References and Notes

(1) Prager, S.; Tirrell, M. *J. Chem. Phys.*, **1981**, *75*, 5194.
(2) Prager, S.; Adolf, D.; Tirrell, M. *J. Chem. Phys.* **1983**, *78*, 7015.
(3) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1789.
(4) Silberberg, A. *J. Colloid Interface Sci.* **1982**, *90*, 86.
(5) Akcasu, A. Z. *Macromolecules* **1982**, *15*, 1321.
(6) Schmidt, M.; Stockmayer, W.; Mansfield, M. *Macromolecules* **1982**, *15*, 1609.

Urethane-Substituted Poly(diacetylene): Electrical Conductivity of Poly[5,7-dodecadiyne-1,12-diol bis([(*n*-butoxycarbonyl)methyl]urethane)] in Amorphous and Single-Crystalline Forms

HIROSHI OHNUMA, KEIJIRO INOUE, KAZUNORI SE,[1] and TADAO KOTAKA*

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

Received June 1, 1983

This note is concerned with anisotropic electrical conductivities of a single-crystalline form poly(diacetylene). In our previous papers,[2,3] we reported the synthesis, characterization, and mechanical and electrical properties of poly[4,6-decadiyne-1,10-diol bis([(*n*-butoxycarbonyl)methyl]urethane)], which has a highly conjugated poly(ene-yne) backbone with the substituent R = $-(CH_2)_3OCONHCH_2COO(CH_2)_3CH_3$. The polymer abbreviated as poly(3BCMU) is soluble in common organic solvents such as $CHCl_3$. $CHCl_3$-cast films of this polymer exhibited an enhancement of the electrical conductivity by doping with iodine from 10^{-12} to 10^{-5} Ω^{-1} cm^{-1}, although the films were poorly crystalline.[3] Another member of this class of poly(diacetylene)s, poly[5,7-decadiyne-1,12-diol bis([(*n*-butoxycarbonyl)methyl]urethane)], having the substituent R = $-(CH_2)_4OCONHCH_2COO(CH_2)_3CH_3$ [abbreviated as poly(4BCMU)] has an intriguing property. Namely, we can obtain, besides solvent-cast amorphous specimens of this poly(4BCMU), single crystals with fully extended chains by a solid-state polymerization of the monomer single crystals.[4] We prepared $CHCl_3$-cast and single-crystalline form specimens of this polymer and compared their electrical properties in the undoped and iodine-doped states.

Experimental Section

4BCMU monomer was prepared through the following four-step reactions: (i) Addition of 4-chloro-1-butanol to ethyl vinyl ether; (ii) reaction of the ether with sodium acetylide in liquid ammonia to obtain 5-hexyne-1-ol [bp 72 °C (10 torr)];[5] (iii) oxidative coupling of the monoalcohol by Hay's method[6] to obtain 5,7-dodecadiyne-1,10-diol; and finally (iv) reaction of the diol with *n*-butyl isocyanatoacetate to obtain 4BCMU (mp 72 °C).

Needlelike and plateletlike single crystals of 4BCMU monomer (typical sizes = 6 × 1 × 0.2 and 3 × 2 × 0.2 mm^3, respectively) were grown from acetone/hexane solution by slowly evaporating the solvent. Powder-form monomer crystallites were obtained by precipitating the monomer from acetone solution in *n*-hexane. These single-crystalline and powder-form specimens were allowed to polymerize by irradiating them with 48-Mrd ^{60}Co γ-rays in high-vacuum ampules (10^{-5} Torr) at room temperature. Unreacted monomer was extracted with acetone. The polymer conversion determined from the absorbance at 470 nm of the $CHCl_3$ solutions (ϵ_{max} = 17 000 L/(mol·cm)) was 94.4% for single crystals and 74.1% for powder-form samples. This method has been shown to give accurate values for the polymer conversion of poly(4BCMU).[7] Poly(4BCMU) films were obtained by casting the powder-form polymer from $CHCl_3$ solution. Both the single-crystalline and powder-form poly(4BCMU)s showed metallic black-gold luster, while the color of the films was red with metallic brilliancy.

Table I
Characteristics of Poly(4BCMU) Samples in Various Forms

samples	$10^{-3}\cdot M_n{}^a$	$10^{-3}\cdot M_w{}^a$	$M_w/M_n{}^a$	ΔH_t, J g^{-1} 380 K	ΔH_t, J g^{-1} 410 K
powder form	93	623	6.7	18.47	4.77
$CHCl_3$ cast	56	339	6.1	6.25	4.16
single crystal	152	984	6.5	21.39	6.66

[a] Molecular weights based on polystyrene standards.

All the samples were characterized with a gel permeation chromatograph (Model HLC-801A, Toyo Soda Mfg. Co.) by using $CHCl_3$ carrier and polystyrene elution standards. Table I lists the molecular weights M_w and M_n of these samples. The single-crystalline sample has the highest M_w, while the $CHCl_3$-cast specimen the lowest among the samples examined. Presumably, as pointed out by Wenz and Wegner,[8] UV-induced chain scission and/or degradation due to oxygen or impurities in $CHCl_3$ had taken place during the casting and film handling processes.

The samples were tested on a differential scanning calorimeter (DSC Model 8055, Rigaku-Denki Co.) with a heating rate of 10 K min^{-1} to estimate the degree of crystallinity. Color change accompanied by crystalline melting was observed by a micromelting point apparatus (Yanagimoto Seisakusho, Kyoto).

A preliminary X-ray diffraction study was carried out on single crystals by using a cylindrical camera with Cu Kα radiation.[9] The relation between the unit cell and habitus of the crystal was determined by two rotation photographs around the mutually perpendicular axes along the length and width of plateletlike crystals. The fiber (*c*) axis is parallel in the width direction and *b* axis (the side groups) in the thickness direction, and thus, the poly(4BCMU) chains are stacked along the length direction of the crystal.

Conductivity experiments were performed in two-electrode configuration. For $CHCl_3$-cast films, two platinum wires were connected to a specimen (usually 9 × 3 × 0.15 mm^3 size) with carbon black containing conductive paste (Dotite XC-12, Fujikura Kasei Co.). On the other hand, single-crystalline specimens were prepared as follows: Plateletlike crystals with good quality were selected by examining them with a polarizing microscope. Gold was evaporated onto each specimen to form electrodes so that we could measure the conductivities $\sigma_\parallel$ and $\sigma_\perp$ in the directions parallel to the *c* and *a* axes of the crystal, respectively. The area and distance between the electrodes were measured with a Peacock dial thickness gauge (0.01 mm) and Ocular micrometer attached to a polarizing microscope. Current was measured from a 1.5- or 130-V dry cell with a Keithley 640 electrometer. Doping of specimens with iodine was carried out by exposing specimens to iodine vapor at 10^{-3} Torr at room temperature. The amount of iodine absorbed in the specimen was determined either by weighing or by elemental analysis. The dopant concentration is expressed by *Y* as the number of moles of I_3^- ions per mol of the monomer unit, because dopant iodine is known to exist mostly in I_3^- form at low dopant concentration level from the measurement of Raman spectra.[3]

The current for the doped specimens under both applied voltages of 1.5 and 130 V was almost constant during more than 200 h as previously shown in the case of poly(3BCMU).[3] This means that the observed conductivity is mostly due to electronic rather than ionic conduction. However, for the undoped specimens, transient current was observed for a few minutes, which may be attributed to the orientation of polar side groups and/or ionic conduction due to a small amount of impurities. Therefore, the current at 5 min after applying the voltage was used for the calculation of conductivity.

Results and Discussion

In DSC tests, $CHCl_3$ cast films and single-crystalline samples usually exhibit two endothermic peaks at about 380 and 410 K, although the 380 K peak for the former is rather weak. The red color of the former slightly changes its tone at 380 K and, further, to yellow at 410 K, while

0024-9297/84/2217-1285$01.50/0

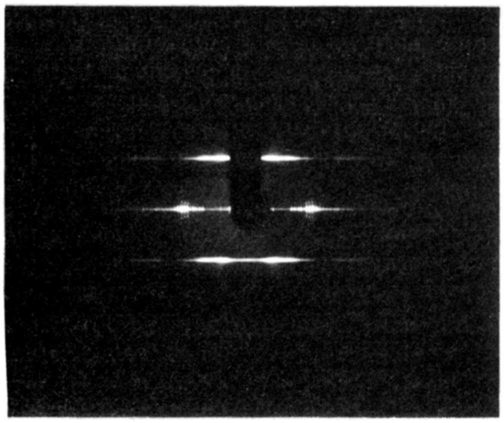


Figure 1. X-ray rotation photograph about the chain axis of poly(4BCMU) single crystal.

the black-purple single crystal turns to red at 380 K and then to yellow at 410 K. According to Patel and Miller,[10] the polymer chains of urethane-substituted soluble poly(diacetylene)s usually assume a planar, flat ribbonlike conformation stabilized by side-by-side hydrogen bondings between the C═O and —NH groups of the adjacent substituents, and these flat ribbons are stacked regularly in the crystallites. The melting peaks accompanying the color changes are due to transitions from planar to nonplanar conformation leading to changes in effective conjugation length of the polymer backbones.[10] These transitions are obviously induced by intermolecular disordering, i.e., the destruction of ribbon stackings at 380 K and by intramolecular melting, i.e., the disruption of hydrogen bondings at 410 K. Table I also lists the values of the enthalpy of transition ΔH_t of these samples estimated from the area under the DSC peaks. From these data, the inter- and intramolecular orderings in $CHCl_3$-cast film are estimated to be decreased to 29% and 62%, respectively, in comparison with those of single-crystalline specimens.

From the preliminary X-ray diffraction analysis,[9] the fiber period (c axis) was found to be 0.488 nm. The subcell dimensions perpendicular to the c axis were $a' = 0.533$ nm and $b' = 5.436$ nm with the assumption of $\gamma' = 90°$. The b' axis is almost parallel to the urethane group direction, and the a' axis perpendicular to both of the main chain and urethane group directions. Figure 1 shows an X-ray rotation photograph about the c axis, in which we see several discrete reflections on the equatorial line and continuous scattering streaks on each layer line. These features suggest that in the crystal the chain backbone has an essentially regular periodic conformation, and the packing of the chains in the a' and b' directions is also periodic, but the mutual level of the chains in the c-axis direction is irregular. A more detailed analysis of the crystal structure is now in progress.[9]

Figure 2 shows temperature dependence of electrical (direct current) conductivity σ for undoped and iodine-doped films. For single crystals, the conductivities along the c axis, $\sigma_\parallel$, and along the a' axis, $\sigma_\perp$, were measured at various dopant concentrations. The values of σ's at 20 °C and the apparent activation energy E_a are compared in Table II. For the doped single crystals of $Y = 0.005$–0.010, the E_a values for $\alpha_\parallel$ and $\sigma_\perp$ were also estimated to be 0.92 and 1.09 eV, respectively. For all samples, the E_a value appears to decrease slightly by doping. Also the E_a value for $\sigma_\parallel$ appears to be slightly smaller than that for $\sigma_\perp$.

Figure 3 compares the conductivities as functions of Y for single crystals with that for $CHCl_3$-cast films at 20 °C. For single crystals, the conductivities rapidly level off at a level of Y by a factor of 100 times lower than that for $CHCl_3$-cast films. The maximum attainable values of $\sigma_\parallel$ and $\sigma_\perp$ are also lower than those for the solvent-cast films. This result is presumably due to the difficulty in effectively doping the highly crystalline specimens. For example, a

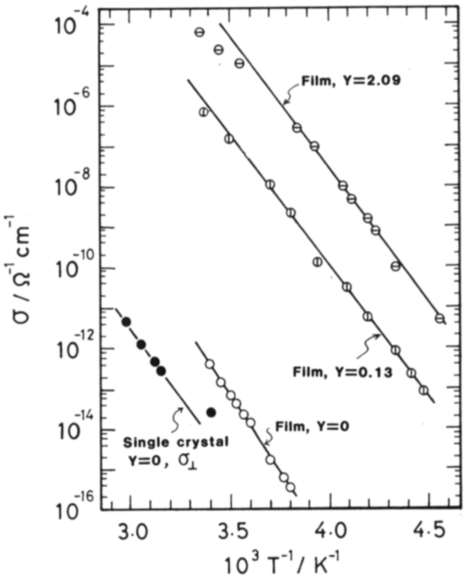


Figure 2. Logarithm of conductivity σ vs. $1/T$ for $CHCl_3$-cast and single-crystalline specimens.

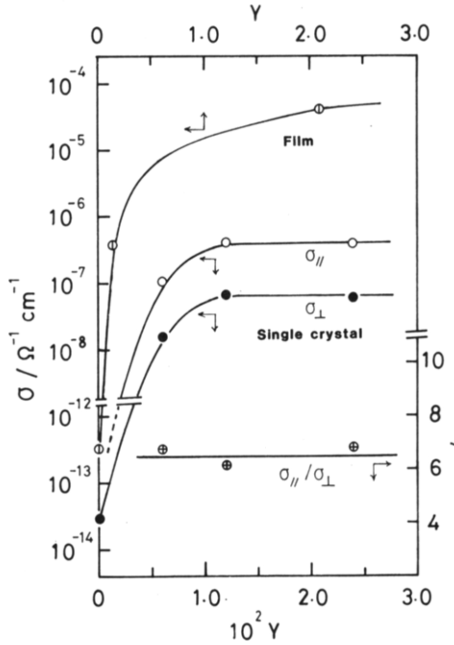


Figure 3. Dependence of conductivities and the ratio $\sigma_\parallel/\sigma_\perp$ on dopant concentration Y for $CHCl_3$-cast and single-crystalline specimens at 20 °C.

Table II
Electrical Conductivities at 20 °C and Their Apparent Activation Energy E_a for $CHCl_3$-Cast Films and Single-Crystalline Specimens with Various Dopant Concentrations

samples	Y	σ, $\Omega^{-1}\,cm^{-1}$	E_a, eV
$CHCl_3$ cast film	0	3.1×10^{-13}	1.48
	0.13	3.6×10^{-7}	1.32
	2.09	4.0×10^{-5}	1.30
single crystal	0	2.8×10^{-14} ($\sigma_\perp$)	1.32[a]
	0.014	4.1×10^{-7} ($\sigma_\parallel$) 6.5×10^{-8} ($\sigma_\perp$)	

[a] Estimated at 50 °C.

cast film could be doped to $Y = 0.13$ after 5-h exposure to iodine, while a single-crystalline specimen gave $Y = 0.026$ even after as long as 50-h exposure. Figure 3 also shows that the anisotropy in the conductivities $\sigma_{\parallel}/\sigma_{\perp}$ of the single crystal is 6.5 ± 0.4 and is independent of Y. This value of anisotropy is comparable to that reported by Schermann and Wegner[11] on dark conductivities of a single-crystalline poly(diacetylene) *p*-toluenesulfonic acid derivative (PDA–TS).

Recently, Siddiqui and Wilson[12] reported that the anisotropy for PDA–TS is $\sigma_{\parallel}/\sigma_{\perp} = 10^3$, which is in sharp contrast with the results obtained by Schermann and Wegner. They pointed out that Schermann and Wegner had used an undesirable arrangement of electrodes on the same face (surface electrodes), in which, when examining currents along the chains, the current must also flow in the directions perpendicular to the chains. This is not the reason for the low anisotropy of poly(4BCMU) single crystal, since we adopted evaporated-gold electrodes covering the edges of the specimen completely. Then, the difference in the anisotropy between poly(4BCMU) and PDA–TS single crystals might have resulted from the difference in their crystal forms. The single crystal of PDA–TS is known to be the most perfect among various poly(diacetylene)s, but poly(4BCMU) single crystal contains the disorder in the mutual level of the chains in the *c*-axis direction as above mentioned.[9] In addition, the nearest-neighbor distance of the chains for poly(4BCMU) is 0.533 nm in the direction of *a′* axis ($\sigma_{\perp}$ direction), which is much shorter than that of 0.75 nm for PDA–TS.[13] This evidence seems to give the reasons for the low anisotropy of poly(4BCMU) single crystal.

From the results given above, we may conclude as follows: (i) The conduction along the polymer chain is prevailing. (ii) The doping takes place mainly in the amorphous regions of the specimens. (iii) The dopant iodine is interacting with and providing charge carriers along the conjugated backbones of poly(4BCMU). (iv) Presumably the dopant may be acting also as bridges for hopping of charge carriers from one chain to another.

Acknowledgment. We thank Dr. Yasuhiro Takahashi of this department for his assistance and helpful discussion on the X-ray structural analysis of poly(4BCMU) single crystals. This work is supported in part by a grant from the Naoji Iwatani Memorial Foundation, which is gratefully acknowledged.

Registry No. 5,7-Dodecadiyne-1,12-diol bis(*n*-butoxycarbonylmethyl)carbamate polymer, 68777-93-5; iodine, 7553-56-2.

References and Notes

(1) Present address: Department of Materials Engineering, The Technological Univeristy of Nagaoka, Nagaoka, Niigata 949-54, Japan.
(2) Se, K.; Ohnuma, H.; Kotaka, T. *Polym. J.* **1982**, *14*, 895.
(3) Se, K.; Ohnuma, H.; Kotaka, T. *Macromolecules*, **1983**, *16*, 1581.
(4) Baughman, R. H.; Yee, K. C. *J. Polym. Sci., Macromol. Rev.* **1978**, *13*, 219.
(5) Brandsma, L. "Preparative Acetylenic Chemistry"; Elsevier: Amsterdam, 1971.
(6) Hay, A. S. *J. Org. Chem.* **1962**, *27*, 3320.
(7) Patel, G. N.; Chance, R. R.; Witt, J. D. *J. Chem. Phys.* **1979**, *70*, 4387.
(8) Wenz, G.; Wegner, G. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 231.
(9) Takahashi, T.; Zakoh, T.; Inoue, K.; Ohnuma, H.; Kotaka, T., unpublished experiments; Preprint of the Kobe Symposium on Polymer Chemistry, Kobe, Japan, July 1983.
(10) Patel, G. N.; Miller, G. G. *J. Macromol. Sci., Phys.* **1981**, *B20*, 111.
(11) Schermann, W.; Wegner, G. *Makromol. Chem.* **1974**, *175*, 667.
(12) Siddiqui, A. S.; Wilson, E. G. *J. Phys. C* **1979**, *12*, 4237.
(13) Kobelt, D.; Paulus, E. F. *Acta Crystallogr.* **1974**, *B30*, 232.

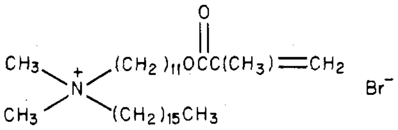
Degree of Polymerization of a Vesicle Membrane[1]

DURGADAS BOLIKAL and STEVEN L. REGEN*

Department of Chemistry, Marquette University, Milwaukee, Wisconsin 53233. *Received September 13, 1983*

Polymerized vesicles are now receiving intense interest as stable models for biological membranes, as carriers of drugs, and as devices for solar energy conversion.[2–9] While considerable attention has focused on the synthetic design, gross morphology, entrapment efficiency, permeability, stability, and dynamic properties of such vesicles, surprisingly little effort has been aimed at characterizing the polymeric nature of the membrane.

In this paper, we report the molecular weight distribution of polymers formed within vesicles of dimethyl-*n*-hexadecyl[11-(methacryloyloxy)undecyl]ammonium bromide (1) via AIBN-induced and photoinduced polymerization.[10]



$$(CH_3)_2\overset{+}{N}[(CH_2)_{11}OC(=O)C(CH_3)=CH_2][(CH_2)_{15}CH_3]\ Br^-$$

Results and Discussion

The preparation of polymerized and nonpolymerized vesicles derived from 1 has been previously described.[2] Characterization was made on the basis of Fourier transform ^1H NMR spectroscopy, turbidity, gel filtration behavior, electron microscopy, stability toward ethanol, and entrapment and permeability toward [^{14}C]sucrose. With use of similar preparative methods, a well-sonicated dispersion of 1 was prepared in distilled water and purified by gel filtration on a Sephadex G-50 column. The yield of vesicles, recovered in the void volume of the column, was ca. 95% (nitrogen analysis). After addition of a free-radical initiator (azobisisobutyronitrile, AIBN) and subsequent heating (80 °C), the resulting dispersion was purified by gel filtration (Sephadex G-50). Nitrogen analysis of the void-volume fraction revealed a 95% recovery of the vesicles. The dispersion was then freeze-dried to give a colorless solid (sample 1). In a second preparation, a similarly prepared aqueous dispersion of 1 was subjected to direct UV irradiation (254 nm, 0.5 h), gel filtered (95% recovery), and freeze-dried to give a colorless solid (sample 2). Both samples 1 and 2 were completely soluble in chloroform (nitrogen analysis) or chloroform containing 0.005 M tetrabutylammonium bromide and were analyzed directly by size-exclusion chromatography.

Elution profiles of samples 1 and 2 in pure chloroform depended significantly on the concentration of injected sample. In sharp contrast, analysis carried out with samples dissolved in chloroform containing 0.005 M tetrabutylammonium bromide yielded chromatograms that were independent of polymer concentration, in the range of 2.0–25.0 mg of polymer per milliliter of solvent. Increasing the salt concentration to 0.05 M had no influence on the elution profile. Retention volumes of polystyrene molecular weight standards (used to derive a universal calibration curve) in chloroform containing 0.05 M tetrabutylammonium bromide were identical with those found in pure chloroform.

Figure 1 reveals a substantial difference in apparent molecular weights between polymers formed from AIBN-initiated and photoinitiated polymerization; the former is substantially higher.[11] Measurement of the intrinsic viscosity of samples 1 and 2 together with these size-exclusion chromatography data and a universal calibration curve

0024-9297/84/2217-1287$01.50/0