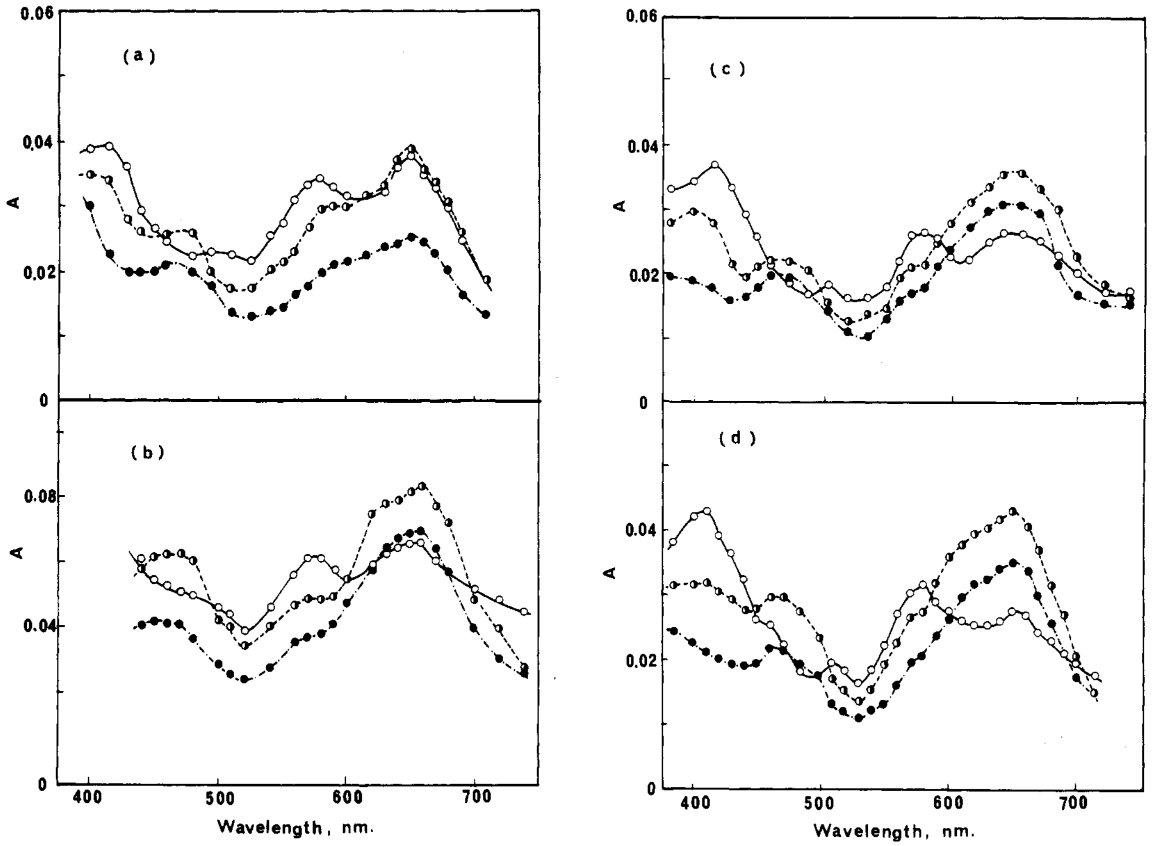

Figure 4. Transient absorption spectra of poly(2-vinylnaphthalene) with molecular weights of (a) 1950, (b) 38 000, (c) 80 000, and (d) 120 000 in methylene chloride immediately (○), 200 (a, b) or 400 ns (c, d) (◑), and 1800 ns (●) after a pulse.

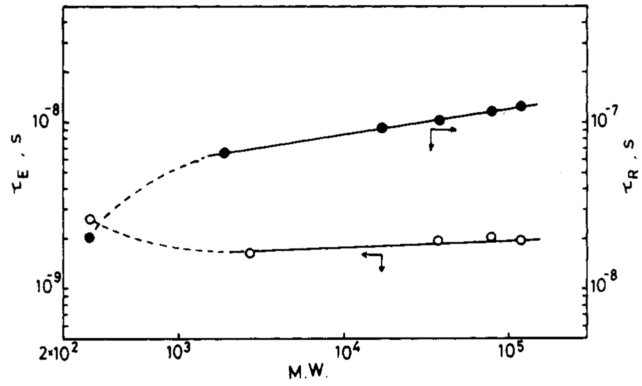

Figure 5. Dependence of the conversion time, τ_R, and excimer formation time, τ_E, on the molecular weight of poly(2-vinylnaphthalene).

value is twice that of the activation energy of excimer formation of 1,3-di(2-naphthyl)propane, 4.0 kcal/mol.[27a] The large activation energy suggests that the process includes cooperative works of several rotations or some kind of hindered rotation, especially in the polymer systems.

These large conformational changes in polymer systems are expected to be dependent on the nature of the solvent. Figure 6 shows the solvent dependence of the transient absorption change of poly(2-vinylnaphthalene). The inset shows the time dependence of the absorptions. In a good solvent, methylene chloride, good correlation between the decay of the 570-nm band and the formation of the 640-nm band is clearly shown. The pronounced increase of the absorption at 660 nm indicates that the polymer has sufficiently high chain flexibility in the good solvent and that the stable dimer geometry can be reached easily by a conformational change of the polymer chains.

In a poor solvent 89/11 (v/v) (methylene chloride/cyclohexane), on the other hand, the interconversion from the 580-nm band to the 660-nm band was scarcely observable. The intensity ratio of the 580- and 660-nm bands remained almost constant except for a small rapid initial change. Population distributions between the two dimer conformations are mainly determined in the formation processes of the two kinds of dimers during the pulse, and conversions between them are prohibited because of the shrunken conformation of the polymer chain in the poor solvent. In the shrunken conformation, the high density

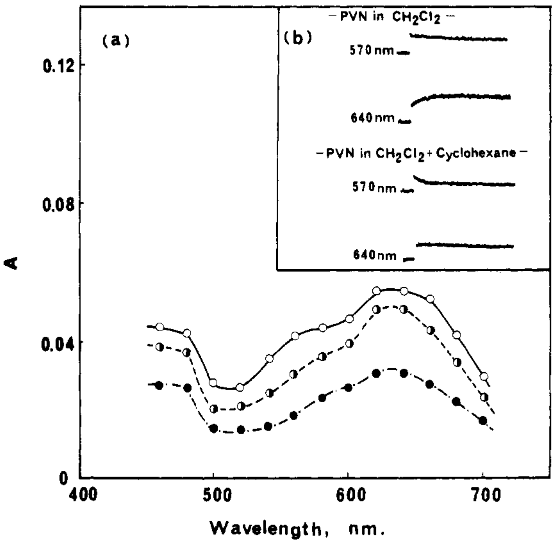

Figure 6. (a) Transient absorption spectra of poly(2-vinylnaphthalene) (MW 38 000) in 89/11 (v/v) methylene chloride/cyclohexane immediately (○), 200 ns (◑), and 1800 ns (●) after the pulse. (b) Typical oscilloscope traces of dimer cation obtained in the pulse radiolysis of poly(2-vinylnaphthalene) (MW 38 000) in methylene chloride solution, and methylene chloride/cyclohexane solution, monitored at 570 and at 640 nm.

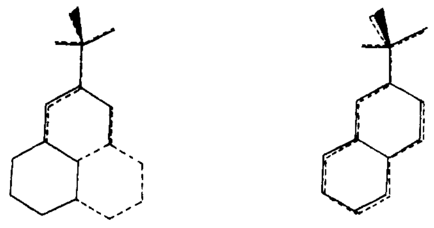

Figure 7. Dimer geometries in 1,3-di(2-naphthyl)propane and poly(2-vinylnaphthalene).

of the polymer chains in the coil prevents the conformational change, which causes the spectral change from 580 to 660 nm.

Discussion

Dimer radical cation is a useful tool for the study of weak intramolecular interaction in polymer systems because small changes in the intermolecular distance and geometrical structures markedly change the spectral shape and absorption peak positions. In addition, the long lifetime of the radical ions enables us to follow the rather slow conformational change in the polymer systems.

The large spectral difference between the two dimer radical cations observed in 1,3-di-(2-naphthyl)propane and poly(2-vinylnaphthalene) suggests that these dimers have geometries with different overlaps between the two naphthyl chromophores (Figure 7), as is well established in the case of excimers of 2,4-di(1-pyrenyl)pentane[8,12] and 1,3-di(1-pyrenyl)propane.[16-18] Fluorescence decay measurements on 2,4-di(1-pyrenyl)pentane clearly showed that one of the eclipsed and partially overlapped excimer conformations gives a longer wavelength emission with a lifetime of 160 ns and the other a shorter wavelength emission with a lifetime of 80 ns. The existence of the two dimer radical cation species with different geometrical structure was also verified for anthracene by absorption measurement in glassy matrices.[31]

These two partially or fully overlapped sandwich structures of naphthyl chromophores can be reached from ($T\bar{G}$, $\bar{G}T$) conformations of the isotactic chain or TT conformations of the syndiotactic chain by a single rotation of the methylene chains. The most probable process is the formation from the ($T\bar{G}$, $\bar{G}T$) conformation in the isotactic chain units in the polymers, which is similar to the excimer formation process. In the case of 1,3-di(2-naphthyl)propane, both the (tg, gt) and (tg$^-$, g$^-$t) conformations can produce the sandwich structure (gg$^-$, gg$^-$) by a single rotation.

During the course of the sandwich structure formation, the probability of formation of the two rotational isomeric states, eclipsed and partially overlapped, is almost the same as in the case of the polymer, although one isomeric state is slightly dominant over the other in the case of 1,3-di(2-naphthyl)propane, as is shown from the initial intensity at 580 and 660 nm. The rotational isomeric state giving absorption at 580 nm is rather unstable thermodynamically compared with the other isomeric state and converts to the stable one at 660 nm. This relaxation process requires double rotations of the chains, unfolding of the chain to the open form and refolding to the sandwich structure, because rotation of the naphthyl chromophores in the sandwich structure is prohibited due to steric hindrance. The double rotation requires a slow relaxation process, especially in the polymer systems.[32]

Although there is no clear evidence at this moment, one may suggest that the partially overlapped structure corresponds to the 580-nm band and the fully overlapped structure corresponds to the 660-nm band, when we compare the spectra with that of 2,4-di(*N*-carbazoyl)pentane.[10] The dimer radical cation spectrum of the sandwich structure of the 2,4-di(*N*-carbazoyl)pentane is similar to the monomeric radical cation spectrum, and the partial overlap spectrum shifted to a shorter wavelength. This correlation may be applied to naphthyl chromophores.

The dimer radical formation process is summarized as follows: the two geometrical structures, the partially and fully overlapped sandwich structures, are produced through a kinetically controlled process by interaction of the monomer radical cation with the ground-state chromophore. They are formed very quickly and stabilized into a transient state. The unstable partially overlapped state slowly converts to a thermodynamically lower free energy state, the fully overlapped state. This thermodynamically driven process may need a higher activation energy than the initial kinetically controlled process.

Acknowledgment. We thank K. Tsumori and N. Kimura for valuable technical assistance in this study.

Registry No. 1,3-Di(2-naphthyl)propane, 75442-70-5; 1,6-di(2-naphthyl)hexane, 64648-99-3; 1,12-di(2-naphthyl)dodecane, 102745-34-6; poly(2-vinylnaphthalene), 28406-56-6.

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One-Dimensional Aromatic Crystals in Solution. 8. Periodic Arrangement of Naphthyl Chromophores along α-Helical Polypeptides with Varying Spacings and Orientations

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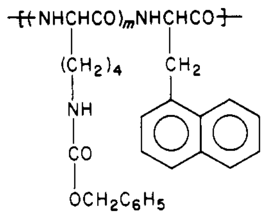
ABSTRACT: Polypeptides having regular sequences of [Lys(Z)$_m$-1-napAla] (m = 1–4) [Lys(Z) = N^ϵ-benzyloxycarbonyl-L-lysine; 1-napAla = L-1-naphthylalanine] were prepared. Infrared spectra of these polymers in trimethyl phosphate solution indicated the occurrence of α-helical main-chain conformation. The polymer solutions showed a strong circular dichroism (CD) at the naphthyl ^1B_b absorption band, indicating a helical arrangement of 1-naphthyl groups along the α-helical main chain. The helical side-chain conformation was analyzed theoretically by the ECEPP conformational energy calculation for poly(Ala$_m$-1-napAla)s assuming α-helical main chains. It was found that the conformational freedom of the 1-naphthylmethyl group is highly restricted and only two regions, i.e., $(\chi_1, \chi_2) = (178 \pm 6°, 257 \pm 1°)$ (form A) and $(273 \pm 6°, 109 \pm 2°)$ (form B), are allowed for the four sequential polypeptides. Theoretical CD curves were computed for the four sequential polypeptides having α-helical main chains with a side-chain conformation in form A or B. The CD curves calculated for form A showed a qualitative agreement with the experimental curves for the four sequential polypeptides.

A one-dimensional chromophoric array is the most basic system on which various aspects of electronic properties of chromophoric assemblies can be studied. The rate of energy transfer and electron transfer will be most simply interpreted in a one-dimensional system in which the complexity arising from the multiple paths of the transfer processes is eliminated. Furthermore, some new electronic interactions that are able to act only in one-dimensional systems have been proposed.[2] For example, Davydov has proposed a soliton state on an α-helical polypeptide chain.[3] Although the Davydov soliton is based on a coupling of an exciton of the amide I vibration with a longitudinal lattice vibration of the α-helix, it is a straightforward extension of the theory to an electronic soliton in which an electronic exciton couples with a longitudinal lattice vibration.[3]

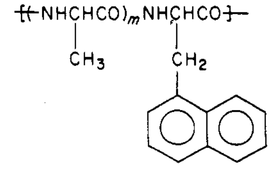
A one-dimensional chromophoric system can be synthesized by covalently attaching chromophores to an α-helical polypeptide chain.[2] A previous papers, we have reported the syntheses and the conformational analyses of poly(L-arylalanine)s which carry 1- and 2-naphthyl and 1-pyrenyl groups as aryl substituents.[4-8] However, these homopolypeptides cannot be considered one-dimensional aromatic systems in a strict sense, since their molecular structure suggests that each aromatic group can interact with more than two neighboring aromatic groups. This multiplicity in the side-chain interaction can be eliminated by inserting spacers between the aromatic amino acid units, keeping the interchromophoric distance between the nearest pair of aromatic groups along the α-helix nearly unchanged.

The present paper describes the synthesis and spectroscopic characterization of a series of sequential polypeptides consisting of N-benzyloxycarbonyl-L-lysine [Lys(Z)] and L-1-naphthylalanine (1-napAla) units (I).



p[Lys(Z)$_m$-1-napAla]
I, m = 1–4

The most probable conformations in solution were determined theoretically by empirical energy calculation and theoretical circular circular dichroism (CD) computation on the sequential polypeptides. In the theoretical calculations, the Lys(Z) unit was replaced by Ala unit for simplicity (II).



p(Ala$_m$-1-napAla)
II

Experimental Section

Synthesis of p[Lys(Z)$_m$-1-napAla]. The sequential polypeptides were prepared by a procedure that is known to minimize racemization. However, some racemization can occur during hydrolysis of peptide methyl esters and during polymerization

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