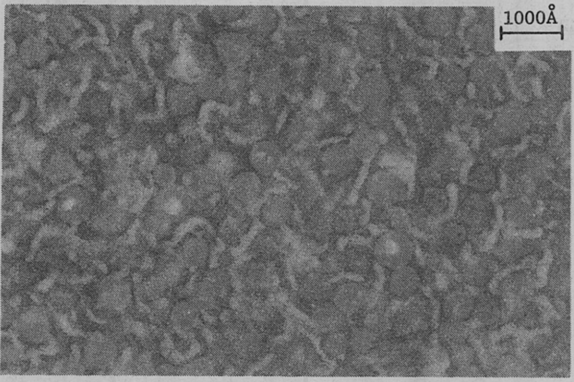
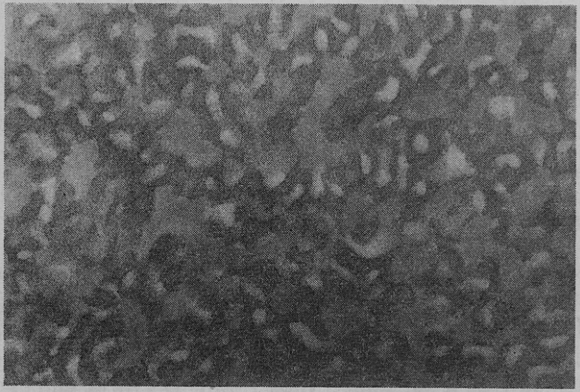


(a) SBP-1/[benzene/methanol(9:1)]



(b) SBP-2/pyridine

Figure 2.

It should be noted that in the above results the morphologies do not comply with a rule given by Molau,[1] namely, that P4VP always forms large globular domains rather than cylindrical or lamellar domains in spite of the P4VP content being varied from 0.10–0.24. In contrast to this, Nagasawa reported that the morphology of an ABC three-block polymer of PS–(poly[(4-vinylbenzyl)dimethylamine])–PI exhibits a combination of Molau's morphologies.[5] We suspect that strong inter- and intrablock coherence of P4VP blocks predominates over other interactions[9,10] and that the P4VP domains tend to keep the interfacial area as small as possible.

To prevent the coagulation of the P4VP phase into globules, we also cast SBP-2 from pyridine, which is a good solvent for P4VP. Figure 2b shows its morphology, in which P4VP formed neither globular domains nor a clear continuous phase but curious amoeba-like domains. This result suggests a possibility of controlling the morphology of SBP's, to some extent, by choosing suitable casting conditions.

Note Added in Proof. Recently we were able to obtain a new morphology, a "three-lager lamellar" structure, in which the three phases alternate as . . .SBP·PBS·SBP. . . in the SBP-1 cast from *n*-butyraldehyde/CHCl$_3$ (9:1 v/v) mixture. The details will be reported soon.

References and Notes

(1) G. E. Molau, Ed., "Colloidal and Morphological Behavior of Block and Graft Copolymers", Plenum Press, New York, 1971.
(2) C. Price, T. P. Lally, and R. Stubbersfield, *Polymer*, **15**, 541 (1974).
(3) W. Cooper, P. T. Hale, and J. S. Walker, *Polymer*, **15**, 175 (1974).
(4) G. S. Fielding-Russel and P. S. Pillai, *Polymer*, 18, 859 (1977).
(5) Y. Matsushita, Y. Higo, H. Choshi, T. Fujimoto, and M. Nagasawa, *Kobunshigakkai-Yokoshu*, 28 (2), 194 (1979).
(6) P. P. Spiegelman and G. Parravano, *J. Polym. Sci., Part A*, 2245 (1964).
(7) K. Arai and T. Kotaka, unpublished experiments, 1979; *Kobunshigakkai-Yokoshu*, **28** (8) (1979).
(8) A. R. Luxton, A. Quig, M.-J. Delvaux, and L. J. Fetters, *Polymer*, **19**, 1320 (1978).
(9) D. J. Meier, *J. Polym. Sci., Part C*, **26**, 81 (1969).
(10) T. Ono, H. Minamiguchi, T. Soen, and H. Kawai, *Kolloid Z. Z. Polym.*, **250**, 394 (1972).

* Address correspondence to this author at Osaka University.

Koichi Arai, Tadao Kotaka,* Yukishige Kitano, and Kenji Yoshimura

Department of Polymer Science, Osaka University,
Toyonaka, Osaka 560, and Toray Research Center,
Sonoyama, Ohtsu 520, Japan

Received September 19, 1979

Formation of Soluble Polyethylene by Hydrogenation of Alkali-Metal-Doped Polyacetylene

The semiconducting organic polymer polyacetylene $[(CH)_x]$ or polyvinylene $[-(CH{=}CH)_x-]$ has recently been the subject of much experimental[1–12] and theoretical[13–20] study because of observations that its conductivity can be changed many orders of magnitude by doping it with various acceptors and donors.

Infrared,[21] Raman,[22] and absorption[22] spectral data are consistent with a linear conjugation of cis and/or trans C=C double bonds. The insolubility and infusibility of this conjugated polymer, however, make it difficult to obtain various information on molecular weight, its distribution, cross-linking, branching, etc. More detailed structural information is necessary for understanding chemical as well as physical properties of the as-prepared polyacetylene.

In this short communication, we present preliminary results on the formation of soluble polyethylene by hydrogenation of alkali-metal-doped polyacetylene.

Recently we have found that the alkali-metal-doped polyacetylene catalyzes the H_2–D_2 exchange reaction under very mild conditions and that hydrogen in the doped polyacetylene is also able to exchange with H_2 in the gas phase at higher temperature (>160 °C).[23] During the course of the hydrogen exchange study, we have observed that the doped film becomes partly transparent after several hours when the reaction is carried out at 200 °C and 85 Torr of H_2, suggesting that there is a possibility of hydrogenation of the conjugated double bonds in the doped polyacetylene.

The sodium doped films were prepared by treating the *trans*-polyacetylene films[24] (0.05–0.1-mm thickness) with a solution of sodium naphthalide in THF (~0.5 M) for about 1 h. The doped films were washed repeatedly with THF by trap-to-trap distillation from the sodium naphthalide solution until the washed solution became colorless. After being dried under vacuum, the films were allowed to react with hydrogen (550 Torr) at 200 °C for 7 h. Silvery films of the sodium-doped polyacetylene turned to transparent pale brown material, which became opaque to some extent on cooling to room temperature. The hydrogenated product was treated with methanol vapor and then immersed into a methanol–water mixture to dissolve the doped sodium in the films. Since hydrogen evolution was observed by this treatment, it was suggested that sodium in the hydrogenated film was present in the form of either the metal or sodium hydride. The entire operation was carried out under vacuum or inert gas.

0024-9297/80/2213-0457$01.00/0 © 1980 American Chemical Society

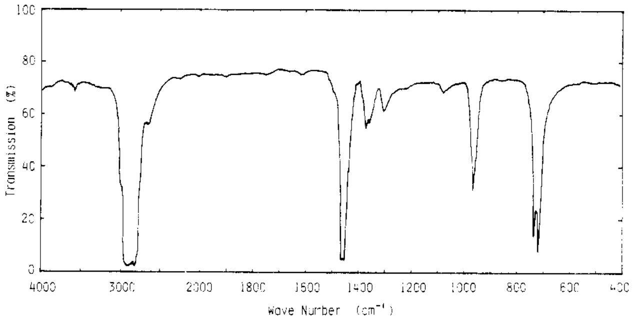


Figure 1. Infrared spectrum of the hydrogenated polyacetylene.

The product was washed with a small portion of the methanol–water mixture until it became neutral to phenolphthalein. The combined solution was titrated by HCl solution to obtain the amount of sodium in the films. The composition of the pristine-doped material was $(CHNa_{0.146})_x$. It is noteworthy to mention that the hydrogenated films are flexible and themoplastic.

Infrared spectra of the hydrogenated films coincided closely to that of high-density polyethylene except for a band at 965 cm^{-1} which may be due to C–H out-of-plane vibration in residual isolated or short, conjugated double bonds (Figure 1).

It is interesting to note that the hydrogenated film does not melt down but maintains the initial shape of the film although the reaction is carried out at a higher temperature than the melting point of polyethylene. This observation strongly suggests that the product might be a highly cross-linked polyethylene. Treating the product (145 mg) with boiling tetralin for 5 h, however, gave a soluble polyethylene (87 mg) whose IR spectrum was identical with that of untreated hydrogenated film. Since the hydrogenated film became opaque upon cooling, it was suggested that this material might be crystalline. In fact, appearance of a doublet at 720 and 730 cm^{-1} due to the CH_2 rocking vibration in the IR spectrum indicated that both soluble and insoluble polymers were highly crystalline (ca. 50%). The melting point of the soluble polymer observed by a microscope was in the range 111.6–120.6 °C. DSC analysis gave an endothermic peak maximum at 120 °C and indicated ca. 40% crystallinity. The number average molecular weight measured by GPC was 6200 with a Q-$(\bar{M}_w/\bar{M}_n)$ value of 3.44 (Figure 2).

Although the hydrogenated product was slightly colored and contained a detectable amount of C=C double bonds in its IR spectrum, elemental analysis gave a H/C ratio of 2.01 and 2.03 for the insoluble and soluble polymers, respectively.

In order to obtain completely hydrogenated polyacetylene, the reaction was carried out in a stainless steel autoclave at a higher pressure of hydrogen (ca. 60 kg/cm^2) at 190 °C for 24 h. Hydrogenation of the sodium-doped polyacetylene $(CHNa_{0.141})_x$ prepared from 854.6 mg of *trans*-polyacetylene film gave 915.0 mg of white opaque film. From the material balance, 99.4% of the double bonds in the polyacetylene were hydrogenated. Its IR spectrum, however, showed absorption at 965 cm^{-1} attributable to residual double bonds. Corresponding absorption was also observed in the ultraviolet region. In addition to a very strong absorption at a shorter wavelength than 260 nm due to the isolated double bonds, very weak shoulders were observed at 306, 322, and 341 nm assignable to $-(CH=CH)_5-$ sequences.[25] Since the H/C ratio of the soluble fraction was 2.02, the amount of the residual C=C double bonds must be very small. However, only 132.0 mg of white soluble powder was recovered from the hot tetralin extract. The insoluble part which also gives the same IR spectrum may be a cross-linked polyethylene.

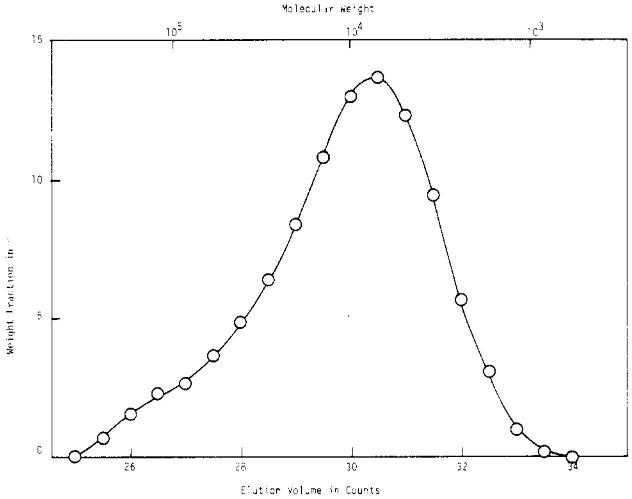


Figure 2. Molecular weight distribution curve of a soluble part of the hydrogenated polyacetylene. The molecular weight distribution was measured by GPC (Toyo Soda Co. TSK-HLC), using a GMH6-S column and trichlorobenzene as the solvent at 145 °C. The calibration curve of the molecular weight was obtained with ten standard samples of monodisperse polystyrene with molecular weights from 1 000 to 3 840 000.

The soluble fraction of the hydrogenated products in a series of hydrogenation reactions scattered over a wide range of 5–80%, although the pristine polyacetylene was taken from the same polymerization batch, suggesting that the cross-linkage may occur during the doping or the hydrogenation processes promoted by some impurities such as oxygen, water, etc. Very recently Chien et al. reported the successful hydrogenation of polyacetylene by several catalyst systems, but the hydrogenated product was insoluble.[26] There is no possibility that the alkali-metal-doped polyacetylene is chemically reduced by the Na/methanol combination, because the doped polyacetylene became transparent by the hydrogenation process before the methanol treatment.

In conclusion, the formation of soluble polyethylene by hydrogenation of polyacetylene strongly suggests that polyacetylene has no cross-linkage. Further studies on the hydrogenation of polyacetylene and the detailed characterization of the hydrogenated products are in progress.

Acknowledgment. Part of this study was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education of Japan (No. 355390).

References and Notes

(1) H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chiang, and A. J. Heeger, *J. Chem. Soc., Chem. Commun.*, 578 (1977).

(2) C. K. Chiang, C. R. Fincher, Jr., Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, S. C. Gau, and A. G. MacDiarmid, *Phys. Rev. Lett.*, **39**, 1098 (1977).

(3) C. K. Chiang, M. A. Druy, S. C. Gan, A. J. MacDiarmid, E. J. Louis, A. G. MacDiarmid, Y. W. Park, and H. Shirakawa, *J. Am. Chem. Soc.*, **100**, 1013 (1978).

(4) C. K. Chiang, Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, and A. G. MacDiarmid, *J. Chem. Phys.*, **69**, 5098 (1978).

(5) Y. W. Park, M. A. Druy, C. K. Chiang, A. G. MacDiarmid, A. J. Heeger, H. Shirakawa, and S. Ikeda, *J. Polym. Sci., Polym. Chem. Ed.*, **17**, 195 (1979).

(6) I. Harada, M. Tasumi, H. Shirakawa, and S. Ikeda, *Chem. Lett.*, 1411 (1978).

(7) T. C. Clarke, R. H. Geiss, J. F. Kwak, and G. B. Street, *J. Chem. Soc., Chem. Commun.*, 489 (1978).

(8) J. F. Kwak, T. C. Clarke, R. L. Green, and G. B. Street, *Solid State Commun.*, **31**, 355 (1979).

(9) R. H. Banghman, S. L. Hsu, G. P. Pez, and A. J. Signorelli, *J. Chem. Phys.*, **68**, 5405 (1978).

(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]

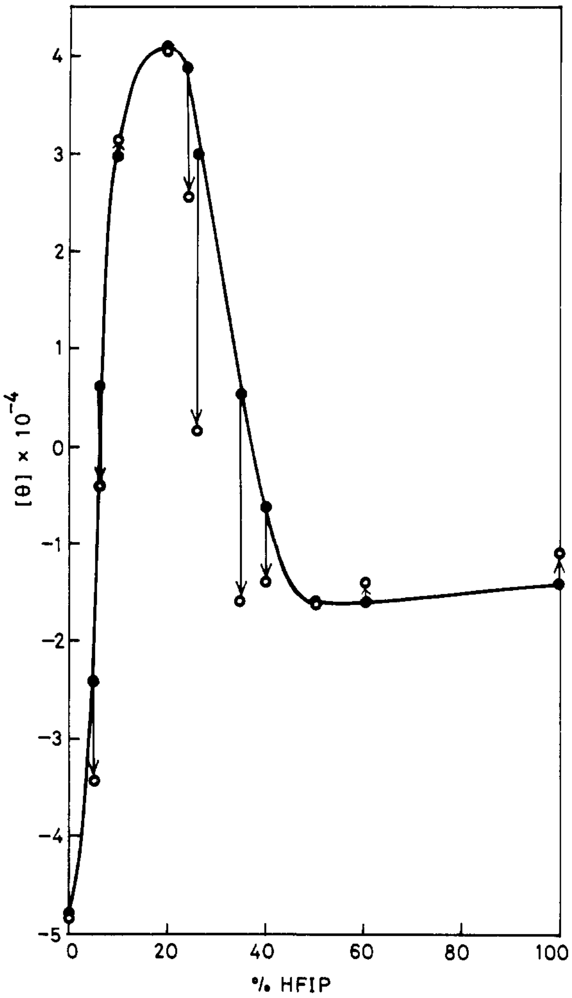
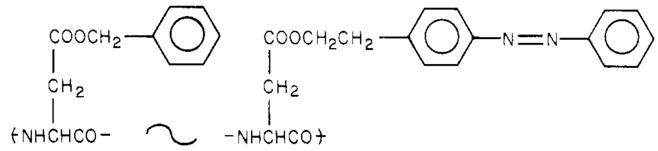


Figure 1. Variation of the molecular ellipticity at 222 nm of I induced by solvent and/or light: (●) before photoirradiation; (○) after photoirradiation.

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