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(20) Laboratoire commun CEA-CNRS.

Patrick Keller
Laboratoire Léon Brillouin,[20] CEN-Saclay
91191 Gif-sur-Yvette Cedex, France

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Anisotropic Electrical Conductivity of Oriented Poly(diacetylene) Films

In recent publications,[1-4] we reported a series of studies on urethane-substituted poly(diacetylenes), $=(\mathrm{RC{-}C{\equiv}C{-}RC}){=}_n$, with $\mathrm{R} = (\mathrm{CH_2})_x\mathrm{OCONHCH_2COO}(\mathrm{CH_2})_y\mathrm{CH_3}$ ($x = 2$–4, $y = 1$ or 3), which are soluble in common organic solvents such as $\mathrm{CHCl_3}$.[5] The electrical conductivity of $\mathrm{CHCl_3}$-cast films of poly[4,6-decadiyne-1,10-diol bis([(*n*-butoxycarbonyl)methyl]urethane)] ($x = 3$, $y = 3$), abbreviated as poly(3BCMU), was enhanced from 10^{-12} to 10^{-5} S cm^{-1} by doping with an electron acceptor such as iodine.[2,4] For poly[5,7-dodecadiyne-1,12-diol bis([(*n*-butoxycarbonyl)methyl]urethane)] ($x = 4$, $y = 3$), abbreviated as poly(4BCMU), single crystals with fully extended chains were prepared by solid-state polymerization of its monomer single crystals. The anisotropy in conductivity, defined as the ratio of the conductivity along the chain axis to that along the chain stacking direction, was 6.5 [illegible] 0.4, independent of iodine concentration Y.[3] However, the poly(4BCMU) single crystals absorbed iodine only up to 3×10^{-4} mol %, and correspondingly, the enhancement in electrical conductivity was very low. Since as-cast films can be doped to a large extent, a study on the anisotropic conductivity of oriented poly(diacetylene) films, if available, should enable us to cover much wider ranges of dopant concentration and conductivity and, thus, is interesting to elucidate the condition mechanism of polymers with conjugated backbones. In this communication, we report the electrical conductivity of uniaxially stretched films of poly(3BCMU) as a function of iodine concentration and the degree of orientation. In this context, the anisotropy in conductivity was reported also for stretch-oriented films of polyacetylene[6] and poly(*p*-phenylenevinylene).[7,8]

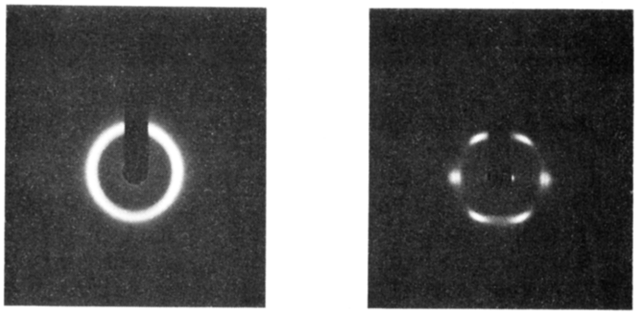
(a) (b)

Figure 1. X-ray diffraction photographs for (a) an as-cast film and (b) a stretched film of λ = 2.9. The X-ray incident beam is perpendicular to the film surface.

Preparation of poly(3BCMU) samples was conducted[1,2] by the method proposed by Patel.[5] In this study, we used a purified poly(3BCMU) sample with number- and weight-average molecular weights 7.7×10^4 and 6.4×10^7, respectively, determined by GPC using polystyrene standards. Poly(3BCMU) films ca. 0.1–0.3 mm thick were cast from 0.7–2.0% (w/v) $\mathrm{CHCl_3}$ solution. Stretched films with various elongation ratios, $\lambda = l/l_0$ (where l and l_0 are the stretched and unstretched length, respectively) were prepared by the following procedures. An as-cast film was placed between two Teflon sheets, gripped by two cramps of an elongation device, and then heated to about 170 °C, near the melting temperature of poly(3BCMU). As soon as the purple-black film changed to yellowish red, it was drawn by the device together with the Teflon sheets and quenched immediately to the room temperature. The color of the film after stretching was green-black with a golden luster, slightly different from the unstretched film. This suggested some changes had taken place in the film morphology. However, the bulk density of the film was almost unchanged (typically 1.165 and 1.169 before and after stretching, respectively).

Wide-angle X-ray measurements were carried out to determine the degree of orientation of the stretched films. Figure 1 shows typical examples of X-ray photographs obtained with a cylindrical camera of radius 35 mm for an as-cast film and a stretched film of λ = 2.9. Both X-ray diffraction patterns show that the films are semicrystalline, but the degree of crystallinity is very low. The diffuse Debye rings observed for the as-cast film change to the diffuse spots for the stretched film. Poly(3BCMU) chains in the solid state are supposed to assume a planar flat ribbonlike conformation stabilized by hydrogen bondings between NH and C=O groups of the neighboring side chains.[9] In the stretched film, such ribbonlike poly(3BCMU) chains are partially oriented along the stretch direction. This was also confirmed from the difference in the intensities of the polarized infrared absorption for the NH stretching band at 3330 cm^{-1}. The spacing calculated from the meridional layer lines is 0.49 nm, corresponding to the length of the repeat unit of the polymer backbone. For stretched films, the intensity distribution of the spots on the equator (i.e., an azimuthal scan) was used to evaluate the orientation function $f = (3\langle\cos^2\alpha\rangle - 1)/2$, where α is the angle between the stretching direction and polymer chain axis.[10] The calculated f values scattered between 0.40 and 0.45 for all the stretched films, although the bulk stretch ratios λ varied from 1.7 to 3.0. This result

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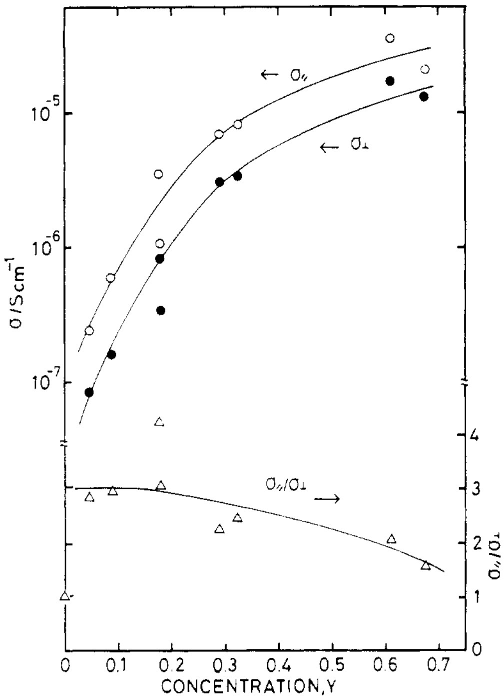

Figure 2. Dependence of the electrical conductivities parallel, $\sigma_\parallel$, and perpendicular, $\sigma_\perp$, to the orientation direction and the anisotropy, $\sigma_\parallel/\sigma_\perp$, on dopant concentration Y for a stretched film of f = 0.44 at 298 K.

Table I
Apparent Activation Energies, E_a, for the Parallel and Perpendicular Conductivities of Stretched Films

direction	Y	f	E_a/eV
parallel	0.05	0.45	1.25
	0.24	0.43	1.18
perpendicular	0.06	0.45	1.21
	0.09	0.45	1.22
	0.24	0.43	1.21

shows that in the films stretched near the melting temperature the crystallites were not completely oriented along the stretch direction but displaced relative to one another.

The electrical conductivity of the stretched films was measured by a two-terminal method. A toluene dispersion of colloidal graphite, Dotite XC-12 (Fujikura Kasei Co.), was used to make electrical contacts to the polymer film. Doping was carried out by exposing the films to iodine vapor in a desiccator evacuated in advance under a vacuum of 10^{-3} torr. The amount of iodine absorbed was determined by the weight increase. The dopant concentration was expressed as the number of moles Y of I_3^- ions per mole of 3BCMU unit, as before.[2-4] Current–voltage characteristics of all the films obeyed Ohm's law.

Figure 2 shows the dependence of the electrical conductivities parallel, $\sigma_\parallel$, and perpendicular, $\sigma_\perp$, to the stretch direction on dopant concentration Y for an oriented film of f = 0.44. Both $\sigma_\parallel$ and $\sigma_\perp$ increase with increasing Y and finally attain the semiconductive range of about 10^{-5} S cm^{-1}, that of the as-cast films.[2] Figure 2 also shows the dependence on Y of the ratio $\sigma_\parallel/\sigma_\perp$, i.e., the anisotropy for the same stretched film. The $\sigma_\parallel/\sigma_\perp$ value is about 3 at low Y and gradually decreases with increasing Y. For the undoped stretched film we found virtually no anisotropy in the conductivity. This result may be an artifact due to the fact that the conductivity of the undoped film is as low as 10^{-12} S cm^{-1} and is apt to be influenced by the surface conduction or the ionic conduction due to impurities in the film. The decrease in the anisotropy with increasing Y may be a consequence that the iodine dopant not only produces charge carriers along the conjugated main chains but also acts as hopping sites, thereby assisting hopping of charge carriers from one chain to another. Accordingly, although the electrical conduction along the conjugated main chains is prevailing in the poly(3BCMU) films, the contribution of lateral conduction might become gradually larger as Y increases, leading to the decline of the anisotropy. The increased dimensionality by doping was reported also for bromine-doped $(SN)_x$ polymers.[10,11]

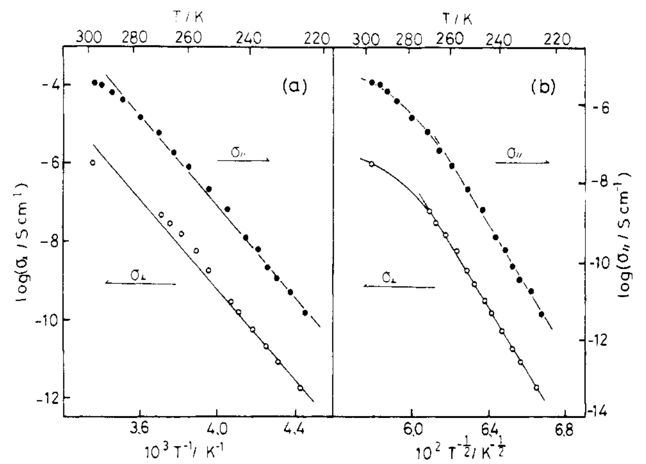

Figure 3. Temperature dependence of $\sigma_\parallel$ and $\sigma_\perp$ for a stretched film of f = 0.43 with Y = 0.24. log $\sigma_\parallel$ or $\sigma_\perp$ is plotted against (a) T^{-1} and (b) $T^{-1/2}$.

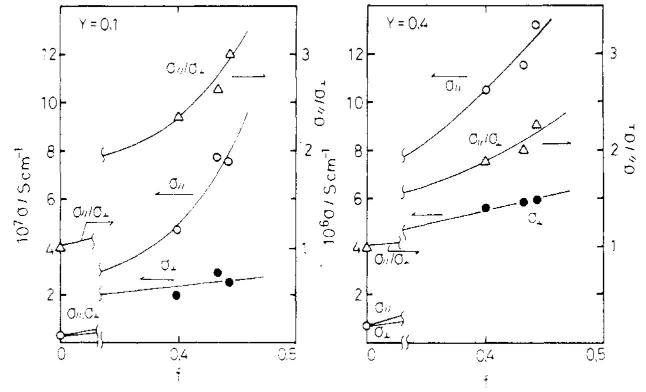

Figure 4. Dependence of $\sigma_\parallel$ and $\sigma_\perp$ on the orientation function f for the films with Y = 0.1 and 0.4 at 298 K.

Figure 3 shows the temperature dependence of $\sigma_\parallel$ and $\sigma_\perp$ for the stretched film of f = 0.43 with Y = 0.24. Both the conductivities decrease with decreasing temperature. The (apparent) activation energy, E_a, was estimated from the slope of the Arrhenius-type plot of log $\sigma_\parallel$ or $\sigma_\perp$ vs. $1/T$, as shown in Figure 3a. Table I shows the E_a values at various Y for the films of f = 0.43 and 0.45. The E_a values are about 1.2 eV and do not differ much between $\sigma_\parallel$ and $\sigma_\perp$. Furthermore, they seem little dependent on either Y or f. This is presumably because, as reported previously,[4] the processes requiring the large activation energy E_a for poly(3BCMU) films appear to be creation of charge carriers along the chains and presumably hopping of the carriers from one chain to another, since the free movement of the charge carriers along the conjugated main chains may be hampered by the chain ends.

To describe the conduction mechanism of disordered semiconductors, Mott[13] proposed the variable-range hopping model, which predicted for the condutivity log $\sigma \sim T^{-1/4}$. The models extended to pseudo-one-dimensional[14] and two-dimensional[15] systems predict log $\sigma \sim T^{-1/2}$ and log $\sigma \sim T^{-1/3}$, respectively.[16] The present data were tested by these theories. The plot according to Mott's original model gave an upward-convex curve and was not fully satisfactory. The plot of log σ vs. $T^{-1/3}$ was also not satisfactory. On the other hand, as shown in Figure 3b, the plot of log σ against $T^{-1/2}$ gives a straight line over a relatively wide range of T below 270 K. This satisfies a requirement for the one-dimensional variable-range hopping model.[14] The departures at high temperatures are also expected from the theory.[14]

Figure 4 shows the dependence of the conductivities on the degree of orientation f for the stretched films with $Y = 0.1$ and 0.4. Unfortunately, the films with the widely varied stretch ratio λ all resulted in a degree of orientation f between 0.40 and 0.45, as mentioned above. Nevertheless, comparing with the data for the unstretched film, we notice that the $\sigma_{\parallel}$ value appears to increase rather rapidly but the $\sigma_{\perp}$ less rapidly with increasing f. As a result, the $\sigma_{\parallel}/\sigma_{\perp}$ value tends to increase with f. The $\sigma_{\parallel}$ may become larger with increasing f due to the conduction along the conjugated chains, while the $\sigma_{\perp}$ is not appreciably affected by the chain orientation, since it may occur mostly through hopping. This conclusion is only tentative since it is derived from data over a limited range of f. More elaborate experiments will be needed before a final conclsuion can be reached.

An increase in $\sigma_{\parallel}$ by stretching was also reported for stretch-oriented films of other conductive polymers,[6-8] while the change in $\sigma_{\perp}$ was somewhat contradictory among them. Park, Shirakawa, and Ikeda[6] reported that the $\sigma_{\perp}$ for polyacetylene films decreases with stretch ratio λ. For poly(p-phenylenevinylene), Gagnon et al.[7] observed a decrease in $\sigma_{\perp}$ with λ, while Murase et al.[8] reported the opposite result. These discrepancies may be attributed to the difference in the morphology and in the crystallinity of the films used in these studies.

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Registry No. Poly(3BCMU), 68777-87-7; I_2, 7553-56-2.

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(17) Present address: Department of Materials Engineering, The Technical University of Nagaoka, Nagaoka, Niigata 949-54, Japan.

Hiroshi Ohnuma, Koh Hasegawa, Kazunori Se,[17] and Tadao Kotaka*

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

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Growth of Large-Area Thin-Film Single Crystals of Poly(diacetylenes)

Poly(diacetylenes) are distinguished from traditional polymeric systems by virtue of their superior crystalline properties. Poly(diacetylenes) are the only known conjugated systems that can be obtained as macroscopic single crystals. As nonlinear optical materials poly(diacetylenes) are competitive with select inorganic systems such as GaAs for many important future applications.[1] Recently, extensive attention has been paid to this unique class of one-dimensional system from the fundamental as well as the technological standpoint,[2-4] and a variety of optical and optoelectronic applications have been proposed.[1,2,5] Specifically for pTS-poly(diacetylene) (see Figure 1), the nonlinear response time in the nonabsorptive region has been estimated to be in the subpicosecond domain, which may have major importance in the emerging ultrafast optical signal processing technologies.[2,6] One critical obstacle in the way of materializing the proposed applications has been the poor quality of the available crystals. The bulk crystals of poly(diacetylenes) that are obtained in the conventional crystallization procedure (such as slow cooling or evaporation from solution) are full of defects such as cracks, grain boundaries, uneven surfaces, stacking faults, etc. and are also produced with uncontrollable dimensions (see Figure 2). In the interest of detailed fundamental optical characterizations as well as practical applications, it is required that the crystals not only are optical quality but also possess some specific desired forms. The most versatile form that would be compatible with the silicon planar technology and also facilitate experimental characterization is the form of a thin-film single crystal with optically flat surfaces. Such thin films on suitable substrates form planar wave guides, which would be ideal for optical signal processing involving nonlinear interactions. Many other important applications would also become amenable if such wave guide structures are fabricated. Additionally, some of the crucial experimental measurements such as the time scale of nonlinear optical response, time-resolved carrier mobility measurements, etc. could be carried out with a great deal of accuracy and facility if good-quality thin-film single crystals were available. Thus, the thin-film crystal growth of diacetylenes is a much longed for research area which may have significant implications in fundamental understanding as well as practical applications of these materials.

At present, thin-film crystal growth of inorganic metal and semiconducting materials (Au, GaAs, Si, etc.) is a very demanding and mature field of research.[7] The basic operational method therein relies on "epitaxy" or lattice matching. Accordingly, a material crystallizes from a mobile phase (melt, solution, or vapor) onto a solid crys-

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