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CONFORMATIONAL CHANGES IN SOLID FILMS AMONG α-HELICES WITH DIFFERENT HELIX SENSES AND π-HELIX FOR COPOLYMERS OF POLY(ASPARTATE ESTERS) WITH BENZYL AND (m-PHENYLAZO)BENZYL SIDE CHAINS

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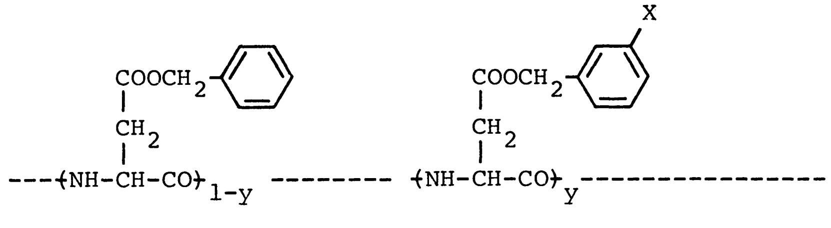
Copolymers of β-(m-phenylazo)benzyl L-aspartate and β-benzyl L-aspartate exist as left-handed α-helix (α_L), right-handed α-helix (α_R) or π-helix (π_L) in solid films at 25 °C. Conformational transitions from α_L to π_L and from α_R to π_L were found to occur by heating.

The conformational versatility of poly(aspartate esters) is the basis for designing photoresponsive systems in which polymer conformation transforms in an on-off fashion by light. Various kinds of photoinduced changes of polypeptide conformation have been shown to occur in solution for poly(aspartates) containing azobenzene moieties.$^{1)}$ In an extension of the work, we have investigated conformational behavior of the azobenzene polypeptides in solid films. It is well known that poly(β-benzyl L-aspartate) (PBLA), which exists as a left-handed α-helix (α_L) in chloroform, shows a transition in the solid state from α_L to a left-handed ω-helix (ω_L) by heating.$^{2)}$ Recently, another type of transition from a right-handed α-helix (α_R) to a left-handed π-helix (π_L) was found to occur in the solid state for poly(β-phenethyl L-aspartate).$^{3)}$ In the present work, the incorporation of m-phenylazo substituent into some of benzyl moieties of PBLA was found to enable an $\alpha_L \rightarrow \pi_L$ transition by heating the films instead of the $\alpha_L \rightarrow \omega_L$ transition of PBLA itself. An $\alpha_R \rightarrow \pi_L$ transition was also found to occur under certain conditions.



X: $-N=N-C_6H_5$

y = 0 (PBLA), 0.10, 0.32, 0.49, 0.67, 0.92

The copolymers of (m-phenylazo)benzyl L-aspartate and benzyl L-aspartate shown above undergo a photoinduced $\alpha_L \rightarrow \alpha_R$ transition in mixed solutions of 1,2-dichloroethane and trimethyl phosphate.$^{1d)}$ The solid films of the copolymers

Table 1. Infrared Band Positions for the Copolymer with 32% m-Phenylazo Substituent and Poly(L-aspartate esters)

	Solvent for film making	Temperature	Band position / cm^{-1}			
			Amide A	Ester C=O	Amide I	Amide II
		Copolymer				
A (α_R)	MS$^{a)}$	25 °C	3291	1741	1656	1553
B (π_L)	MS$^{a)}$	150 °C	3332	1730	1672	1538
C (α_L)	chloroform	25 °C	3299	1734	1664	1556
D (π_L)	chloroform	150 °C	3334	1729	1672	1538
		Esters				
$\alpha_R$$^{b)}$			3296	1741	1659	1553
$\alpha_L$$^{b)}$			3302	1735	1666	1557
$\omega_L$$^{b)}$			3296	1731	1675	1536
$\pi_L$$^{c)}$			3332	1731	1674	1536

a) MS: mixed solvent of chloroform and trimethyl phosphate (3:2 by volume).
b) Ref. 5. c) Ref. 3.

obtained from chloroform solutions show an IR pattern which is typical for the α_L form (Table 1).$^{3-5)}$ The spectra have peaks around 3300 cm^{-1} for the amide A, 1735 cm^{-1} for the ester carbonyl, 1665 cm^{-1} for the amide I and 1550 cm^{-1} for the amide II frequency.

Heating the films at 150 °C for 30 min in vacuo changed the spectral pattern to that of π_L with peaks around 3330 cm^{-1} for the amide A, 1730 cm^{-1} for the ester carbonyl, 1671 cm^{-1} for the amide I and 1537 cm^{-1} for the amide II frequency. The behavior is different from that of PBLA since the same treatment for PBLA resulted in the conformational change from α_L to ω_L helix as previously reported.$^{2)}$ It should be noted that the introduction of only 10% m-phenylazo substituent into PBLA is enough to cause such different behavior.

Another interesting aspect is the solvent effect of trimethyl phosphate on the conformations of the copolymers. The solid films obtained from the mixed solutions of chloroform and trimethyl phosphate (3:2 by volume)$^{6)}$ showed different IR patterns depending on the copolymer composition; the typical α_R pattern was observed for the copolymers with 10% and 32% of m-phenylazo substituent whereas the π_L pattern was observed for the copolymers with more substituent ratios. The reversion of helix was previously reported for PBLA when the solvent was changed from chloroform to trimethyl phosphate.$^{7)}$ In this study, the same result was obtained for PBLA although the mixed solvent of chloroform and trimethyl phosphate was used in place of pure trimethyl phosphate. Therefore, we may say that the copolymers with smaller amounts of m-phenylazo substituent behave in the same fashion as PBLA to the solvent change, but the copolymers with greater amounts of m-phenylazo substituent ($\geq$49%) behave

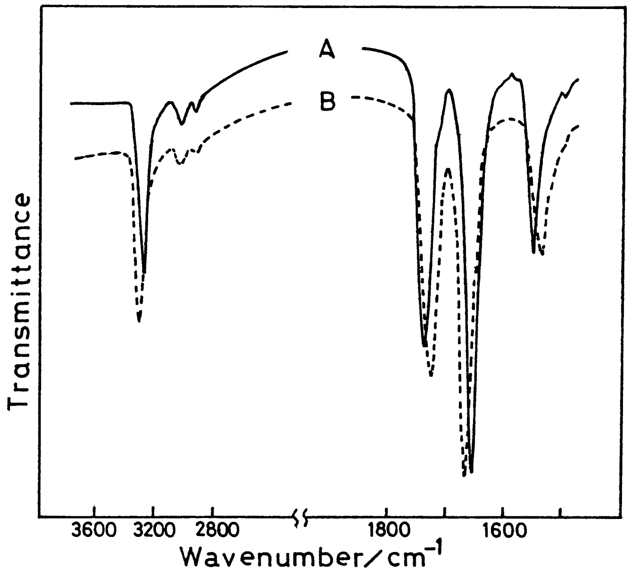


Fig. 1. Infrared spectra of the film of the copolymer with 32% m-phenylazo substituent prepared by casting the mixed solution of chloroform and trimethyl phosphate (3:2) on a KRS-5 plate. A: 25 °C; B: 150 °C (annealing temperature).

quite differently, forming the π_L helix from the mixed solutions. The π_L helix formation at 25 °C contrasts to the behavior of poly(β-phenethyl L-aspartate) which forms the π_L helix above 140 °C.$^{3)}$

Heating the films at 150 °C for 30 min in vacuo caused no conformational change except for the copolymer with 32% m-phenylazo substituent which showed an $\alpha_R \rightarrow \pi_L$ transition (Table 1 and Fig. 1); the α_R form of the copolymers with smaller contents of m-phenylazo substituent ($\leq$10%) and the π_L form of the copolymers with greater contents of m-phenylazo substituent ($\geq$49%) were kept unchanged. The α_R helix of the 32% m-phenylazo copolymer observed at 25 °C, therefore, may be regarded as the form which is in a delicate energy balance, so it seems reasonable that the conformation changes into the π_L helix by heating.

The azobenzene moieties of the copolymers undergo trans-cis photoisomerization, but the attained cis contents were smaller than 30% probably because of the limited mobility in the solid state.$^{8)}$ Although the effect of photoirradiation was checked by IR measurements on all the samples, no conformational change was found to occur.

We are still trying to find photoresponsive films in which polypeptide conformation changes in an on-off fashion by light.

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