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### Functional Monomers and Polymers. 165. Dehydrochlorination of Head-to-Tail 1,4-rans-Poly-(-1-Chlorobutadiene) Prepared by Inclusion Polymerization in Deoxycholic Acid Canals

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**FUNCTIONAL MONOMERS AND POLYMERS. 165.<sup>†</sup>  
DEHYDROCHLORINATION OF HEAD-TO-TAIL 1,4-*trans*-POLY-  
(-1-CHLOROBUTADIENE) PREPARED BY INCLUSION  
POLYMERIZATION IN DEOXYCHOLIC ACID CANALS**

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**ABSTRACT**

Thermal and chemical dehydrochlorination of head-to-tail 1,4-*trans*-poly(-1-chlorobutadiene) prepared by inclusion polymerization in deoxycholic acid canals resulted in formation of a *trans*-polyacetylene-type polymer. The dehydrochlorinated polymer was characterized by UV/VIS, IR, Raman, and ESR spectroscopy. The number of conjugated double bonds in the polymer was about 10-20. Doping with iodine was also studied.

**INTRODUCTION**

Highly conjugated polymers, especially polyacetylene, have been investigated intensively for their interest as a "synthetic metal" in the last decade [1, 2]. Indirect routes for the synthesis of polyacetylene include the forma-

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<sup>†</sup>Part 164: W. Goonewardena, M. Miyata, and K. Takemoto, In preparation.

tion of precursor polymers, such as poly(vinyl chloride) [3] and poly(-7.8-bis(trifluoromethyl)tricyclo[4,2,2,0<sup>2,5</sup>] deca-3,7,9-triene) [4].

We found that poly(-1-chlorobutadiene) (PCB) with a head-to-tail 1,4-*trans* structure can serve as a new precursor polymer [5, 6]. The highly stereoregular polymer was prepared by inclusion polymerization in deoxycholic acid (DCA) canals, whereas the usual free-radical polymerization gives a polymer with both 3,4- and 1,4-structures [7]. The former polymer dehydrochlorinated more completely and smoothly than poly(vinyl chloride).

It is known that the physical properties of polymers are influenced by their structure and morphology [1]. Therefore, morphological control is very important to obtain tailor-made polymers. In the present case, dehydrochlorination of PCB can be done in various states, such as the inclusion state, the nascent state (immediately after separation of host molecules), in solution, and the film state, leading to the formation of conjugated polymers with various morphologies.

The present paper deals with a detailed study of the thermal and chemical dehydrochlorination of PCB in various states, as well as the characterization of the resulting polyacetylene-type polymer.

## EXPERIMENTAL

### Materials

1-Chlorobutadiene was prepared according to the literature [8]. PCB with almost 100% of head-to-tail *trans* 1,4-structure was prepared by inclusion polymerization in DCA canals as the host molecules [5, 6]. Postpolymerization at 0°C for 2-8 days afforded polymers with molecular weights from 10 000 to 20 000 on the basis of gel permeation chromatography.

### Thermal Dehydrochlorination

PCB or the polymer-DCA adduct was heated at the desired temperature under nitrogen. The degree of dehydrochlorination of the polymer was determined by elemental analysis.

### Dehydrochlorination by Treatment with DBU

Dehydrochlorination of PCB in chloroform solution was carried out with DBU (1,8-diazabicyclo-[5,4,0]-7-undecene). To 2 mL of the polymer solu-

tion (1.14 mg/mL, 13 mmol/L), 20  $\mu$ L of DBU (0.13 mmol) was added, and the mixture was stirred rapidly.

### Doping

Dehydrochlorinated polymer was doped with iodine at room temperature for 1 day. The iodine content in the polymer was determined by elemental analysis.

### Measurements

IR and Raman spectra of polymer-DCA adducts and polymers were measured on KBr dispersions and on films, respectively. IR and Raman spectra were measured on a JASCO IR 810 spectrophotometer and a JASCO R-500 laser Raman spectrophotometer (excitation 514.5 nm), respectively. Powder diffusion reflection spectra of polymer-DCA adducts and polymers were performed on a JASCO 660 UV/VIS spectrophotometer with an integrating sphere attachment. UV/VIS spectra of PCB solutions were measured continuously in a 1-cm quartz cell. Thermogravimetry (TG) and differential thermal analysis (DTA) were carried out at heating rate of 10 K/min under nitrogen with a SEIKO 580 thermal analysis system. ESR spectra were recorded on a JEOL JES FX1X ESR spectrometer.

## RESULT AND DISCUSSION

### Morphology of Polymers

Figure 1 shows the morphology of the polymers schematically. Figure 1(a) shows the PCB-DCA adducts prepared by inclusion polymerization. When the dehydrochlorination is done in the inclusion state, crosslinking reactions between dehydrochlorinated polymer chains may be prevented by the host molecules which lie between the polymer chains. Orientation of the conjugated polymer chains is also expected. Figure 1(b) shows the PCB chains immediately after separation of the host molecules by thorough washing with methanol, still in the oriented state of the polymer chains [5]. Figure 1(c) presents the solution of the PCB schematically. In the solution state the dehydrochlorination of the polymer can proceed with an organic base, such as DBU. In the film state obtained by simple casting from chloroform solution, the configuration of the polymer chains is random, as shown in Fig. 1(d). However orientation of the polymer chains can be caused by elongation of the film (Fig. 1e).

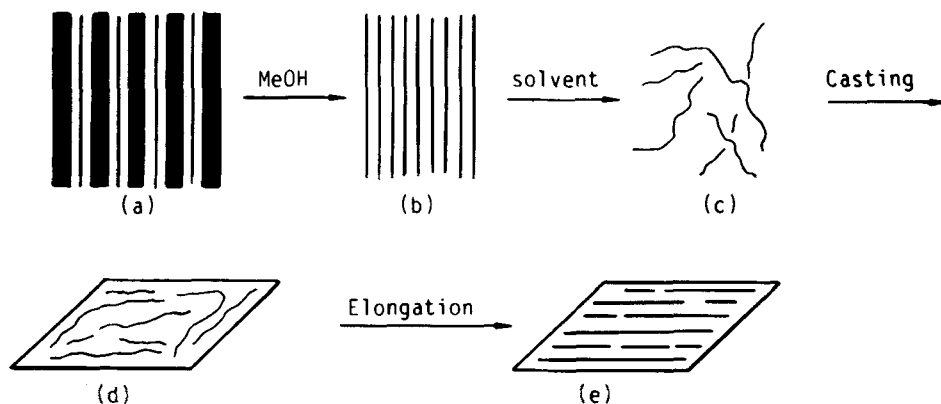


FIG. 1. Schematic presentation of poly(-1-chlorobutadiene) in various states: (a) inclusion state, (b) nascent state, (c) solution state, (d) film state, and (e) film state after elongation. The vertical bars represent the host molecule and the vertical lines represent the polymer.

#### Thermal Dehydrochlorination of Poly(-1-Chlorobutadiene)-DCA Adducts

PCB-DCA adducts tend to change gradually from colorless to purple, finally even to black at 0°C. X-ray diffraction of the adduct clearly showed uniaxial orientation of the polymer chains in the DCA canals [5].

According to TG and DTA of the PCB-DCA adduct (Fig. 2), the release of 1-chlorobutadiene can be observed at about 159°C. In the TG and DTA traces of the PCB-DCA adduct in Fig. 2, a small peak was observed at 152°C, where the weight loss began also. Two main endothermic peaks at 184 and 370°C accompany the weight loss. Therefore, the lower temperature peaks may be due to both the release of residual monomer in the DCA canals and the elimination of hydrogen chloride from the polymer, presumably due to the decomposition of DCA.

The powder diffusion reflection spectrum of the previously heated polymer-DCA adduct is shown in Fig. 3. Peaks were observed at 282, 324, 358, 414, 435, 461, and 496 nm. Studies of electron spectra of model polyenes containing 3 to 12 conjugated double bonds showed that they have a set of three bands of about equal intensity separated by 15 to 25 nm [9, 10] so that the spectrum suggests that conjugated double bonds of various lengths are formed in the polymer chains in the DCA canals.

The Raman spectrum of the PCB-DCA adduct after thermal dehydro-

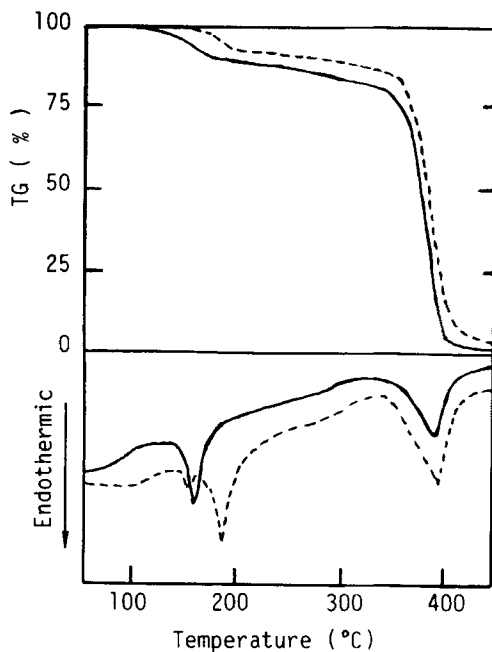


FIG. 2. TGA and DTA diagrams of (a) 1-chlorobutadiene-DCA adduct (—) and (b) poly(1-chlorobutadiene)-DCA adduct (---) at a heating rate of 10 K/min in a nitrogen atmosphere.

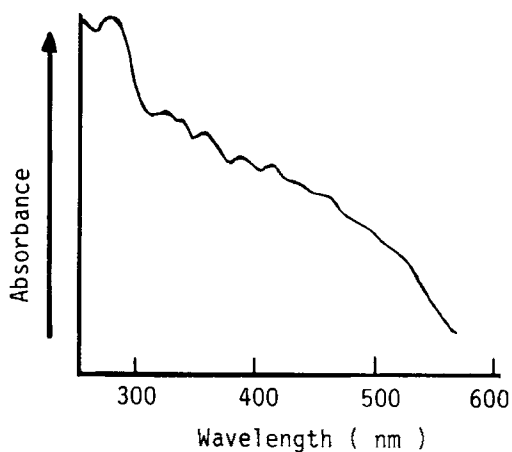


FIG. 3. Powder diffusion reflection spectrum of poly(-1-chlorobutadiene)-DCA adduct after heating at 70°C for 90 h.

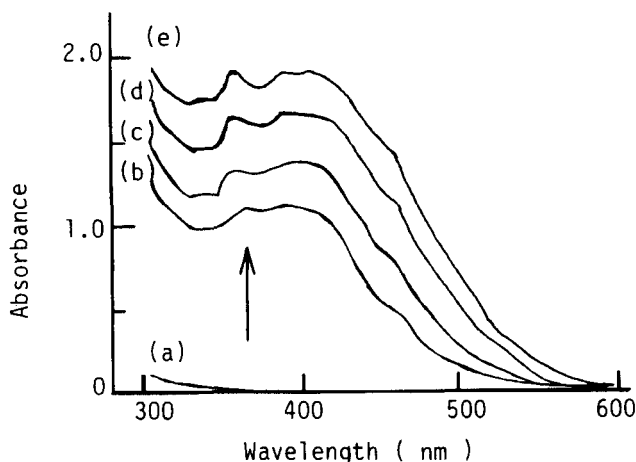


FIG. 4. UV/VIS spectra of poly(-1-chlorobutadiene) in chloroform solution in the presence of DBU at 26°C. Reaction times in minutes: (a) 0, (b) 4, (c) 20, (d) 32, and (e) 40.

chlorination shows a peak at  $1500\text{ cm}^{-1}$ , which can be assigned to C=C stretching. According to the relationship between the wavelength of C=C stretching and the length of conjugated double bonds [11], there are about 15-20 conjugated double bonds in the polymer chain.

#### Dehydrochlorination of Poly(-1-Chlorobutadiene) in Chloroform Solution with DBU

The PCB was dehydrochlorinated in chloroform solution by treatment with DBU. The absorbance and the number of the peaks in the UV/VIS spectra (Fig. 4) increase with the reaction time, which indicates that a system of conjugated double bonds develops in the polymer chains. Formation of a black precipitate was observed. The number of the conjugated double bond is about 5-6 [9, 10].

#### Thermal Dehydrochlorination of Poly(-1-Chlorobutadiene) in the Nascent State

The nascent PCB after extraction of DCA with excess methanol showed a slow change from colorless to purple and finally black, as for the polymer-DCA adduct.

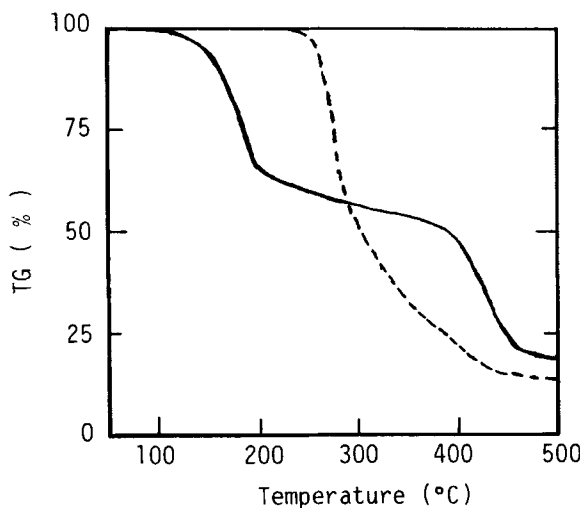


FIG. 5. TGA traces of poly(-1-chlorobutadiene) (—) and poly(vinyl chloride) (---) at a heating rate of 10 K/min in a nitrogen atmosphere.

The TG diagram in Fig. 5 shows that there is a marked weight loss above 130°C. The activation energy of the first stage of weight loss calculated by the method of Freeman et al. [12] is 71 kJ/mol, which is smaller than that for poly(vinyl chloride), 84–138 kJ/mol [13]. Dehydrochlorination of the PCB occurs at lower temperature than that of poly(vinyl chloride) (Fig. 5). Reaction at lower temperature would prevent decomposition and/or cross-linking reactions of the polymer.

Dehydrochlorination was achieved by heating of the nascent polymer at 100°C in a nitrogen atmosphere. The degree of dehydrochlorination of polymer was 53% in 2 days and 65% in 7 days.

The volatile products of the dehydrochlorination reaction were mostly hydrogen chloride and a smaller amount of cyclohexane.

The IR spectrum of PCB (Fig. 6) showed bands at 2950  $\text{cm}^{-1}$  due to C–H stretching in  $-\text{CH}_2-$  and at 640  $\text{cm}^{-1}$  due to C–Cl stretching. After thermal dehydrochlorination, the intensities of these bands decreased and bands appeared at 3010 and 996  $\text{cm}^{-1}$ . *trans*-Polyacetylene shows bands at 3013 and 1015  $\text{cm}^{-1}$ , which are assigned to C–H stretching and C–H out-of-plane deformation in the *trans* configuration, respectively [14]. After dehydrochlorination, these peaks are similar to those of polyacetylene.



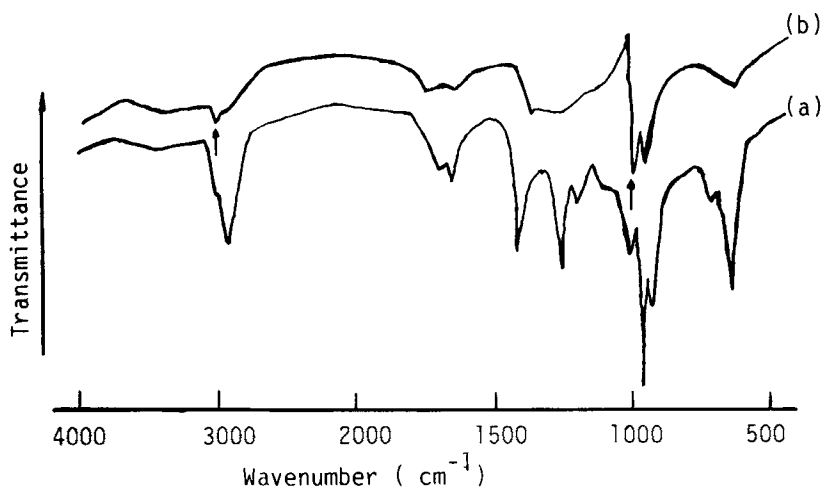


FIG. 6. IR spectra of poly(-1-chlorobutadiene) before (a) and after (b) thermal dehydrochlorination at 100°C for 2 days. Degree of dehydrochlorination: 53%.

The Raman spectrum of the polymer after thermal dehydrochlorination in Fig. 7 shows two main peaks at 1125 and 1510  $\text{cm}^{-1}$ , which are assigned to C—C and C=C stretching, respectively. It is known that *cis*-rich polyacetylene shows bands at 1542, 1253, and 910  $\text{cm}^{-1}$ , while the *trans*-rich polymer shows bands at 1475 and 1113  $\text{cm}^{-1}$  [15]. The structure of the PCB after thermal dehydrochlorination is similar to that of *trans*-rich polyacetylene. The number of conjugated double bonds amounts to about 15–20 [11], which is similar to that of the PCB-DCA adduct after thermal dehydrochlorination.

After  $\text{I}_2$  doping, two Raman bands are observed at 107 and 160–170  $\text{cm}^{-1}$  (Fig. 8). The former peak is assigned to the symmetric stretching vibration of  $\text{I}_3^-$ . The latter band is formed by two overlapping peaks; that at 163  $\text{cm}^{-1}$  may be attributed to the  $\text{I}_5^-$  ion. Two Raman bands which can be assigned to  $\text{I}_3^-$  and  $\text{I}_5^-$  are observed at these points on iodinated polyacetylene [15] and iodine-starch [16] or iodine-poly(vinyl alcohol) complexes [17].

The ESR spectrum of the thermally dehydrochlorinated polymer (Fig. 9) has a Lorentzian line shape, and the line width at maximum slope ( $\Delta H_{\text{msl}}$ ) is 11.1 G. The investigation of  $\gamma$ -ray-irradiated polymer with polyenyl-type radicals (I) showed that the delocalization of the unpaired electron increases while the  $\Delta H_{\text{msl}}$  value decreases when the number of conjugated double

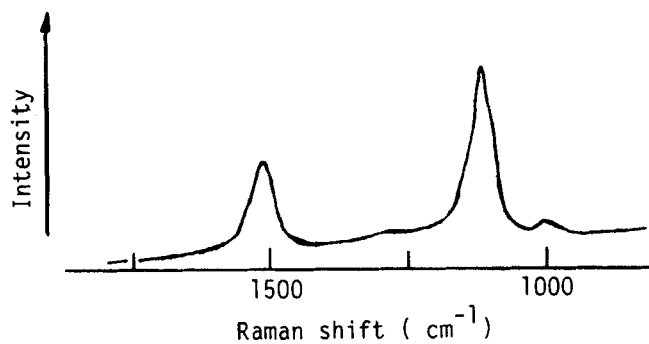


FIG. 7. Raman spectrum of poly(-1-chlorobutadiene) film after thermal dehydrochlorination at 100°C for 2 days. Degree of dehydrochlorination: 53%.

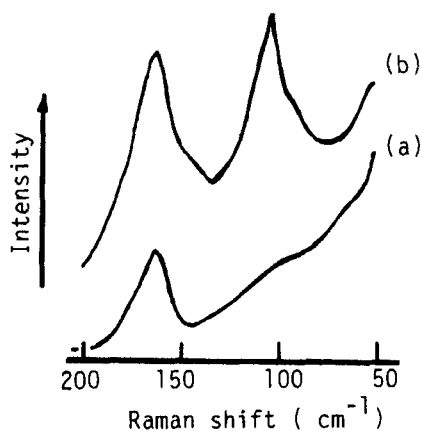


FIG. 8. Raman spectra of thermally dehydrochlorinated poly(-1-chlorobutadiene) (degree of dehydrochlorination: 53%) before (a) and after (b) doping with iodine. Iodine content: 8.39%.

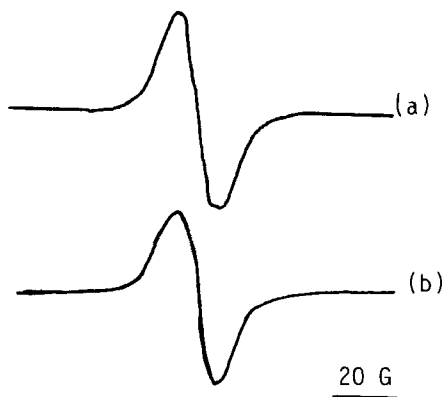
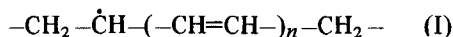


FIG. 9. ESR spectra of thermally dehydrochlorinated poly(1-chlorobutadiene) (degree of dehydrochlorination: 53%) before (a) and after (b) doping with iodine. Iodine content: 8.39%.

bonds ( $n$ ) increases [18]. The  $\Delta H_{msl}$  value is roughly proportional to  $n$ ; for example, when  $\Delta H_{msl} = 17$  G,  $n$  is nearly equal to 11.



For PCB after thermal dehydrochlorination, the number of conjugated double bonds is calculated to be about 26. This result is similar to that obtained by Raman spectroscopy.

In the ESR spectrum of the iodine-treated PCB (Fig. 9), the line shape has not changed. It is known that the line becomes asymmetric when polyacetylene is highly doped with iodine [19], owing to the growth of the size of the metallic domains. Therefore, it is concluded that the dehydrochlorinated polymer may not have a length of conjugated double bonds sufficient to develop metallic domains.

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