7.30 (4 H, phenyl group). Anal. for $C_{20}H_{27}NOSFe_2$ = 441.26; Fe, 25.48 (25.31).

**Copolymerization of 4 and 5.** In a typical experiment, 1 mmol of AIBN was added to a solution (25 mL) containing 0.2 mmol of the organometallic monomer and 20 mmol of styrene, methyl methacrylate (MMA), or *N*-[tris(hydroxymethyl)methyl]acrylamide (Tris-A). After the solution was heated under $M_2$, with stirring, for 24 h at 65 °C, the copolymer was precipitated by addition of a nonpolar solvent to the cooled solution. Copolymers were purified by the classical dissolution-precipitation technique. Their characteristics are listed in Table I.

**Copolymer 12a**: 70% conversion, solvent benzene, precipitation by hexane, purification from $CH_2Cl_2$-$CH_3OH$.

**Copolymer 12b**: 75% conversion; same experimental conditions as for **12a**.

**Copolymer 12c**: 60% conversion, solvent *N*-methylpyrrolidone, precipitation by diethyl ether, purification by addition of a mixture of acetone and diethyl ether (1/1) to an aqueous solution.

**Copolymer 13**: 75% conversion; same experimental conditions as for **12a**.

**Reaction of $Fe_2(CO)_9$ with Polymers.** To a solution of 1 g of copolymer 8, 9, or 10 in acetone (acetone-benzene (1/1) in the case of homopolymer 9) was added $Fe_2(CO)_9$ (50% excess based on the known composition of the polymer). The mixture was reacted, with stirring, for 24 h at room temperature in the dark and under $N_2$. After filtration, the mixture was poured into methanol, and the resulting precipitate was collected and purified by the usual dissolution-precipitation technique ($CH_2Cl_2$-$CH_3OH$) or washed by $CH_2Cl_2$ and acetone in the case of cross-linked polymers. The characteristics of the modified polymers are listed in Table I for the synthesis of the starting materials, see ref 12.

**Registry No.** 1, 56986-31-3; 2, 79631-36-0; 3, 5977-87-7; 4, 80137-07-1; 5, 86689-20-5; 6, 80137-05-9; 7, 86695-73-0; **12a**, 86689-17-0; **12b**, 86689-18-1; **12c**, 86689-19-2; **13**, 86689-21-6.

## References and Notes

(1) Carraher, C. E.; Sheats, J. E.; Pittman, C. U. "Organometallic Polymers"; Academic Press: New York, 1978.

(2) Pittman, C. U. In "Polymer Supported Reactions in Organic Synthesis"; Hodge, P., Sherrington, D. C., Eds.; Wiley: New York, 1980.

(3) (a) Seriya, A.; Stille, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 5096 and references therein. (b) Kaneka, M.; Tsuchida, E. *J. Polym. Sci., Macromol. Rev.* **1981**, *16*, 397.

(4) Macomber, D. W.; Hart, W. L.; Rausch, M. D.; Priesterand, R. D.; Pittman, C. U. *J. Am. Chem. Soc.* **1982**, *104*, 884.

(5) Gressier, J. C.; Levesque, G.; Patin, H. *Polym. Bull.* **1982**, *8*, 55 and references therein.

(6) Nagy, A. G.; Dezsi, I.; Hillman, M. *J. Organomet. Chem.* **1976**, *117*, 55. Hillman, M.; Nagy, A. G. *Ibid.* **1980**, *184*, 433.

(7) Ruby, S. L.; Zabransky, B. J.; Flinn, P. A. *J. Phys. (Paris)* **1976**, *37*, C6, 745.

(8) Patin, H.; Mahe, C.; Renoist, M.; le Marouille, J. Y. *J. Organomet. Chem.* **1981**, *218*, C67.

(9) Alper, H.; Chan, A. S. K. *J. Chem. Soc., Chem. Commun.* **1973**, 724.

(10) Muetterties, E. L. *J. Organomet. Chem.* **1980**, *200*, 177.

(11) Darchen, A.; Mahe, C.; Patin, H. *J. Chem. Soc., Chem. Commun.* **1982**, 243.

(12) (a) Haraoubia, R.; Gressier, J. C.; Levesque, G. *Makromol. Chem.* **1975**, *176*, 2. (b) Haraoubia, R.; Bonnans-Plaisance, C.; Levesque, G. *Ibid.* **1981**, *182*, 2409. (c) Haraoubia, R.; Bonnans-Plaisance, C.; Gressier, J. C.; Levesque, G. *Ibid.* **1982**, *183*, 2317, 2383.

(13) Alper, H.; Foo, C. K. *Inorg. Chem.* **1975**, *14*, 2928.

(14) Mahe, C. Thesis, Rennes, 1982.

(15) See, for instance: Gutlich, P.; Link, R.; Trautwein, A. "Mössbauer Spectroscopy and Transition Metal Chemistry"; Springer-Verlag: West Berlin, 1978.

(16) (a) Pittman, C. U., Jr.; Lai, J. C.; Vanderpool, D. P.; Good, M.; Prado, R. *Macromolecules* **1970**, *3*, 706. (b) Corfield, G. L.; Brooks, J. S.; Plimley, S. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1981**, *22* (1), 3.

(17) Mignani, G. Thesis, Rennes, 1980.

(18) Greenwood, N. K.; Gibb, T. C. "Mössbauer Spectroscopy"; Chapman and Hall: London, 1971; p 230.

(19) van Diepen, A. M.; Popma, J. J. A. *J. Phys. (Paris)* **1976**, *37*, C6, 755.

(20) Janot, C. "L'Effet Mössbauer et ses Applications"; Masson: Paris, 1972; p 12.

(21) van Krevelen, D. W.; Hoftyzer, P. J. "Properties of Polymers"; Elsevier: Amsterdam, 1976.

---

# Urethane-Substituted Poly(diacetylenes): Structure and Electrical Properties of Poly[4,6-decadiyne-1,10-diol bis([(*n*-butoxycarbonyl)methyl]urethane)]

**Kazunori Se, Hiroshi Ohnuma, and Tadao Kotaka***

*Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan.*

*Received December 13, 1982*

ABSTRACT: A study on the relation between molecular characteristics and electrical conductivity was carried out on a urethane-substituted poly(diacetylene), poly[4,6-decadiyne-1,10-diol bis([(*n*-butoxycarbonyl)methyl]urethane)], abbreviated as poly(3BCMU), prepared by $^{60}$Co $\gamma$-ray irradiation of the powder-form monomer. Two samples were employed: one obtained at 45-Mrd dose and having a relatively low molecular weight (MW) and broad molecular weight distribution (MWD), and the other obtained at 0.09-Mrd dose and having a relatively high MW and narrow MWD. The effects of dopant iodine on the mechanical and electrical properties were examined in particular. Raman spectra indicated the presence of iodine in the form of $I_3^-$ and $I_5^-$ in poly(3BCMU). The doping increased the glass transition temperature $T_g$ as much as 27 K. An X-ray diffraction study suggested that the doping mostly occurs in the amorphous regions. The direct-current conductivity $\sigma_{dc}$ of undoped poly(3BCMU) was of the order of $10^{-11}\ \Omega^{-1}\ cm^{-1}$, while the doping enhanced the $\sigma_{dc}$ by about $10^7$-fold. The activation energy $E_a$ was virtually unchanged by doping but decreased abruptly at a certain temperature as $T$ was decreased: The $E_a$ was also different between the two samples. The $\sigma_{dc}$ of doped poly(3BCMU) was found to obey Ohm's law. This and all other evidence suggested that the conduction is mainly electronic, involving such processes as the activation of charge carriers from dopant to the conjugated backbones of poly(3BCMU) and the transfer of the carrier from one chain to another.

## Introduction

Although common polymeric materials are generally insulators of electricity, some conductive polymers have been attracting attention in recent years.[1] These conductive polymers have two intriguing characteristics besides their rather high conductivity. One is the anisotropy of the conductivity. Therefore, these materials may be called linear-chain conductors or one-dimensional conductors.[2] The other is the possibility of easy processability. They may be molded into thin films that might be utilized

0024-9297/83/2216-1581$01.50/0

as solar cell materials and/or rechargeable organic batteries. Among the various synthetic polymeric conductors examined along these lines, polyacetylene (PA) is one of the simplest organic polymers having conjugated $\pi$-electron backbones. In particular, the interest in PA was stimulated by a successful demonstration of doping with halogens or $AsF_5$ to control the electrical properties over a wide range.[1,3-5] However, most of these materials, including polyacetylene, can be neither dissolved nor melted. Hence, they can hardly be characterized adequately with regard to the molecular weight and its distribution without some laborious manipulation.[6] In addition to this difficulty, neither solvent-cast films nor oriented fibrous specimens can be obtained from these polymers to test their anisotropic conductivity.

Recently, Patel et al.[7,8] reported the synthesis of soluble poly(diacetylene) derivatives, which consist of conjugated main chains analogous to polyacetylene. One of the major differences between PA and the poly(diacetylenes) is that the former has a polyene-type backbone, while the latter has a poly(ene-yne)-type backbone with an admixture of the butatriene structure. The other difference is that the latter has two bulky substituent groups R in the monomer unit.[9,10] One such poly(diacetylene) is poly[4,6-decadiyne-1,10-diol bis([(*n*-butoxycarbonyl)methyl]urethane)], abbreviated as poly(3BCMU), whose R has the form $-(CH_2)_3OCONHCH_2COOC_4H_9$. Because the conjugated main chain is surrounded by the bulky side groups, poly(3BCMU) is fusible and soluble in common organic solvents. Therefore, poly(3BCMU) could be a convenient model of linear-chain conductors to study the relationship between the molecular characteristics and electrical conductivity.[11]

Poly(diacetylenes) as well as polyacetylene are insulators of electricity, unless they are doped adequately with some electron acceptors (or donors) such as halogens and arsenic pentafluoride ($AsF_5$). A key problem is undoubtedly the mechanism of enhancing the conductivity by doping. However, it was often pointed out that doping makes the polymer conductive but deteriorates mechanical properties. In this article we discuss these two major problems on the effects of dopant, particularly iodine, on poly(3BCMU). First, we examine the dopant effect on the glass transition temperature $T_g$ of poly(3BCMU) by carrying out mechanical and dielectric relaxation studies on pure (or undoped) and doped specimens. Second, we describe the dependence of electrical conductivity of poly(3BCMU) on the dopant concentration and temperature. Particularly, we examine the conductivities for direct (dc) and alternating current (ac).[12] These tests were carried out on two samples reported earlier.[11] One of them had a relatively high number-average molecular weight and narrow molecular weight distribution and the other was contaminated heavily with low molecular weight components and thus had a very broad molecular weight distribution.

## Experimental Section

**Materials.** The 3BCMU monomer was prepared through a four-step reaction reported previously.[11] The poly(3BCMU) was obtained by a solid-state polymerization exposing the powder-form monomer to $^{60}Co$ $\gamma$-rays. The unreacted monomer was removed by extracting with acetone, and the monomer-free powder-form poly(3BCMU) was obtained. Among several samples obtained at various doses, we employed two samples in this study: The sample codes and the characteristics are summarized in Table I. The average molecular weights were estimated on a gel permeation chromatograph (GPC, Toyo Soda Mfg. Co., Model HLC 801A) with a low-angle laser light scattering monitor (Toyo Soda Mfg. Co., Model LS-8). The carrier solvent was $CHCl_3$. Narrow-distribution polystyrenes (TSK polystyrenes, Toyo Soda Mfg. Co.) were used as the elution standards.[11] Figure 1 shows GPC chromatograms of the two samples.

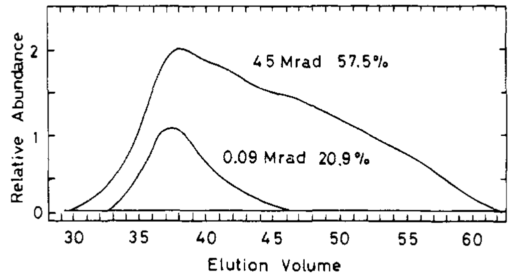

**Figure 1.** GPC chromatograms of poly(3BCMU) specimens used in this study. The numerical values in this figure represent both the dose level and polymer conversion.

Table I
Molecular Characteristics of Poly(3BCMU) Samples Used in This Study

| polymer | $10^{-6}M_n$ | $10^{-6}M_w$ | $M_w/M_n$ |
|---|---|---|---|
| poly(3BCMU)/45 Mrd | 0.080 | 3.2 | 40 |
| poly(3BCMU)/0.09 Mrd | 1.3 | 3.9 | 3.0 |

Among several organic solvents tested, $CHCl_3$ was the best solvent,[11] which dissolved the polymer nearly up to 5% concentration at room temperature. Films of 0.2–0.3-mm thickness were cast from 2% (w/v) $CHCl_3$ solution of the purified poly(3BCMU). The solvent was allowed to evaporate slowly at room temperature over a period of 80 h. The films showed a metallic black-gold luster.

**Doping with Iodine.** Specimens could be easily doped with a strong electron acceptor, iodine, simply by exposing them to the vapor in a desiccator that had been evacuated in advance under a vacuum of $10^{-3}$ torr. The iodine-doped specimens were relatively stable even in air, where the dopant was lost very slowly. $AsF_5$ was very unstable and must be handled under vacuum. Therefore only iodine was used as a dopant in this study, though $AsF_5$ was a much more effective dopant. The dopant concentration was varied from 1 to 60 wt % by adjusting the doping time from 1 min to 30 h. The amount of iodine absorbed was determined by measuring the weight increase of the specimen. The dopant concentration $Y$ was expressed as the number of moles of $I_3^-$ ions per mole of the 3BCMU unit.

**Methods.** Differential scanning calorimetry was carried out on a DSC apparatus (Rigaku Denki Co., Model 8055) with a heating rate of 10 K min$^{-1}$. X-ray diffraction patterns were obtained by a cylindrical camera of 3.5-cm radius. The radiation used was Ni-filtered Cu K$\alpha$. Raman spectra were obtained with a triple-monochromator Raman spectrometer (Japan Spectrometric Co., Model R750). Dynamic mechanical measurements were made on a Rheovibron DDV-II (Toyo-Baldwin Co.) at 110 Hz. Both complex dielectric permittivity $\epsilon^*$ and alternating-current (ac) conductivity $\sigma_{ac}$ were measured with a transformer bridge (General Radio Model 1615A) in the range 0.1–100 kHz. The direct-current (dc) conductivity $\sigma_{dc}$ (or simply $\sigma$) was determined by a four-terminal method. A certain voltage was applied to the two outer contacts, and then the electric current of the circuit and the potential difference between the two inner contacts were measured, respectively, with a Keithley 640C electrometer as an ammeter and with a Keithley 610 electrometer as a potentiometer.

## Results

**Differential Scanning Calorimetry (DSC) and X-ray Diffraction.** DSC measurements were carried out for a poly(3BCMU)/45 Mrd powder specimen and two cast-films of poly(3BCMU)/45 Mrd and poly(3BCMU)/0.09 Mrd. For the powder specimen, two endotherms were observed at about 450 and 420 K. However, the thermograms of the cast films showed one endotherm at 450 K, which has the tailing on the low-temperature side. A similar result was also reported by Patel et al.[13] On the

Table II
Enthalpies of Fusion[a] and *d* Spacings[b] for the Various Poly(3BCMU) Specimens

| | poly(3BCMU)/45 Mrd | | | poly(3BCMU)/0.09 Mrd |
|---|---|---|---|---|
| | powder | undoped film | doped film | undoped film |
| enthalpy of fusion/J g$^{-1}$ | 28.5 (450 K)<br>8.8 (420 K) | 5.4 (450 K) | | 11.5 (450 K) |
| *d* spacings/nm | 1.33 (s) | 1.40 (s) | | |
| | 0.90 (vw) | | | |
| | 0.53 (w) | 0.45 (w) | 0.45 (w) | |
| | 0.43 (s) | 0.42 (s) | 0.42 (s) | |
| | 0.38 (w) | | | |
| | 0.34 (vw) | | | |
| | 0.22 (vw) | 0.23 (vw) | 0.23 (vw) | |
| | 0.20 (vw) | 0.20 (vw) | | |

[a] The temperatures in the parentheses correspond to the melting peaks, from which the enthalpies of fusion were estimated. [b] In the parentheses, each intensity of the X-ray diffractions is indicated by three symbols: s = strong, w = weak, and vw = very weak.

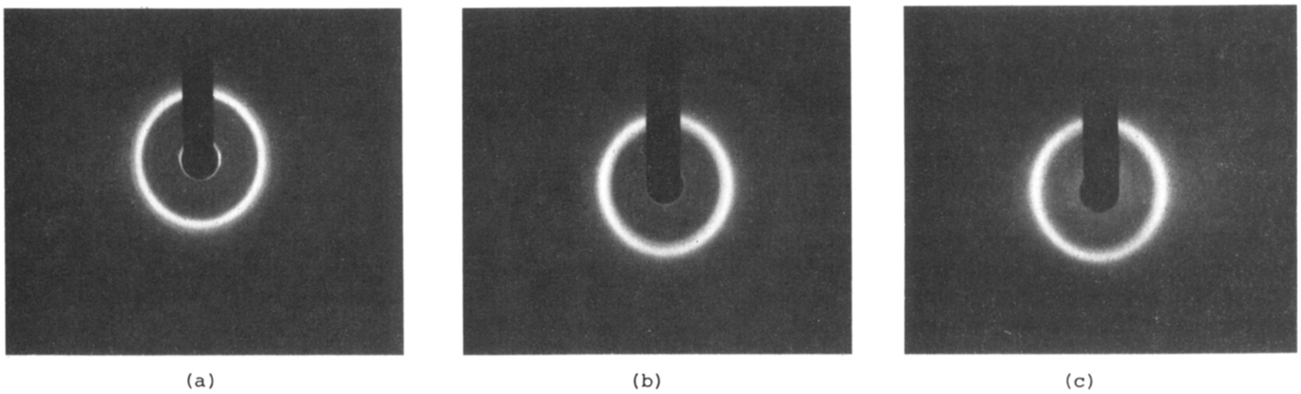
(a) (b) (c)

**Figure 2.** Debye–Scherrer photographs for (a) the poly(3BCMU) powder specimen, (b) the undoped poly(3BCMU)/45 Mrd film, and (c) the doped poly[3BCMU$(I_3)_{0.42}$]/45 Mrd film.

basis of their finding that the poly(3BCMU) film was totally amorphous in their X-ray diffraction study, they concluded the following: (i) The endotherm at 420 K is due to the destruction of intermolecular order (intermolecular melting), and the endotherm at 450 K is due to destruction of the intramolecular hydrogen bonds between the C=O and N–H functionalities of the adjacent side groups (intramolecular melting). (ii) The endotherm at 420 K corresponds to a change in the crystallinity of the sample. We estimated values of the enthalpy of fusion from the areas of the melting peaks at 420 and 450 K. The results are summarized in Table II. Unfortunately, since the enthalpy of fusion for the perfectly crystalline specimen is not known, the degree of crystallinity for these specimens could not be quantitatively determined. We can safely say that the powder specimen has the highest degree of crystallinity and that of the poly(3BCMU)/45 Mrd film is the lowest among the three specimens.

Parts a and b of Figure 2 show the Debye–Scherrer photographs of the powder specimen and the undoped poly(3BCMU)/45 Mrd film, respectively. Both photographs are characteristic of unoriented crystalline polymers. For the powder specimen, eight diffraction rings could be detected, while only five diffraction rings could be detected for the film specimen. The photograph of the latter suggests that the film specimen has a very low degree of crystallinity. This result is consistent with the DSC result. An X-ray photograph of the doped poly[3BCMU$(I_3)_{0.42}$]/45 Mrd film is shown in Figure 2c. Only three diffraction rings were detected for the doped film due to the pronounced background scattering. The *d* spacings calculated from the X-ray diffraction patterns are also listed in Table II. The difference in the *d* spacings between the powder and film specimens suggests that their crystal forms may be different. On the other hand, all the *d* spacings in the doped film were found to be the same values as those in the undoped film, and the difference in relative intensities of the corresponding diffraction between the undoped and doped film was not observed. These results imply that the doping does not affect the crystal form. Thus, we may conclude that the doping took place mostly in the amorphous regions.

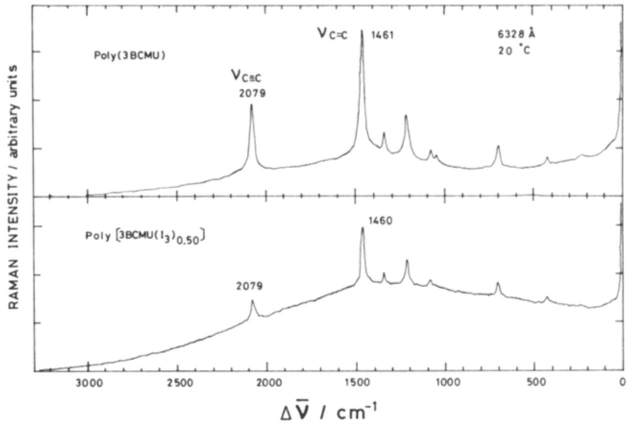

**Figure 3.** Raman spectra of poly(3BCMU) (upper curve) and poly[3BCMU$(I_3)_{0.50}$] (lower curve).

**Raman Scattering.** We obtained spectra at room temperature and at liquid nitrogen temperature for pure and doped poly(3BCMU)/0.09 Mrd films. The 514.5-nm line from an Ar$^+$ laser was used as the excitation source. As shown in Figure 3, the Raman spectrum of the pure (undoped) specimen at room temperature has two very strong bands due to a resonance Raman effect.[14] On the basis of results reported on poly(diacetylene) deriva-

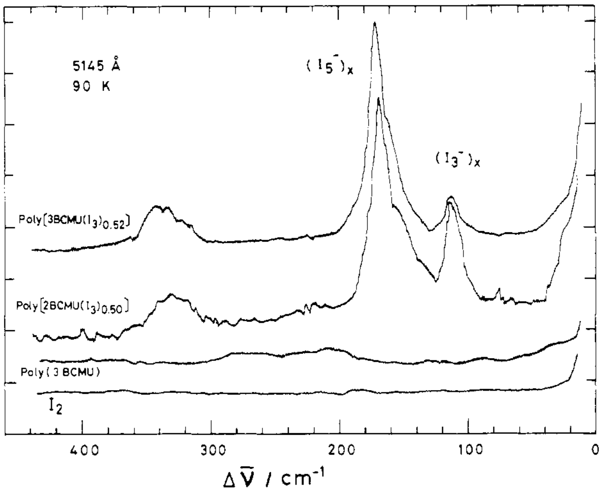

**Figure 4.** Low-frequency region of Raman spectra at 90 K of iodine in pure and doped specimens. Iodine-doped poly[3,5-decadiyne-1,8-diol bis([(*n*-butoxycarbonyl)methyl]urethane)], abbreviated as poly(2BCMU),[7,8] also shows the same additional bands in the Raman spectra.

tives,[15,16] one absorption at 2079 cm$^{-1}$ may be assigned to the $C\equiv C$ vibration and the other at 1461 cm$^{-1}$ to the $C=C$ vibration.

The doped specimen also exhibited the same two bands as those of the pure specimen. However, the doped specimen exhibited rather high background intensity. This increment may be regarded either as the fluorescent background[14] due to some impurities or as that due to charge-transfer complex[17] between conjugated main chains and dopant ions.

Figure 4 shows Raman spectra in the range of small wavenumber obtained at liquid nitrogen temperature. The doped specimen ($Y = 0.52$) shows additional bands in the range of wavenumber below 400 cm$^{-1}$. Comparing these results with those reported for iodine-doped polyacetylene,[18] we concluded that one absorption at 105 cm$^{-1}$ was due to the $I_3^-$ vibration and the other at 160 cm$^{-1}$ to the $I_5^-$ vibration. Moreover, we could observe their overtones, whose intensities were less than that of the original absorptions. The results clearly indicate the existence of $I_3^-$ and $I_5^-$ ions.

**Dynamic Mechanical and Dielectric Properties.** Figure 5 shows the temperature dependence of the storage Young's moduli $E'$, the loss moduli $E''$, and tan $\delta$ for poly(3BCMU), poly[3BCMU(I$_3$)$_{0.09}$], and poly[3BCMU-(I$_3$)$_{0.23}$]. The polymer is the 45-Mrd sample. The $E'$ of undoped poly(3BCMU) decreases gradually with increasing temperature from 140 to 240 K and then somewhat more rapidly from 240 to 300 K. The specimen began to flow at about 420 K. This result coincides with that of differential scanning calorimetry (DSC), in which poly(3BCMU) exhibited a sharp melting point at about 450 K. The dynamic mechanical behavior of poly(3BCMU) is similar in nature to that of common semicrystalline polymers. The $E''$ and tan $\delta$ curves exhibit a broad transition having a maximum temperature $T_{\max}$ at 270 K, which presumably corresponds to the glass transition temperature $T_g$. The temperature dependence of the complex Young's moduli were measured also on the doped specimens of poly(3BCMU)/45 Mrd. The behavior of poly[3BCMU(I$_3$)$_{0.09}$] and poly[3BCMU(I$_3$)$_{0.23}$] is similar to that of the undoped poly(3BCMU), except that the $T_{\max}$ shifted to the higher temperature side. The $T_{\max}$ increases as $Y$ increases up to $Y = 0.09$ and reaches a constant of approximately 300 K in the range of $Y$ from 0.09 to 0.23. In doped specimens, the $I_3^-$ ions might coordinate to several conjugated main chains or polar side chains and might form ionic clusters as those usually found in ionomers.[17] This strong intermolecular interaction under the presence of $I_3^-$ might cause the $T_{\max}$ to increase with increasing dopant concentration.

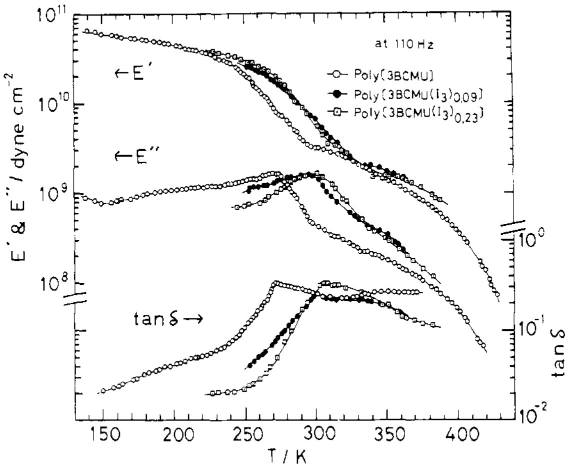

**Figure 5.** Temperature dependence of the storage Young's moduli $E'$, the loss moduli $E''$, and tan $\delta$ at 110 Hz for pure and doped poly(3BCMU) specimens.

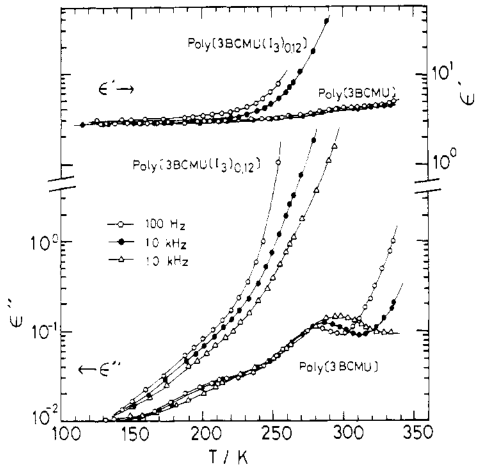

**Figure 6.** Temperature dependence of the dielectric permittivity $\epsilon'$ and loss $\epsilon''$ for poly(3BCMU) and poly[3BCMU(I$_3$)$_{0.12}$].

Figure 6 shows the temperature dependence of the dielectric permittivity $\epsilon'$ and loss $\epsilon''$ for undoped poly(3BCMU)/45 Mrd and doped poly[3BCMU(I$_3$)$_{0.12}$]. The loss curve of the poly(3BCMU) has a small peak at 210 K (designated as the $\beta$-peak), a peak at 280 K (the $\alpha$-peak), and a steep rise in the high-temperature side. The $\alpha$-peak temperature is roughly the same as the $T_{\max}$ of dynamic mechanical transition and may be attributed to the primary relaxation due to the glass transition. The $\beta$-peak temperature is also roughly the same as that of the dynamic mechanical $\beta$-relaxation. The $\beta$-relaxation may be ascribed to the motion of polar side groups.[19] The frequency and temperature dependence of the $\alpha$-peak follows a Williams–Landel–Ferry (WLF) law. From the slope of the plot at 1 kHz, the apparent activation energy was estimated to be 163 kJ mol$^{-1}$. The $\epsilon'$ and $\epsilon''$ curves of the doped poly[3BCMU(I$_3$)$_{0.12}$] exhibit a steep rise in the high-temperature side, as the conductivity steeply increases with increasing dopant concentration. The dielectric $\alpha$-relaxation peak was obscured because of this steep rise.

**Direct-Current Conductivity.** The electrical conductivity $\sigma$ of undoped poly(3BCMU)/45 Mrd and poly(3BCMU)/0.09 Mrd films is of the order of $10^{-11}$ Ω$^{-1}$ cm$^{-1}$, though they have the metallic appearance of golden color.

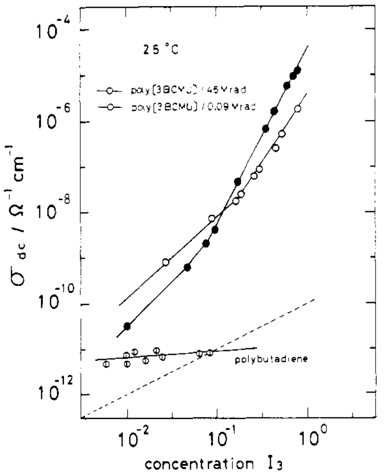

**Figure 7.** Dc conductivity of poly(3BCMU)/45 Mrd, poly(3BCMU)/0.09 Mrd, and polybutadiene as a function of dopant concentration *Y*.

After about 4 h of evacuation of the four-terminal cell at $10^{-3}$ torr, $\sigma_{dc}$ decreased from $2.3 \times 10^{-11}$ to $0.8 \times 10^{-11}$ $\Omega^{-1}$ $cm^{-1}$. The $\sigma_{dc}$ became constant after 50 h of evacuation. Then air was introduced into the cell and the $\sigma_{dc}$ increased to the initial value of $2.3 \times 10^{-11}$ $\Omega^{-1}$ $cm^{-1}$ after about 4 h. This increase in $\sigma_{dc}$ may be a result of oxygen acting as a dopant.[20] However, such an increase in the $\sigma_{dc}$ was usually far less than that due to iodine doping. Hence, the $\sigma_{dc}$ of iodine-doped specimens was usually measured in the presence of air.

Figure 7 shows the dependence of the $\sigma_{dc}$ on dopant concentration *Y* for poly(3BCMU)/45 Mrd, poly(3BCMU)/0.09 Mrd, and polybutadiene at 25 °C. The $\sigma_{dc}$ of both poly(3BCMU)/45 Mrd and poly(3BCMU)/0.09 Mrd increase rapidly with increasing *Y* and finally reach about $10^{-5}$ $\Omega^{-1}$ $cm^{-1}$ at a *Y* of about 0.7. This result[21] may be the first demonstration that the $\sigma_{dc}$ of a poly(diacetylene), among a variety of other derivatives,[22-25] reaches as high as a semiconductor level by adequate doping. For comparison, we studied polybutadiene doped with iodine as a reference. The $\sigma_{dc}$ of doped polybutadiene remains almost constant in the range of *Y* about $10^{-2}$–$10^{-1}$. These results suggest that iodine is not acting as an ionic charge carrier but interacts strongly with the conjugated main chains of doped poly(3BCMU) to increase the $\sigma_{dc}$.

The behavior of the $\sigma_{dc}$ increments may be represented by

$$\sigma_{dc}(Y) = AY^{\alpha} \tag{1}$$

where *A* and $\alpha$ are parameters independent of the dopant concentration. According to Drude, the $\sigma_{dc}(Y)$ is generally given by[26]

$$\sigma_{dc}(Y) = qn\mu \tag{2}$$

where $q$, $n$, and $\mu$ are, respectively, the amount of charge, the number density, and the mobility of the charge carrier. If the dopant iodine is acting merely as an ionic carrier, the $q$ and $\mu$ would be virtually constant and $n$ would be directly proportional to the carrier concentration *Y*. However, the $\sigma_{dc}$ for poly(3BCMU)/45 Mrd first increases in proportion to $Y^{2.0}$ and later in proportion to $Y^{3.0}$, while the $\sigma_{dc}$ for poly(3BCMU)/0.09 Mrd increases in proportion to $Y^{2.0}$ in the region of low dopant concentration and in proportion to as much as $Y^{3.9}$ in the region of high dopant concentration. In any case, the values of $\alpha$ are larger than one. Hence the dopant iodine must be interacting with the conjugated main chains of poly(3BCMU), thereby producing active electrons and/or positive holes as the charge carriers along the main chains. The dopant may also act as a bridge for the hopping of charge carriers from one chain to the other or between chain ends.

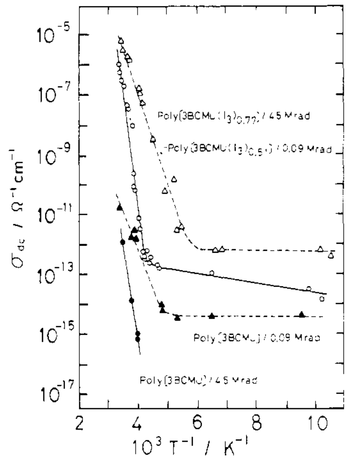

**Figure 8.** Temperature dependence of the dc conductivity for pure and doped poly(3BCMU)/45 Mrd and poly(3BCMU)/0.09 Mrd specimens.

In particular, in the range of high dopant concentration the exponent $\alpha$ for poly(3BCMU)/0.09 Mrd was about 30% larger than that of poly(3BCMU)/45 Mrd. This result is resonable, because poly(3BCMU)/45 Mrd is heavily contaminated with low molecular weight components and has an extremely broad molecular weight distribution. The higher molecular weight components excited with the dopant might be more effective semiconductive components, while the chain ends provide the electrical resistance either by acting as localized trap sites or by reducing the degree of crystallinity or by both reasons.

Comparing these results with those of iodine-doped polyacetylene (PA),[1-5] we see three characteristics in their behavior: (1) An undoped and doped PA have a semiconductive $\sigma_{dc}$ of $10^{-6}$ $\Omega^{-1}$ $cm^{-1}$ and a metallic value of 10 $\Omega^{-1}$ $cm^{-1}$, respectively, while poly(3BCMU)/0.09 Mrd and poly[3BCMU$(I_3)_{0.8}$/0.09 Mrd] have an insulative $\sigma_{dc}$ of $10^{-12}$ $\Omega^{-1}$ $cm^{-1}$ and a semiconductive value of $10^{-5}$ $\Omega^{-1}$ $cm^{-1}$, respectively. (2) The $\sigma_{dc}$ of PA is substantially saturated at a *Y* of about 0.1, while that of poly(3BCMU) is saturated at a *Y* of about 0.9. Finally, there is a similarity in their behavior that (3) the doping of both PA and poly(3BCMU) results in an increase in $\sigma_{dc}$ by the same factor of about $10^7$. These characteristics may be attributed to the difference in the molecular and/or crystal structure between PA and poly(3BCMU) films. In the latter, only 10% of the total molecular volume is conjugated main chain, with the remaining 90% insulative side chains. Furthermore, the former has a particular foamlike fibrillar structure with a high degree of crystallinity,[27] while the latter, especially the cast-film, is a semicrystalline film with a very low degree of crystallinity.

Figure 8 shows a few examples of the temperature dependence of the $\sigma_{dc}$ for undoped and doped poly(3BCMU) specimens. The $\sigma_{dc}$ of poly[3BCMU$(I_3)_{0.51}$]/0.09 Mrd and poly(3BCMU)/0.09 Mrd decrease with decreasing temperature and then become almost constant below a certain temperature. In the high-temperature region, plots of log $\sigma_{dc}$ vs. $1/T$ give approximately straight lines, from which the approximate thermal activation energy $E_a$ can be determined. Both undoped and doped specimens of the 0.09-Mrd sample give $E_a$ of the same order of magnitude, 0.54 eV $mol^{-1}$. Unlike $\sigma_{dc}$, $E_a$ does not depend on the dopant concentration. The undoped and doped ($Y = 0.77$) specimens of the 45-Mrd sample also give the same $E_a$ of

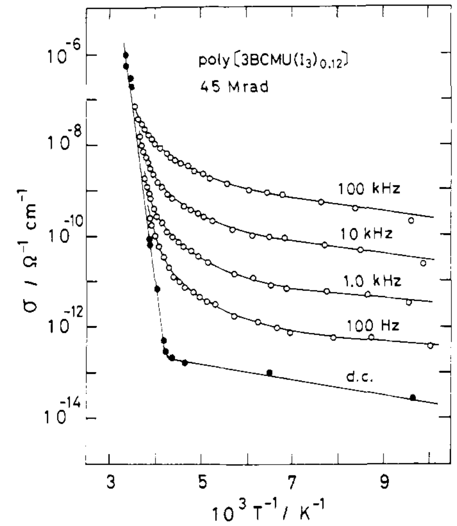

**Figure 9.** Temperature dependence of the ac conductivity at 0.1, 1, 10, and 100 kHz (open circles) and the dc conductivity (solid circles) for poly[3BCMU$(I_3)_{0.12}$].

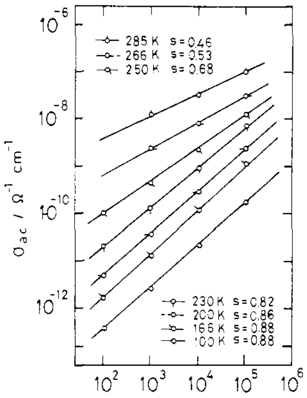

**Figure 10.** Frequency dependence of the ac conductivity for poly[3BCMU$(I_3)_{0.12}$]. The values of *s* indicated are the slopes of the curves at the corresponding temperature.

about 1.61 eV mol$^{-1}$. The value is about 3 times larger than that of poly(3BCMU)/0.09 Mrd and is much larger than that of 0.09–0.35 eV mol$^{-1}$ for polyacetylene.[3-5] On the other hand, in the low-temperature region, the $E_a$ is nearly zero for the 0.09-Mrd sample and is as small as 0.012 eV mol$^{-1}$ for the doped 45-Mrd sample. The $\sigma_{dc}$ was too low to be measured accurately for the undoped 45-Mrd sample at the low temperature.

**Alternating-Current Conductivity.** Measurements of the conductivity $\sigma_{ac}$ for alternating current often provide important information on the mechanism of electrical conductivity of materials. Figure 9 shows the temperature dependence of the ac conductivity $\sigma_{ac}$ of poly[3BCMU$(I_3)_{0.12}$]/45 Mrd. The $\sigma_{ac}$ is much larger than the $\sigma_{dc}$, and the difference becomes progressively greater as temperature is lowered. A similar temperature dependence of $\sigma_{ac}$ was found in some inorganic semiconductors[26,28] such as a single-crystalline silicone.

Figure 10 shows the frequency dependence of the $\sigma_{ac}$ for poly[3BCMU$(I_3)_{0.12}$]/45 Mrd obtained at various temperatures. The data may be cast into the form[12]

$$\sigma_{ac}(f) = Af^s \qquad (3)$$

where $A$ and $s$ are constants and $f$ is the frequency. The $\sigma_{ac}$ of an insulator is directly proportional to $f$ ($s = 1$), while the $\sigma_{ac}$ of a metal does not depend on $f$ ($s = 0$). As seen in Figure 10, the value of $s$ decreases from 0.88 to 0.46 as the temperature is raised from 100 to 285 K.

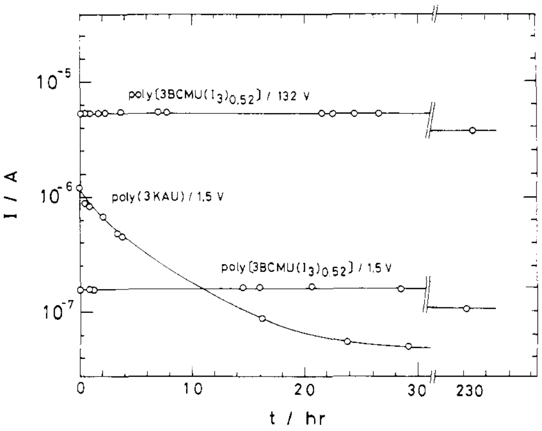

**Figure 11.** Electric current vs. applied time for doped poly(3BCMU) specimens under constant applied voltages. For comparison, the figure shows data for poly(3KAU), which is a KOH-hydrolyzed poly(3BCMU)/45 Mrd specimen.

## Discussion

Phenomenologically the electric conduction of doped poly(3BCMU) might involve two mechanisms; one is an ionic conduction due to the migration of iodine ions, while the other is due to hole conduction linked to the band created by the main chain. In order to estimate the relative contribution of these two mechanisms, the electric current was measured as a function of time under constant voltage. If the ionic conduction is dominant, the current would decrease with applied time, as the ionic carriers are eventually purged from the system. It is also known that for ionic conductions, Ohm's law does not hold but the sine-hyperbolic law becomes valid.[26]

The behavior due to ionic conduction is seen for the potassium salt of KOH-hydrolyzed poly(3BCMU), coded as poly(3KAU).[31] For the poly(3KAU) specimen under an applied voltage of 1.5 V the current rapidly decreases, as is seen in Figure 11. The voltage vs. current relation was not ohmic for the poly(3KAU) specimen. On the other hand, for iodine-doped poly(3BCMU), as is seen in Figure 11, the current under the applied voltage of 1.5 V and that under 132 V are almost constant up to about 230 h. The slight drop of the current after a prolonged application of the voltage to the doped poly(3BCMU) may be attributed to iodine desorption during the period, as judged from the absorption and desorption feature of iodine by the poly(3BCMU)–iodine system mentioned previously. We also found that the current was proportional to the applied voltage. That is, the conduction is approximately ohmic. These results strongly suggest that the electronic conduction is the main process in the doped poly(3BCMU).

Under an applied voltage of 132 V, the constant current was about 5.0 × $10^{-6}$ A. The transported charges during 230 h, then, amount to 4.1 C. The dimension of this specimen was 3.15 × 1.70 × 0.13 mm$^3$ and the dopant concentration $Y$ was 0.52. If we assume that the polymer density is 1 and the dopant exists only in the form of $I_3^-$ ion, all the ionic charges in this specimen are as small as 4.2 × $10^{-2}$ C. The observed value is larger than that of the estimated ionic charges by a factor of 100. This observation suggests that electronic conduction may be the dominant factor in this specimen.

The mechanisms of electronic conduction in polymer semiconductors are very complex, because they are aggregates of chain molecules, partially crystalline but partially amorphous. Although the detailed nature of the interaction between dopant species and conjugated main chains is not yet well understood,[25,29,30] iodine ions in the form of $I_3^-$ and/or $I_5^-$ existing in doped poly(3BCMU) specimens of presumably amorphous regions are apparently playing a key role. Dopant iodines withdraw electrons from the conjugated main chains to become anions. Hence, extra holes can be produced in the chain. This structural model is consistent with the observation in the mechanical properties of doped poly(3BCMU) specimens, in which strong intermolecular interactions resulted in an increase in $T_{\max}$.

The characteristic features of the conductivity of the present systems are summarized as follows: (i) the conductivity increases with increasing dopant concentration, while (ii) the activation energy of the conductivity is independent of the dopant concentration, (iii) but is dependent on the molecular weight and its distribution and/or the degree of crystallinity. The results suggest that the iodine doping affects both the carrier mobility $\mu$ and the carrier density $n$, whereas the molecular weight and its distribution apparently influence $\mu$. (iv) The activation energy changes abruptly at a certain temperature from a substantially large value to nearly zero with decreasing temperature. An electronic process such as a tunneling mechanism may be playing a role in determining the conductivity at the low temperature.

Comparing these results, we may conclude that the most dominant processes in the semiconductivity of the doped poly(3BCMU) are the activation of charge carriers, i.e., free electrons and/or holes from dopant iodines to the conjugated backbones, and the transfer of the carriers from one chain to another, presumably by hopping at high temperature and by tunneling at low temperature in the crystalline (ordered) regions and/or in the amorphous regions through dopant iodine ions, although the detailed mechanism is not unknown. A more detailed analysis of the effects of molecular weight and its distribution and the degree of crystallinity on the conductivity of poly(3BCMU) is now in progress in our laboratory.

**Acknowledgment.** We thank Dr. Y. Takahashi of the Department of Macromolecular Science, Osaka University, for his kind help in taking and interpreting the X-ray diffraction patterns of poly(3BCMU) samples.

**Registry No.** Poly[4,6-decadiyne-1,10-diol bis([(*n*-butoxycarbonyl)methyl]urethane)] (homopolymer), 68777-87-7; iodine, 7553-56-2.

## References and Notes

(1) Street, G. B.; Clarke, T. C. "IBM Symposium on Highly Conducting Polymers and Graphite", San Jose, 1979 (*Synth. Met.* 1980, *1*, 99–347).

(2) Park, Y. W.; Druy, M. A.; Chiang, C. K.; MacDiarmid, A. G.; Heeger, A. J.; Shirakawa, H.; Ikeda, S. *J. Polymn. Sci., Polym. Lett. Ed.* **1979**, *17*, 203.

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

(4) Chiang, C. K.; Heeger, A. J.; MacDiarmid, A. G. *Ber. Bunsenges. Phys. Chem.* **1979**, *83*, 107.

(5) Park, Y. W.; Heeger, A. J.; Druy, M. A.; MacDiarmid, A. G. *J. Chem. Phys.* **1980**, *73*, 946.

(6) Shirakawa, H.; Sato, M.; Hamano, A.; Kawakami, S.; Soga, K.; Ikeda, S. *Macromolecules* **1980**, *13*, 457.

(7) Patel, G. N.; Chance, R. R.; Witt, J. D. *J. Chem. Phys.* **1979**, *70*, 4387.

(8) Patel, G. N.; Walsh, E. K. *J. Polym. Sci., Polym. Lett. Ed.* **1979**, *17*, 203.

(9) Wegner, G. *Makromol. Chem.* **1971**, *145*, 85; **1972**, *154*, 35.

(10) Baughman, R. H. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 1511.

(11) Se, K.; Ohnuma, H.; Kotaka, T. *Polym. J.* **1982**, *14*, 895.

(12) Diaconnu, I.; Dumitrescu, S.; Simionescu, C. R. *Eur. Polym. J.* **1980**, *16*, 511.

(13) Patel, G. N. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1979**, *20* (2), 452. Khana, Y. P.; Patel, G. N. *Ibid.* **1979**, *20* (2), 457. Patel, G. N.; Miller, G. G. *J. Macromol. Sci., Phys.* **1981**, *B20*, 111.

(14) Ivin, K. J. "Structural Studies of Macromolecules by Spectroscopic Methods"; Wiley: New York, 1976; Chapter 8.

(15) Baughman, R. H.; Witt, J. D.; Yee, K. C. *J. Chem. Phys.* **1974**, *60*, 4755.

(16) Bloor, B.; Ando, D. J.; Hubble, C. L.; Williams, R. L. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 779.

(17) Eisenberg, A.; King, M. "Ion-Containing Polymers"; Academic Press: New York, 1977.

(18) Lefrant, S.; Lichtmann, L. S.; Temkin, H.; Fitchen, D. B.; Miller, D. C.; Whitfwell, G. E.; Burlitch, J. M. *Solid State Commun.* **1979**, *29*, 191.

(19) For example: McCrum, N. G.; Read, B. E.; Williams, G. "Anelastic and Dielectric Effects in Polymeric Solids"; Wiley: New York, 1967.

(20) Pohan, J. M.; Gibson, H. W.; Bailey, F. C. *J. Polym. Sci., Polym. Lett. Ed.* **1980**, *18*, 447.

(21) Se, K.; Ohnuma, H.; Kotaka, T. *Rep. Prog. Polym. Phys. Jpn.* **1981**, *24*, 209.

(22) Schermann, W.; Wegner, G. *Makromol. Chem.* **1974**, *175*, 667.

(23) Chance, R. R.; Baughman, R. H. *J. Chem. Phys.* **1976**, *64*, 3889.

(24) Lochner, K.; Reimer, B.; Bassler, H. *Chem. Phys. Lett.* **1976**, *41*, 388.

(25) Day, D. R.; Lando, J. B. *J. Appl. Polym. Sci.* **1981**, *26*, 1605.

(26) See, for example: Blythe, A. R. "Electrical Properties of Polymers"; Cambridge University Press: New York, 1979; Chapter 5.

(27) Shirakawa, H.; Ikeda, S. *Synth. Met.* **1980**, *1*, 175. Akaishi, T.; Miyasaka, K.; Ishikawa, K.; Shirakawa, H.; Ikeda, S. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 745.

(28) Sze, S. M. "Physics of Semiconductor Devices"; Wiley: New York, 1969.

(29) MacDiarmid, A. G.; Heeger, A. J. *Synth. Met.* **1979**, *1*, 101.

(30) Fincher, C. R., Jr.; Ozaki, M.; Heeger, A. J.; MacDiarmid, A. G. *Phys. Rev. B* **1979**, *19*, 4140.

(31) Bhattacharjee, H. R.; Prezios, A. F.; Patel, G. N. *J. Chem. Phys.* **1980**, *73*, 1478.