(10) S. L. Hsu, A. J. Signorelli, G. P. Pez, and R. H. Banghman, *J. Chem. Phys.*, **69**, 106 (1978).

(11) S. Lefrant, L. S. Lichmann, H. Temkin, D. B. Fitchen, D. C. Miller, G. E. Whitwell II, and J. M. Burlitch, *Solid State Commun.*, **29**, 191 (1979).

(12) A. Snow, P. Brant, D. Weber, and N. -L. Yang, *J. Polym. Sci., Polym. Lett. Ed.*, **17**, 263 (1979).

(13) C. B. Duke, A. Paton, W. R. Salaneck, H. R. Thomas, E. W. Plummer, A. J. Heeger, and A. G. MacDiarmid, *Chem. Phys. Lett.*, **59**, 146 (1978).

(14) M. Kertesz, J. Koller, and A. Azuman, *J. Chem. Soc., Chem. Commun.*, 575 (1978).

(15) M. J. Rice, *Phys. Lett. A*, 71, 152 (1979).

(16) W. P. Su, J. R. Schrieffer, and A. J. Heeger, *Phys. Rev. Lett.*, **42**, 1698 (1979).

(17) P. M. Grant and I. P. Batra, *Solid State Commun.*, **29**, 225 (1979).

(18) A. Karpfen and J. Petkov, *Solid State Commun.*, **29**, 251 (1979).

(19) T. Yamabe, K. Tanaka, H. Terama-e, K. Fukui, A. Imamura, H. Shirakawa, and S. Ikeda, *Solid State Commun.*, **29**, 329 (1979).

(20) T. Yamabe, K. Tanaka, H. Terama-e, K. Fukui, A. Imamura, H. Shirakawa, and S. Ikeda, *J. Phys. C: Solid State Phys.*, **12**, L257 (1979).

(21) H. Shirakawa and S. Ikeda, *Polym. J.*, **2**, 231 (1971).

(22) H. Shirakawa, T. Ito, and S. Ikeda, *Polym. J.*, **4**, 460 (1973).

(23) H. Shirakawa, A. Hamano, S. Kawakami, M. Sato, K. Soga, and S. Ikeda, to be submitted.

(24) T. Ito, H. Shirakawa, and S. Ikeda, *J. Polym. Sci, Polym. Chem. Ed.*, **12**, 11 (1974).

(25) J. H. C. Nayler and M. C. Whiting, *J. Chem. Soc.*, 3037 (1965).

(26) B. Chacko, J. C. W. Chien, F. E. Karasz, A. G. MacDiarmid, and A. J. Heeger, *Bull. Am. Phys. Soc.*, **24**, 480 (1979).

Hideki Shirakawa,* Masaru Sato, Akito Hamano, So-ichiro Kawakami, Kazuo Soga, and Sakuji Ikeda

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta-Cho, Midori-ku, Yokohama 227, Japan

Received October 19, 1979

Conformational Changes of Azoaromatic Polyaspartate Induced by Solvent and/or Light

Stereochemical changes induced in the photochromic molecules incorporated into polymer chains can cause conformational variations of the polymers.[1] The photochromic moieties act as photoregulated "switches" changing reversibly from one geometric isomer to another under the influence of light. Azo compounds can undergo both trans → cis photoisomerization and reversion of the cis isomer back to the trans in the dark or on irradiation and were successfully adopted as photochromic moieties to produce conformational changes of vinyl polymers.[2,3]

Among many polymers containing azoaromatic moieties, polypeptides seemed to be extremely interesting to us from the point of view that polypeptides can take various conformations whose chiroptical properties are distinctly different from each other, and the effect of light on their conformations can be easily evaluated by spectral measurements such as ORD and CD.

Goodman et al. prepared azoaromatic polypeptides from L-*p*-(phenylazo)phenylalanine and investigated the effect of photoisomerization of the azoaromatic side chains on the ORD spectra.[4] Similar investigations were carried out by us for azoaromatic polyaspartates[5-7] and by Ciardelli for azo-modified poly(L-glutamic acid).[8,9]

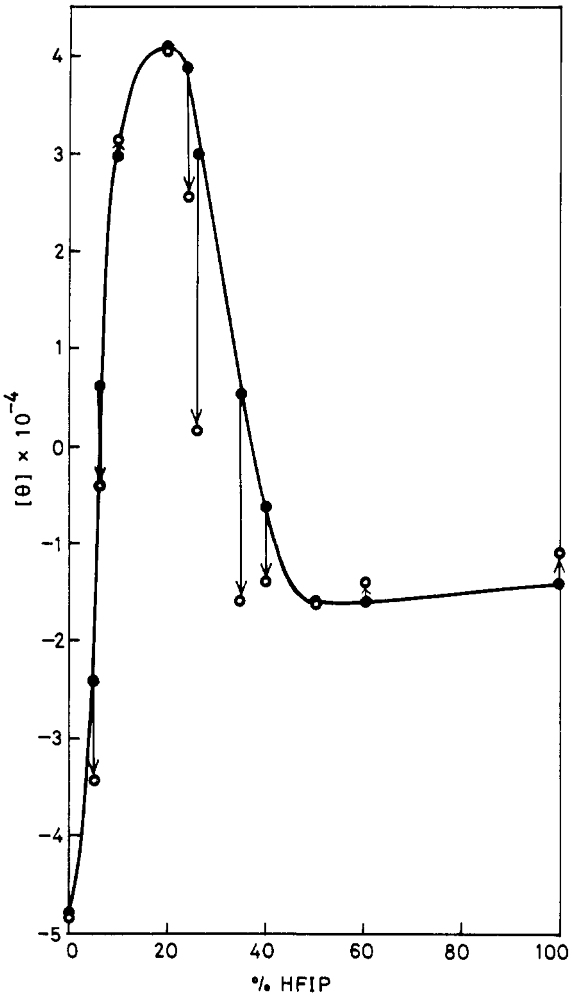
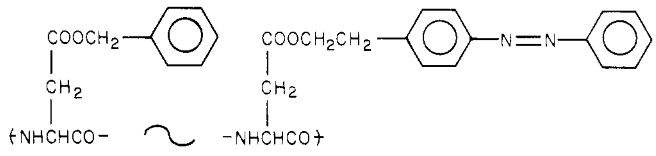


Figure 1. Variation of the molecular ellipticity at 222 nm of I induced by solvent and/or light: (●) before photoirradiation; (○) after photoirradiation.

The light-induced conformational changes of polypeptides were first accomplished by us for copolymers derived from *m*- and *p*-(phenylazo)benzyl L-aspartate.[5-7] These polymers were designed based on the fact that substituted benzyl esters of poly(L-aspartic acid) show conformational versatility, and the conformation can be perturbed by changing the nature and the position of the substituent. This system resembles visual purple rhodopsin whose polypeptide part opsin undergoes a conformational change coupled with the cis-trans photoisomerization of an incorporated chromophore retinal. In a continuation of these investigations, a copolymer I composed of β-benzyl L-aspartate and β-*p*-(phenylazo)phenethyl L-aspartate (33:67) was found to undergo right-handed helix → left-handed helix → random coil transition on addition of hexafluoro-2-propanol (HFIP) to its 1,2-dichloroethane (DCE) solution. Thus there arises one interesting problem of how the conformation of I is affected by the trans-cis photoisomerization of the side-chain azobenzene moieties at different HFIP contents. We wish to report here the results of CD measurements of I in the mixed solutions of DCE and HFIP before and after photoirradiation.



I

Copolymers of β-benzyl L-aspartate and β-*p*-(phenylazo)phenethyl L-aspartate were prepared as photoresponsive polypeptides.[10] The conformation of this polymer

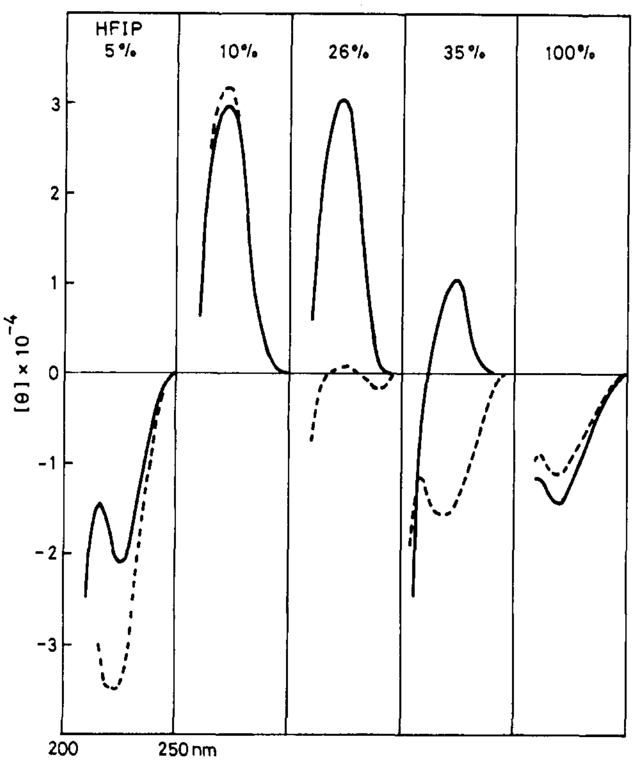


Figure 2. Circular dichroism spectra associated with the amide $n-\pi^*$ transition before (—) and after (- - -) photoirradiation in the mixed solvents of various DCE/HFIP compositions.

series in DCE is left hand helical for the copolymers with less than 40% azo [β-p-(phenylazo)phenethyl L-aspartate] residues whereas it is right hand helical for the copolymers with more azo residues. The polymer with 100% azo residues exhibits poor solubility in DCE. Thus I is the polymer with the highest azo residues among the soluble polymers prepared. In an attempt to check the solvent effect on the conformation[11] of *trans*-I, HFIP was added up to 20% to the DCE solution of I. This led to a solvent-induced right-handed helix → left-handed helix transition as shown in Figure 1. Upon further addition of HFIP, I undergoes a left-handed helix → random coil transition. Bradbury et al. reported similar phenomenon, though in their case the conformational transition was induced by addition of trifluoroacetic acid or dichloroacetic acid to chloroform solutions of copolymers of β-ethyl L-aspartate and β-benzyl L-aspartate.[11b] The random form of I yielded the anomalous value of $[\theta] \sim -15\,000$, which is also in agreement with the result of Bradbury et al. This solvent-induced conformational transition may arise from an alteration of the energy balance as a consequence of hydrogen bonding of HFIP to the side-chain ester group.

Photoirradiation was carried out on the solutions of I at various solvent compositions, using a Corning 7-37 filter which passes the light of 320–390 nm with a 500-W Xenon lamp (percent cis: 70–80 in the photostationary state). The results of photoirradiation are shown in Figures 1 and 2. The trend of light-induced conformational change around 5% HFIP is the one from the left-handed helix to the right-handed helix. At 10% HFIP the trend is inverted and the polymer tends to take a fully left-handed helix. The fully left-handed helix at 20% HFIP is insensitive to light. On further increase in the HFIP content, I again becomes sensitive to light, showing a tendency of conformational change from left-handed helix to random coil with the attainment of maximum ellipticity difference $\Delta[\theta] \sim 28\,500$ at 26% HFIP. When the HFIP content reaches 50%, I is in a random-coil conformation and is hardly affected by photoirradiation. Further increase in the HFIP content causes no significant conformational change although there exists a slight decrease in the absolute ellipticity.

These phenomena suggest the important role of environment in realizing remarkable photoresponsive behavior on natural and synthetic photosensitive macromolecular systems. We are currently investigating the decay process from cis to trans configuration in the mixed solvents in connection with the main-chain conformation.

References and Notes

(1) B. F. Erlanger, *Ann. Rev. Biochem.*, **45**, 267 (1976).

(2) R. Lovrien, *Proc. Natl. Acad. Sci. U.S.A.*, **57**, 236 (1967).

(3) G. Van der Veen and W. Prins, *Photochem. Photobiol.*, **19**, 191 (1974).

(4) (a) M. Goodman and A. Kossoy, *J. Am. Chem. Soc.*, **88**, 5010 (1966). (b) M. Goodman and M. L. Falxa, *ibid.*, **89**, 3863. Goodman et al. investigated chiroptical properties of other azoaromatic polypeptides which lack the ability of photoisomerization.[4c–e] (c) M. Goodman and E. Benedetti, *Biochemistry*, **7**, 4226 (1968). (d) E. Benedetti, A. Kossoy, M. L. Falxa, and M. Goodman, *ibid.*, **7**, 4234 (1968). (e) E. Benedetti and M. Goodman, *ibid.*, **7**, 4242 (1968).

(5) A. Ueno, J. Anzai, T. Osa, and Y. Kadoma, *J. Polym. Sci., Polym. Lett. Ed.*, **15**, 407 (1977).

(6) A. Ueno, J. Anzai, T. Osa, and Y. Kadoma, *Bull. Chem. Soc. Jpn.*, **50**, 2995 (1977).

(7) A. Ueno, J. Anzai, T. Osa, and Y. Kadoma, *Bull. Chem. Soc. Jpn.*, **52**, 549 (1979).

(8) F. Ciardelli, E. Chiellini, C. Carlini, O. Pieroni, P. Salvadori, and R. Menicagli, *J. Polym. Sci., Polym. Symp.*, **62**, 143 (1978).

(9) J. L. Houben, O. Pieroni, A. Fissi, and F. Ciardelli, *Biopolymers*, **17**, 799 (1978).

(10) The amino acid β-p-(phenylazo)phenethyl L-aspartate was synthesized from L-aspartic acid and p-(phenylazo)phenethyl alcohol according to the procedure described previously. (a) Y. Kadoma, A. Ueno, K. Takeda, K. Uno, and Y. Iwakura, *J. Polym. Sci., Polym. Lett. Ed.*, **12**, 715 (1974). All polymers were prepared by the usual *N*-carboxyanhydride (NCA) method with various ratios of β-benzyl L-aspartate *N*-carboxyanhydride and β-p-(phenylazo)phenethyl L-aspartate *N*-carboxyanhydride. Polymerization was carried out in dioxane at room temperature, using triethylamine as an initiator (NCA/initiator molar ratio 50:1). The reduced specific viscosity of the copolymer I stated mainly in this report is 2.50 for a 0.1% DCE solution at 25 °C. The mole percentage of azo amino acid residues in the copolymer was estimated to be 67.24% from the nitrogen content obtained by elemental analysis. Anal. Calcd for I: C, 66.26; H, 5.33; N, 11.54. Found: C, 65.72; H, 5.42; N, 11.54.

(11) There are many reports concerning solvent effects on polypeptide conformation, some of which are: (a) M. Hashimoto, *Bull. Chem. Soc. Jpn.*, **39**, 2713 (1966); (b) E. M. Bradbury, B. G. Carpenter, C. Crane-Robinson, and H. Goldman, *Macromolecules*, **4**, 557 (1971); (c) V. Giancotti, F. Quadrifoglio, and V. Crescenzi, *J. Am. Chem. Soc.*, **94**, 297 (1972); (d) H. Yamamoto and T. Hayakawa, *Biopolymers*, **16**, 1593 (1977); (e) F. Heitz and G. Spach, *Macromolecules*, **10**, 520 (1977); (f) F. Heitz, P. D. Cary, and C. Crane-Robinson, *Macromolecules*, **10**, 526 (1977).

A. Ueno,* K. Takahashi, J. Anzai, and T. Osa

Pharmaceutical Institute, Tohoku University, Aobayama, Sendai 980, Japan

Received June 7, 1979

Variable Temperature High-Resolution Carbon-13 NMR Spectra of Solid Fluoropolymers

It is now well-established that ^{13}C NMR spectra in which resolution approaches that of the liquid state can be obtained for solid hydrocarbon polymers by employing a combination of resolution (dipolar decoupling and magic-angle spinning) and sensitivity (cross-polarization) enhancement techniques.[1–5] In this communication, we re-

0024-9297/80/2213-0460$01.00/0 © 1980 American Chemical Society