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SYNTHESIS AND SPECTROSCOPIC PROPERTIES OF POLY(L-1-PYRENYLALANINE)1)

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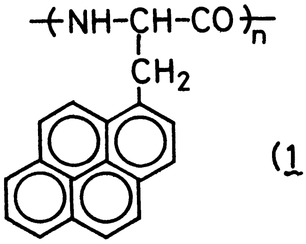
A novel aromatic poly(amino acid), poly(L-1-pyrenylalanine), was synthesized as a block copolymer with poly(γ-benzyl DL-glutamate). The circular dichroism of the block copolymer in trimethyl phosphate indicated a helical arrangement of the pyrenyl groups along the polypeptide chain. The excimer emission was weaker than that from the corresponding racemic copolymer. Two different species of excimers were found by the circularly polarized fluorescence spectrum.

Extensive interest has been focused on one-dimensional array of aromatic chromophores as materials of electric conductivity or as microscopic electron conductors.2,3) In the latter case the chromophoric array may be used as a molecular conductor which can transport electrons across a biological membrane. Aromatic poly(α-amino acid)s are potential candidates as the molecular conductor, if the chromophores are regularly arranged along a helical polypeptide chain. Previously, syntheses and spectroscopic properties of poly(L-1- and 2-naphthyl alanine)s have been reported by us.4,5) In the two kinds of polymers the naphthyl groups were found to take a helical arrangement along the polypeptide helix. Very little excimer formation found in these polymers is especially noteworthy, since the excimer sites may work as energy or electron traps which interrupt the transportation of energy or electron along the polymer chain. In this communication, synthesis and spectroscopic properties of another novel poly(amino acid), poly(L-1-pyrenylalanine) [poly(L-PyrAla)] (**1**), will be described. Since the π-orbital system of pyrenyl chromophore is spatially extended, one may expect more effective interchromophore interaction than in the case of the naphthyl polymers.



(**1**)

Optically active pyrenylalanine (PyrAla) derivatives were prepared as follows. Ethyl 2-benzamido-3-(1-pyrenyl)-2-propenoate6) was hydrogenated with palladium carbon to yield N-benzoyl-DL-pyrenylalanine ethyl ester (mp 168-170°C). Acid hydrolysis followed by acetylation gave N-acetyl-DL-1-pyrenylalanine, which was deacetylated by the action of acylase.7) The free amino acid obtained was optical active and assumed to be an L-isomer.

Alternatively, the optically active derivative of PyrAla was obtained from the racemic mixture of N-benzoyl-1-pyrenylalanine by the complex formation with (+)-1-phenylethylamine. The diastereomeric complex with the L-isomer was less soluble in ethanol than the complex with the D-isomer. N-benzoyl-L-pyrenylalanine: mp 230-234 °C decomp, $[\alpha]_D = -232.5°$ in dimethylformamide. The optical purity was tested for the amino acid methyl ester by ^{1}H NMR chemical shift of the O-CH_3 peak in the presence of a chiral shift reagent.$^{4,5)}$ It was found that the L-isomer contained ca. 2% of the optical antipode.

The free amino acid was converted with phosgene dimer to N-carboxyanhydride (NCA) (mp 199-204°C decomp. Found: C, 75.90; H, 4.25; N, 4.30%. Calcd for $C_{20}H_{13}O_3N$: C, 76.18; H, 4.16; N, 4.44%). The NCA was polymerized with preformed poly(γ-benzyl DL-glutamate) [poly(DL-Glu(OBzl)] (the degree of polymerization = 150)] as initiator, an NCA to initiator molar ratio being kept at 20. After completion of the polymerization, the polymer solution was diluted with an appropriate solvent and subjected to spectroscopic measurements. A gel-chromatographic examination indicated the absence of low molecular weight components having pyrenyl groups in the polymer solution. Thus the formation of a block copolymer represented below was proven.

$$(\text{L-PyrAla})_{20}[\text{DL-Glu(OBzl)}]_{150}$$

Since the poly[DL-Glu(OBzl)] unit does not affect the spectroscopic properties of the pyrenyl chromophores, the block copolymer will be referred to simply as poly(L-PyrAla) hereafter.

A racemic copolymer, $(\text{DL-PyrAla})_{20}[\text{DL-Glu(OBzl)}]_{150}$, was also prepared in a similar manner and will be referred to as poly(DL-PyrAla). As a monomeric model compound, N-acetyl-L-1-PyrAla methyl ester (Ac-L-PyrAla-OMe) was also prepared.

Figure 1 shows UV absorption spectra (bottom) and circular dichroism (CD) (top) of poly(L-PyrAla) and its model compound in dichloroethane. The polymer shows large ellipticities; $[\theta]_{353.5} = 1.23\times10^5$ deg cm^2 (dmol of pyrenyl group)$^{-1}$ at the ^1L_a band, $[\theta]_{286} = 6.5\times10^4$ at the ^1B_b band, and $[\theta]_{249} = -1.62\times10^5$ at the ^1B_a band. These ellipticities are much larger than those of the monomeric model compound. The enhanced CD intensity indicates a helical conformation of poly(L-PyrAla), in which the pyrenyl chromophores are arranged regularly and interact with each other. The interchromophoric interaction is also evident from a marked hypochromicity observed in the absorption spectra (Fig. 1, bottom).

Fluorescence spectra of poly(L-PyrAla), poly(DL-PyrAla), and Ac-L-PyrAla-OMe are compared in Fig. 2 (bottom). Excimer fluorescence which is predominant in the racemic polymer is suppressed in the stereoregular polymer. The reduced excimer formation in poly(L-PyrAla) indicates the reduced encounter of the chromophoric side chains as a result of the regular arrangement along the helical main chain.

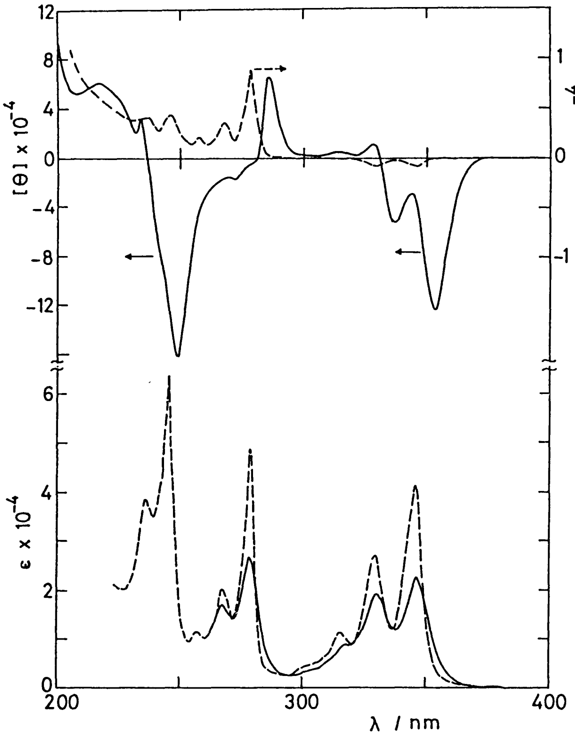


Fig.1. UV absorption (bottom) and CD (top) spectra of poly(L-PyrAla) in dichloroethane containing 10% of dimethylformamide (——, [Pyr] = 5.0x10^{-3} mol dm^{-3}) and of Ac-L-PyrAla-OMe in dichloroethane (----, [Pyr] = 2.0x10^{-3} mol dm^{-3}) at room temperature.

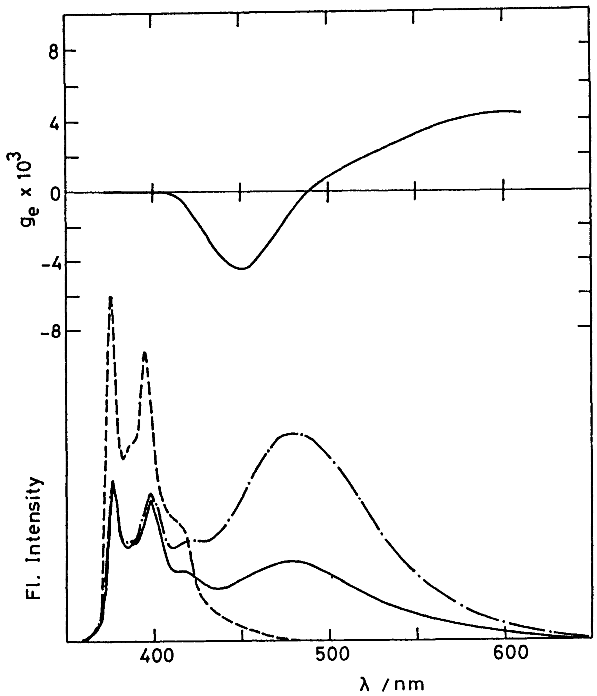


Fig.2. Fluorescence (bottom) and CPF (top) spectra of poly(L-PyrAla) (——), poly(DL-PyrAla) (—·—), and Ac-L-PyrAla-OMe (----) in N_2-bubbled dimethylformamide at room temperature. Fluorescence spectra, [Pyr] = 1.0x10^{-5} mol dm^{-3}; CPF spectrum, [Pyr] = 4.0x10^{-5} mol dm^{-3}.

Conformation or configuration of the excimer can be discussed most adequately from circularly polarized fluorescence (CPF) spectroscopy (Fig.2, top).[8,9] The ordinate of the CPF spectrum is represented with the Kuhn's dissymmetry factor, $g_e = 2(I_L - I_R)/(I_L + I_R)$, where I_L and I_R are intensities of left- and right-circularly polarized fluorescence, respectively.

No detectable CPF signal was observed in the monomer fluorescence region either with poly(L-PyrAla) or with the monomeric model compound. The absence of the fluorescence dissymmetry in poly(L-PyrAla) indicates that the monomer excited state of the lowest energy is virtually localized on a pyrenyl group.

At the excimer fluorescence region, the CPF spectrum of poly(L-PyrAla) indicates the presence of two different fluorescent species ($g_{e\ 450} = -4.5\text{x}10^{-4}$, $g_{e\ 600} = +4.4\text{x}10^{-4}$). A possible interpretation for the dual excimers could be the coexistence of the second excimer and the sandwich-type excimer in the chromophoric polymer. The second excimers have been observed in some polymers[10] and in bichromophoric compounds,[11] and are characterized by the partial overlapping of the chromophores and by the shorter fluorescence wavelength than the sandwich-type excimers. However, this interpretation, although not thoroughly discarded, seems inadequate for poly(L-PyrAla). A preliminary result$^{12)}$ of the temperature-dependence of the CPF spectrum indicated that an enhancement of the helical regularity increased the component which fluoresces at longer wavelengths and reduced the shorter-wavelength component. It was thus shown that the pyrenyl chromophores in the helical part of the polymer emit at longer wavelengths and those in the disordered part fluoresces at shorter wavelengths. Time-resolved fluorescence analyses indicated that the shorter-wavelength component behaves much like the ordinary sandwich-type excimers, whereas the longer-wavelength component shows much shorter lifetime than the ordinary excimers. Therefore, a tentative assignment at present is that the shorter-wavelength component is a sandwich-type excimer formed at irregular part of the polymer and the longer-wavelength component is emitted from the helical part. The geometrical and electronic nature of the latter excimer is uncertain at present.

The above assignment should be confirmed by further study of the temperature and chain-length dependences of the CPF spectrum and of the kinetics of excimer formation, which are in progress.

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