

The Effect of Syndiotacticity on the Structure and Properties of Dehydrochlorinated Poly(vinyl Chloride) Films

TETSUYA DANNO, KEN-ICHI FURUHATA, and KEIZO MIYASAKA,
*Department of Textile and Polymeric Materials, Faculty of Engineering,
Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan*

Synopsis

The dehydrochlorination of a syndiotacticity-enriched poly(vinyl chloride) (s-PVC) gave polyene materials and the structure and properties of dehydrochlorinated specimens were studied. The results were compared with those obtained for polyene materials formed from a commercial poly(vinyl chloride) (c-PVC). The crystallinity of the s-PVC was higher than that of the c-PVC as revealed by the infrared analysis and X-ray diffraction studies. The dehydrochlorinated specimens from the s-PVC were crystalline to some extent while those from the c-PVC were amorphous. The molecular orientation in the original films was preserved in the dehydrochlorinated specimens. The polyene films from the s-PVC had larger conductivities and showed better doping properties as compared with those from the c-PVC. These results were explained in terms of the larger crystallinity and the increased structural regularity of the s-PVC as compared with those of the c-PVC.

INTRODUCTION

It is well known that poly(vinyl chloride) (PVC) is converted into polyene materials by dehydrochlorination.¹⁻³ Recently, we showed that a high degree of dehydrochlorination of PVC films could be achieved in the two-step treatment using 1,8-diazabicyclo[5,4,0]undec-7-ene in polar solvents.⁴ In the first step with a controlled degree of swelling, the amorphous phase in the PVC film was dehydrochlorinated. The swelling which was necessary for the dehydrochlorination must be confined in the amorphous phase; if the crystalline phase was swollen as well as the amorphous phase, the specimen films would no longer keep the shape, and our aim was to obtain polyene films from PVC. In the second step, some solvents for PVC were used to swell crystalline phase, which remained unreacted after the first-step reaction, thus enabling them to be dehydrochlorinated. The amorphous phase which had been dehydrochlorinated in the first-step reaction was unswollen during the second-step reaction because the solvent for PVC is not the solvent for the polyenes formed. In the second step, the amorphous phase played a role in keeping the shape of the film, which had been played by the crystalline phase in the first step.

One of the most interesting results in the previous study was that the molecular orientation in the original PVC film was preserved to some extent after the two-step treatment. However, the electrical conductivities of the films obtained were disappointingly small, in the order of 10^{-9} S/cm at the largest, in spite of the comparatively high degree of dehydrochlorination

and of the molecular orientation. Although the iodine doping increased the conductivity, the largest value observed was in the order of 10^{-4} S/cm. These values of conductivity both before and after the iodine doping are several orders of magnitude smaller than those of the polyacetylene films⁵ prepared by the method of Shirakawa and co-workers.⁶ The low conductivity of the dehydrochlorinated film was supposed to be due to the less delocalized unpaired electrons and to the very small crystallinity as revealed by the X-ray diffraction studies.

It is well known that commercial (atactic) PVCs contain structural irregularities such as branching^{7,8} and head-to-head linkage⁹ along with the irregular stereostructure. These irregularities make the crystallinity much smaller than those of other crystalline polymers such as polyethylene and polyamides. The small crystallinity may be further decreased by the dehydrochlorination of the crystalline phase. The dehydrochlorinated films were found to be noncrystalline.⁵ In addition, the structural irregularities are known to act as termination points in the dehydrochlorination, preventing the uniform reaction.¹⁰ On the other hand, the syndiotacticity-enriched PVCs prepared by the low-temperature polymerization¹¹ are more regular in the molecular structure than the atactic PVCs and, as a result, are more highly crystalline.¹²⁻¹⁴ The former gave longer polyene sequences in the thermal^{15,16} and photodegradation¹⁷ than the latter. This made us expect that the electrical conductivities of dehydrochlorinated films from PVCs with enriched syndiotacticity must be larger than those of the films made from atactic PVCs. Therefore, a syndiotacticity-enriched PVC sample was prepared by the low-temperature polymerization and films made from it were dehydrochlorinated in a similar manner as described in the previous article.⁴ In the present paper, the degree of dehydrochlorination, the structure, and electrical properties of the dehydrochlorinated films made from the syndiotacticity-enriched PVC are reported.

EXPERIMENTAL

Preparation of Syndiotacticity-Enriched PVC

A syndiotacticity-enriched PVC (s-PVC) was prepared by the low-temperature redox polymerization using hydrogen peroxide, ferrous sulfate, and L-ascorbic acid:¹⁸ 0.26 g of ascorbic acid and 0.4 g of sodium dodecylbenzenesulfonate were dissolved in 150 mL of aqueous methanol (50 vol %). The mixture was cooled to -30°C and was completely purged with nitrogen. Then 100 g of vinyl chloride was added under stirring. To the emulsion formed, 50 mg of 35 wt % H_2O_2 was added dropwise, and subsequently 2.5 mg of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (1 wt % aqueous solution) was added. The reaction mixture was held at -30°C for 2 h. The polymers formed were salted out with an aqueous NaCl solution at room temperature and were then washed repeatedly with water in order to exclude chloride ions. Finally, they were dried *in vacuo*.

The commercial PVC (c-PVC) used in this study was the same as that used in the previous paper ($\overline{DP} = 1100$, Mitsubishi Kasei Co.).⁴

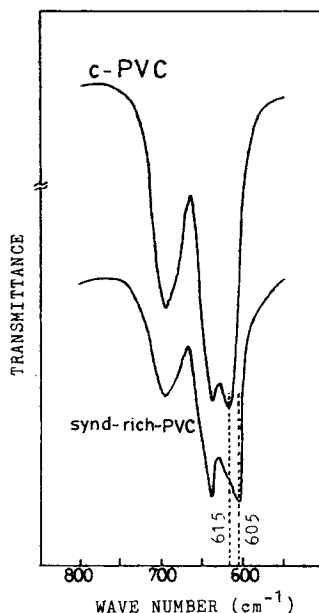


Fig. 1. IR spectra of (a) PVC film prepared by the low temperature redox polymerization and (b) commercial PVC film in the region from 800 to 600 cm^{-1} .

Characterization of PVC Specimens

Figure 1 compares the IR spectrum of the s-PVC with that of the c-PVC. The ratio of the absorbance at 638 cm^{-1} to that at 690 cm^{-1} is a measure of syndiotacticity: The larger the ratio (D_{638}/D_{690}), the higher the degree of syndiotacticity.¹⁹ The ratios cited in Table I indicate that the s-PVC has a higher degree of syndiotacticity than the c-PVC. The s-PVC has a larger crystallinity than the c-PVC: The crystalline C—Cl stretching band at 605 cm^{-1} ²⁰ was strong and the amorphous one at 615 cm^{-1} ²⁰ was weak for the s-PVC. This high crystallinity may be the reason for the insolubility of the s-PVC in tetrahydrofuran and acetone even at their boiling points. The c-PVC was easily soluble in these solvents. The intrinsic viscosities of PVC specimens were calculated from the data of viscosity measurements in cyclohexanone solutions at 30°C , and the average degrees of polymerization were calculated using an empirical equation of Inagaki and Nakazawa.²¹ The results are also summarized in Table I. The degree of polymerization of the s-PVC thus calculated was four times larger than that of the c-PVC.

TABLE I

The Ratios of Absorbance at 638 cm^{-1} to That at 690 cm^{-1} and the Intrinsic Viscosities of s- and c-PVCs

Sample	D_{638}/D_{690}	$[\eta]^a$	\overline{DP}
s-PVC	2.23	2.50	4400
c-PVC	1.65	0.89	1100

^a 30°C in cyclohexanone.

Films of the s-PVC, about 10 μm thick, were cast from cyclohexanone solutions at 60°C under nitrogen. Strips, 15 mm wide and 35 mm long, were cut from the films and were drawn six times using a manually operated device in boiling water. The X-ray diffraction studies showed that the crystals were highly oriented in the drawn samples [Fig. 3(c)].

Measurements

Infrared spectra were recorded on a Hitachi EPI-G3 Spectrometer under a nitrogen stream in order to prevent the oxidation of the dehydrochlorinated specimens.

X-ray diffraction photographs were taken using a Rigaku Denki RU-3 instrument with a Ni-filtered $\text{CuK}\alpha$ radiation (40 kV \times 50 mA), and intensity curves were obtained using Zr-filtered $\text{MoK}\alpha$ (25 kV \times 35 mA) and a scintillation counter. The small absorption coefficient of $\text{MoK}\alpha$ for chlorine made the intensity measurements easier.

The electrical conductivities of the dehydrochlorinated specimens were measured using a four-probe technique in the same manner as in previous studies.^{4,22}

Dehydrochlorination

Cyclohexanone (CHN), methanol (MeOH), and 1,8-diazabicyclo[5,4,0]-undec-7-ene (DBU) were all purified by distillation and were stored under nitrogen. CHN and MeOH were used as a solvent and a nonsolvent. The dehydrochlorination of s-PVC films was carried out in the two-step treatment which was described in detail in our previous paper.⁴ In a typical treatment, an s-PVC film (15 mg, 2.4×10^{-4} mol of repeating units), about 10 cm^2 in area, was placed in 100 mL of CHN–MeOH mixture (1:1) in a Schlenk flask. The amorphous region of the specimen was swollen in the mixture. After the equilibrium swelling had been reached, 10 mL of DBU (6.8×10^{-2} mol) was added to the system. The reaction was carried out at 50°C under nitrogen for 36 h with shaking. After the first-step reaction was over, the reaction medium was replaced with pure CHN and the second-step reaction was carried out at 90°C for 24 h with the same amount of DBU as in the first step. The reaction temperature of 90°C was chosen in order to swell sufficiently the crystalline phase. When the reaction was over, the film was washed with MeOH several times under nitrogen and dried *in vacuo*. The increase in the reaction time from 36 h to 67 h in the first step and from 24 h to 48 h in the second step caused no significant changes in conversions and in infrared spectra. These results indicate that secondary reactions of the polyenes such as inter- and intramolecular cyclizations were negligible under the experimental conditions studied.

Since the polyenes formed reacted easily with oxygen, they were treated carefully under nitrogen in subsequent experiments.

For comparison, c-PVC films cast from tetrahydrofuran solutions were dehydrochlorinated. In this case, the ratio of CHN to MeOH was 2:3 in the first-step reaction, and both reactions were carried out at 50°C. The drawn specimens were fixed to stainless-steel holders during the treatment in order to avoid the shrinkage which might decrease the molecular orientation to a great extent.

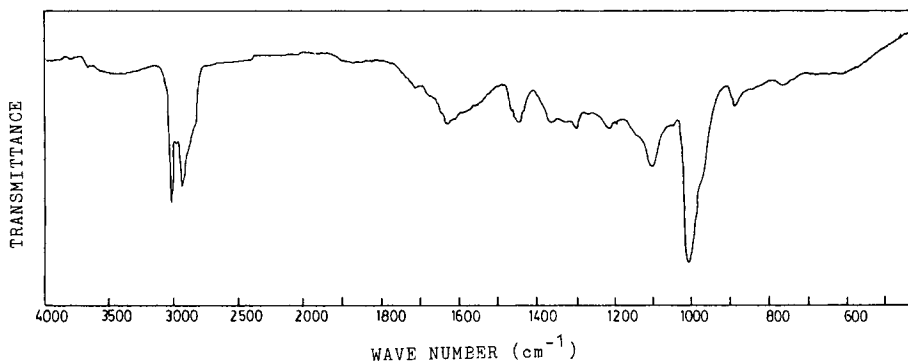


Fig. 2. IR spectrum of dehydrochlorinated s-PVC film ($\chi = 0.94$).

The degree of dehydrochlorination, χ , was calculated from the data of elemental analysis.

RESULTS AND DISCUSSION

Structure of the Dehydrochlorinated s-PVC

The films turned from transparent to yellow, red, and finally shiny black during the course of the dehydrochlorination, as in the case for the c-PVC.⁴ The degree of the dehydrochlorination of the undrawn s-PVC films was 0.94 at the highest after the two-step treatment. Figure 2 shows the IR spectrum of the most highly dehydrochlorinated sample obtained from the undrawn s-PVC film. The intense bands at 1010 and 3015 cm^{-1} were observed which have been assigned to the C—H out-of-plane vibration in conjugated trans double bonds of polyacetylene and to the C—H stretching vibration of the unsaturated carbons, respectively.²³ The C—Cl stretching bands in 700–600 cm^{-1} almost disappeared. This spectrum indicates that the s-PVC was converted into conjugated trans polyenes by the dehydrochlorination, as in the case of the c-PVC films studied in the previous paper.⁴ It should be remarked that the dehydrochlorinated specimens were tough enough for IR, X-ray, and electrical conductivity measurements in the form

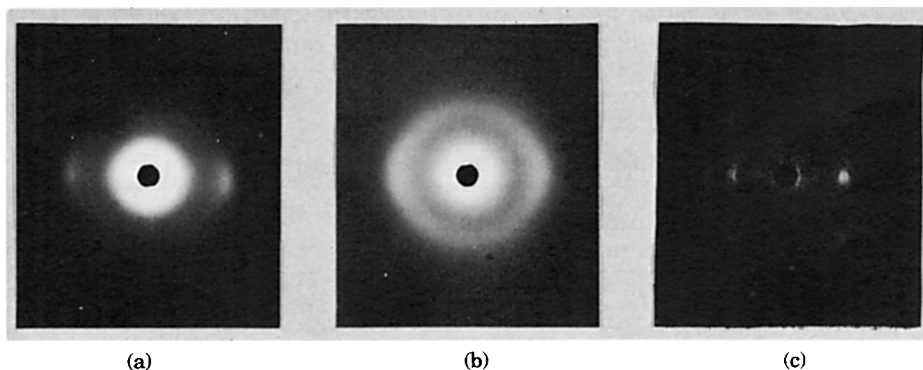


Fig. 3. WAXD photographs of dehydrochlorinated drawn films and s-PVC film. Draw direction is vertical: (a) s-polyene ($\lambda = 6$, $\chi = 0.93$); (b) c-polyene ($\lambda = 6$, $\chi = 0.94$); (c) s-PVC ($\lambda = 6$).

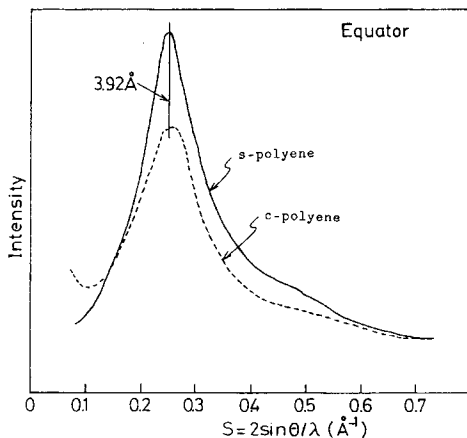


Fig. 4. Equatorial WAXD intensity curves of dehydrochlorinated PVC films: (—) s-polyene; (---) c-polyene.

of film. The highest degree of the dehydrochlorination for the drawn specimen was 0.93, which was nearly equal to that for the undrawn specimen.

Figure 3 shows the WAXD photographs of (a) dehydrochlorinated s-PVC (s-polyene), (b) dehydrochlorinated c-PVC (c-polyene), and (c) original s-PVC films. In the photographs of the two dehydrochlorinated films, the diffractions from PVC crystallites vanished almost completely, and a broad diffraction appeared on the equator instead. This indicates that the polyene molecules were still oriented uniaxially after the dehydrochlorination. The equatorial diffraction from the s-polyene was less broad than that from the c-polyene, and the meridional diffuse halo of the s-polyene was much weaker than that of the c-polyene. These results indicate that the s-polyene was crystalline, although the crystallinity was low, and that the molecular orientation was higher than that of the c-polyene.

Figure 4 shows the equatorial X-ray diffraction intensity curves of s- and c-polyene films. The intensities were normalized at $S = 0.7 \text{ \AA}^{-1}$ at which no significant crystalline diffraction but the background scattering was observed. For both polyene films, a peak at $S = 0.255 \text{ \AA}^{-1}$ corresponding to a spacing of 3.92 \AA was observed. However, the intensity of the peak of the s-polyene was much greater than that of the c-polyene and the half-widths were 0.10 and 0.14 \AA^{-1} for the s- and c-polyenes, respectively. These

TABLE II
Electrical Conductivities of Dehydrochlorinated PVC Films

Sample	Conductivity (S/cm)		
	Undrawn	Drawn ^a	After iodine doping ^b
s-Polyene	1.6×10^{-10}	4.4×10^{-10}	5.7×10^{-4}
c-Polyene	4.4×10^{-12}	1.0×10^{-11}	1.8×10^{-4}

^a The term "drawn" means that the specimens were obtained from PVC films drawn six times which were fixed to holders during the treatment.

^b Doped at 25°C for 60 min at the saturated vapor pressure of iodine.

X-ray observations indicate that the s-polyene was semicrystalline while the c-polyene was almost completely amorphous. This is what we anticipated, but it should be remarked that the crystallinity of the s-polyene was still much smaller than that of the polyacetylene film obtained from gaseous acetylene which was about 0.8 as estimated in our previous paper.²⁴

Electrical Conductivity

Table II shows the electrical conductivity of s- and c-polyene films measured *in vacuo* at room temperature. The conductivities of specimens obtained from drawn PVC films were those in the direction of molecular orientation (the draw direction in the original PVC film). The molecular orientation increased significantly the electrical conductivity, as has been shown for the drawn polyacetylene.²⁵ The conductivity of s-polyene film was about 40 times larger than that of the c-polyene film both for originally drawn and undrawn specimens. For the c-PVC, the conductivity increased by 4-6 orders of magnitude after the dehydrochlorination, but it was still about 6 orders of magnitude smaller than that of the trans polyacetylene films.⁴ The low conductivity of the dehydrochlorinated specimens was supposed to be due to the lower degree of delocalization of unpaired electrons and to the poor crystallinity due to irregular chain structures. The ESR spectra of both the s- and c-polyenes showed a singlet signal, and there were no significant differences in the spin concentration and in the half-width between the two. These ESR data imply that the larger conductivity of the s-polyene film as compared with that of the c-polyene film was related to the higher crystallinity due to more regular chain structures. Figure 5 shows the change in the electrical conductivity of the s- and c-polyene films as a function of iodine doping time. The iodine doping was carried out at 25°C and at the saturated vapor pressure of iodine. The conductivity increased by several orders of magnitude at the earliest stage of doping, and

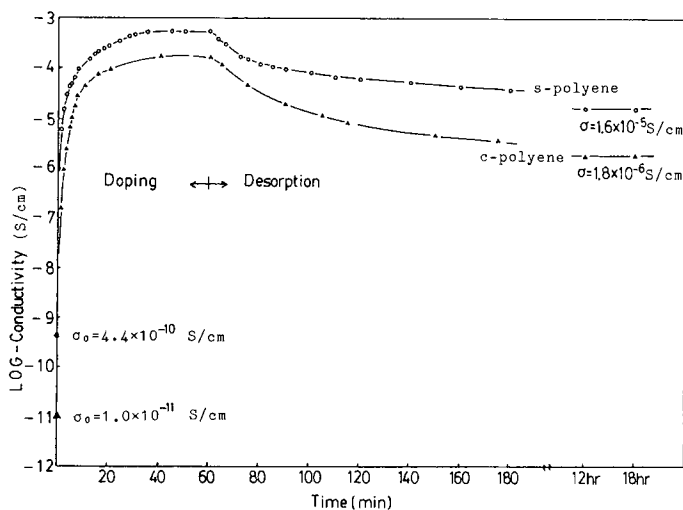


Fig. 5. Change in conductivity during iodine doping and desorption. (○) s-polyene ($\lambda = 6$); (△) c-polyene ($\lambda = 6$).

then it increased gradually. The conductivity after 60 min doping is also shown in Table II. The value for the s-polyene film at this stage was 5.7×10^{-4} S/cm, three times larger than that for the c-polyene film. The system was then evacuated to examine the desorption behavior. The conductivity decreased gradually with evacuation for both polyene films, and the ultimate value (after 17 h evacuation) for the s-polyene film was 1 order of magnitude larger than that for the c-polyene film.

The amounts of the residual iodine after the evacuation were 11 and 6 mol % for s- and c-polyene films, respectively. The amounts of iodine sorbed after 60 min doping were about 15 mol % for both polyene films. We reported previously that iodine penetrated into crystals of *trans*-polyacetylene and "iodine-PA" cells were formed at the iodine pressure higher than a threshold value of about 0.08 Torr at room temperature, and that the iodine once incorporated into the crystal in the form of the "iodine-PA" cell was very difficult to remove by evacuation.²² The larger residual amount of iodine for the s-polyene film should be due to its higher crystallinity. However, it should be noted again that, even for the s-polyene film, the crystallinity was much smaller than that of the polyacetylene film prepared by the polymerization of gaseous acetylene.

ESR measurements showed that the spin concentration in the iodine-doped s-polyene film after the evacuation increased twice as much as that before doping, and the half-width decreased from 10 (before doping) to 8 G after doping. These results show that the increase in the electrical conductivity is related to both the concentration of the carrier and its mobility.

CONCLUSION

Films of a syndiotacticity-enriched poly(vinyl chloride) could be sufficiently dehydrochlorinated by the two-step treatment using 1,8-diazabicyclo[5,4,0]undec-7-ene as a reagent for the dehydrochlorination. The polyene films obtained were crystalline to some extent, and the molecular orientation in the original films was preserved after the reaction. These polyene films had larger electrical conductivities both before and after the iodine doping than those of polyene films obtained from a commercial atactic poly(vinyl chloride).

References

1. E. Tsuchida, C. H. Shin, I. Shinohara, and S. Kambara, *J. Polym. Sci. A*, **2**, 3347 (1964).
2. K. Soga, M. Nakamaru, H. Ooshima, and Y. Kobayashi, *Polym. Prepr. Jpn.*, **31**, 2061 (1982).
3. T. Yamamoto, K. Nishiki, M. Yamashita, T. Takayama, and M. Ookawara, *Prepr. Chem. Soc. Jpn.* 1492 (1982).
4. T. Danno, H. Kondo, K. Furuhashi, and K. Miyasaka, *J. Appl. Polym. Sci.*, **29**, 3171 (1984).
5. C. K. Chiang, Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, and A. G. MacDiarmid, *J. Chem. Phys.*, **69**, 5098 (1978).
6. T. Ito, H. Shirakawa, and S. Ikeda, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 11 (1974).
7. T. Hjertberg and E. M. Sörvik, *Polymer*, **24**, 673 (1983).
8. W. H. Starnes, Jr., F. C. Schilling, I. M. Plitz, R. E. Cais, D. J. Freed, R. L. Hartless, and F. A. Bovey, *Macromolecules*, **16**, 790 (1983).
9. T. Hjertberg, E. Sörvik, and A. Wendel, *Makromol. Chem., Rapid Commun.*, **4**, 175 (1983).
10. K. B. Abbas and E. M. Sörvik, *J. Appl. Polym. Sci.*, **20**, 2395 (1976).

11. M. Asahina and S. Enomoto, *Nippon Kagaku Zasshi*, **81**, 1011 (1960).
12. H. Watanabe, Y. Toyota, and Y. Amagi, *Kogyo Kagaku Zasshi*, **61**, 893 (1961).
13. E. V. Gouinlock, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 961 (1975).
14. C. Baker, W. F. Maddams, and J. E. Preedy, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 1041 (1977).
15. G. Martinez, C. Mijangos, J.-L. Millán, D. L. Gerrard, and W. F. Maddams, *Makromol. Chem.*, **180**, 2937 (1979).
16. G. Martinez, C. Mijangos, and J. Millán, *J. Macromol. Sci. Chem.*, **A17**, 1129 (1982).
17. K. Mitani and T. Ogata, *J. Appl. Polym. Sci.*, **18**, 3205 (1974).
18. H. Watanabe and Y. Amagi, *Jpn. Pat.* 35-7588 (1960).
19. N. Yamazaki, K. Sakai, and S. Kambara, *Kogyo Kagaku Zasshi*, **68**, 881 (1965).
20. M. Tasumi and T. Shimanouchi, *Spectrochim. Acta*, **17**, 731 (1961).
21. M. Kurata, Y. Tsunashima, M. Iwama, and K. Kamada, *Polymer Handbook*, J. Bandrup and E. H. Immergut, Eds., Wiley, New York, 1975, p. IV-14.
22. T. Danno, K. Miyasaka, and K. Ishikawa, *J. Polym. Sci., Polym. Phys. Ed.*, **21**, 1527 (1983).
23. H. Shirakawa and S. Ikeda, *Polym. J.*, **2**, 231 (1971).
24. T. Akaishi, K. Miyasaka, K. Ishikawa, H. Shirakawa, and S. Ikeda, *J. Polym. Sci., Polym. Phys. Ed.*, **18**, 745 (1980).
25. H. Shirakawa, S. Ikeda, T. Akaishi, K. Miyasaka, and K. Ishikawa, *Polym. Prepr. Jpn.*, **27**, 1780 (1978).

Received May 23, 1984

Accepted July 13, 1984