Photobiol. **1980**, *31*, 527. (c) Turro, N. J.; Tanimoto, Y. *Photochem. Photobiol.* **1981**, *34*, 173. (d) Turro, N. J.; Aikawa, M.; Yekta, A. *J. Am. Chem. Soc.* **1979**, *101*, 772. (e) Atik, S.; Nam, M.; Singer, L. *Chem. Phys. Lett.* **1979**, *67*, 75. (f) De Schryver, F. C.; Vandendriessche, J.; Toppet, S.; Demeyer, K.; Boens, N. *Macromolecules* **1982**, *15*, 406.

(8) (a) Schore, N. E.; Turro, N. J. *J. Am. Chem. Soc.* **1975**, *97*, 2488. (b) Chandross, E. A.; Dempster, C. J. *J. Am. Chem. Soc.* **1970**, *92*, 3586.

(9) Ware, W. R. In "Creation and Detection of the Excited State"; Marcel Dekker: New York, 1971; Vol. 1, Part A.

(10) Turro, N. J.; Okubo, T. *J. Am. Chem. Soc.* **1981**, *103*, 7224.

Electrical Conductivity of Urethane-Substituted Poly(diacetylenes): Effect of Substituent Side Groups and Molecular Weights

Kazunori Se,[1] Hiroshi Ohnuma, and Tadao Kotaka*

Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan. *Received October 27, 1983*

ABSTRACT: Direct-current conductivity σ_{dc} of $CHCl_3$-cast films of three urethane-substituted poly(diacetylenes) [poly(*x*ACMU)] was studied as a function of dopant (iodine) concentration Y, temperature T, and molecular weight. The polymers were poly[4,6-decadiyne-1,10-diol bis([(*n*-butoxycarbonyl)methyl]urethane)], poly[4,6-decadiyne-1,10-diol bis([(ethoxycarbonyl)methyl]urethane)], and poly[3,5-octadiyne-1,8-diol bis([(*n*-butoxycarbonyl)methyl]urethane)], abbreviated as poly(3BCMU), poly(3ECMU), and poly(2BCMU), respectively. In all cases, the doping increased the σ_{dc} of $CHCl_3$-cast films, which were poorly crystalline. The substituent side groups affected the conductivity very little. The log σ_{dc} vs. log Y curves showed a break at characteristic dopant concentrations Y_c, which were roughly the same for the three poly(*x*ACMUs). The log σ_{dc} vs. log $1/T$ curves also showed a break at characteristic temperatures T_c. There appeared to be two different conduction regimes above and below T_c. Possible conduction mechanisms were discussed. The dependence of σ_{dc} on molecular weight was investigated for $CHCl_3$-cast films of seven poly(3BCMU) samples. The σ_{dc} at given Y was proportional to the number-average molecular weight M_n. The thermal activation energy E_a of conduction in the region $T > T_c$ was independent of Y but proportional to M_n^{-1}, and the value at $M_n \rightarrow \infty$ was approximately 0.44 eV.

Introduction

In recent years the electrical conduction of fully conjugated linear polymers has been attracting attention as a model of low-dimensional conductors.[2-4] One of such polymers is poly(diacetylenes) having a highly conjugated poly(enyne) backbone with an admixture of the butatriene structure.[5,6]

The solid-state polymerization of diacetylenes ($RC\equiv C—C\equiv CR$) with various substituent groups R has been studied and reviewed by many authors.[7-9] Since some poly(diacetylenes) were obtained as almost perfect single crystals without macroscopic defects, impurities, and dislocations, they have been used as model substances for investigation of the properties of conjugated polymers.[6,10] Usually, poly(diacetylenes) have very low dark conductivities and photoconductivities.[11-13] However, recent findings on the enhancement of electrical conductivity of polyacetylene by doping has stimulated studies of the conductivity of doped poly(diacetylenes).[4,14,15] These findings also motivated us to carry out a series of studies on some poly(diacetylenes) soluble in organic solvents such as $CHCl_3$.[16] The soluble poly(diacetylenes) are appropriate for the studies of the relationship between molecular characteristics and electrical conductivity because they can be easily characterized by dilute solution techniques. The poly(diacetylenes) studied here have the substituent R = $-(CH_2)_xOCONHCH_2COO(CH_2)_yCH_3$ with x = 1–4 and y = 1 or 3. They are referred to as poly(*x*ACMU), standing for the number of methylene groups, and [(*a*lkoxycarbonyl)*m*ethyl]*u*rethane side chain.

We have reported the synthesis, characterization, and mechanical and electrical properties of poly[4,6-decadiyne-1,10-diol bis([(*n*-butoxycarbonyl)methyl]urethane)], abbreviated as poly(3BCMU), for which x = 3 and B = butoxy (y = 3).[17,18] The results of our study of poly(3BCMU)[18] were as follows. (i) The glass transition temperature T_g of $CHCl_3$-cast film is increased by doping with iodine. (ii) The electrical conductivity of the film is largely increased from 10^{-12} to 10^{-5} Ω^{-1} cm^{-1} by doping with iodine. (iii) The conductivity may depend on the molecular weight and its distribution and/or the degree of crystallinity, although the films are poorly crystalline. (iv) The conduction appears to occur mainly through an electronic mechanism; the iodine dopant interacts with and provides charge carriers along the conjugated main chains.

Recently, we also examined $CHCl_3$-cast films and single crystals of poly[5,7-dodecadiyne-1,12-diol bis([(*n*-butoxycarbonyl)methyl]urethane)], abbreviated as poly(4BCMU), for which x = 4 and y = 3.[19] From a preliminary X-ray diffraction analysis on poly(4BCMU) single crystals, the following conclusions were deduced.[19] The fiber period (c axis) and the subcell dimensions perpendicular to the c axis are c = 0.488 nm, a' = 0.533 nm, and b' = 5.436 nm, respectively. The b' axis is almost parallel to the urethane group, and the a' axis is perpendicular to both of the main chain and urethane group directions and hence corresponds to the chain stacking direction. The electrical conductivity of $CHCl_3$-cast films of this polymer was increased from 10^{-13} to 10^{-5} Ω^{-1} cm^{-1} by doping with 2 mol of I_3^- per 4BCMU unit in a manner similar to that of poly(3BCMU). However, a single-crystal specimen could be doped only to a level of 2×10^{-2} mol, and the maximum attainable conductivities along the c axis, $\sigma_{\parallel}$, and along the a' axis, $\sigma_{\perp}$, were 4.1×10^{-7} and 6.5×10^{-8} Ω^{-1} cm^{-1}, re-

0024-9297/84/2217-2126$01.50/0

spectively. The anisotropy $\sigma_{\parallel}/\sigma_{\perp}$ of the single-crystal poly(4BCMU) was 6.5 ± 0.4, independent of the dopant concentration. These results suggested the following additional conclusions: (i) the conduction along the polymer chain is easier than that along the chain stacking direction; (ii) doping takes place to a greater extent in amorphous regions of the specimens than in the crystalline regions.

In order to achieve better understanding of the nature and mechanism of electrical conduction in fully conjugated linear polymers, we have synthesized two other soluble poly(*x*ACMUs): poly[4,6-decadiyne-1,10-diol bis([(ethoxycarbonyl)methyl]urethane)] [poly(3ECMU); *x* = 3 and *y* = 1] and poly[3,5-octadiyne-1,8-diol bis([(*n*-butoxycarbonyl)methyl]urethane)] [poly(2BCMU); *x* = 2 and *y* = 3]. We have investigated the effect of their substituent side groups on the electrical conductivity of $CHCl_3$-cast films in comparison with poly(3BCMU) and poly(4BCMU). In addition, the dependence of electrical conductivity on molecular weight was examined, using $CHCl_3$-cast films of seven poly(3BCMU) samples with different molecular weights. The results are reported in this article.

Experimental Section

Materials. 4-Pentyn-1-ol was synthesized by the reaction reported previously.[17] 3-Butyn-2-ol was obtained from Tokyo Kasei Co., Ltd., Tokyo, Japan. The precursors 4,6-decadiyne-1,10-diol and 3,5-octadiyne-1,8-diol were prepared by Hay's method of oxidative coupling[20] of 4-pentyn-1-ol and 3-butyn-1-ol, respectively. The diacetylene diols were allowed to react with either *n*-butyl isocyanatoacetate or ethyl isocyanatoacetate in purified THF using triethylamine and dibutyltin di-2-ethylhexanoate as catalysts to obtain 3BCMU, 2BCMU, and 3ECMU monomers. The structures of the monomers were confirmed by IR, NMR, DSC, and elemental analysis. Poly(*x*ACMUs) were obtained by solid-state polymerization, exposing the respective powdered monomers to ^{60}Co γ-ray irradiation. The polymer powders were purified by extracting unreacted monomers with acetone.

The purified poly(*x*ACMUs) were cast from 2% (w/v) $CHCl_3$ solution into films about 0.2 mm thick. The solvent was allowed to evaporate slowly at room temperature over a period of 80 h. The films obtained showed metallic black-gold luster for poly(3BCMU), metallic black-purple luster for poly(3ECMU), and metallic black-red luster for poly(2BCMU).

Doping with Iodine. Poly(*x*ACMU) films were doped with iodine by exposing them to iodine vapor; this doping method is referred to as the vapor method. The procedure has been described elsewhere.[18] The amount of iodine absorbed by the specimen was determined by weighing. For poly(3BCMU), doping was also carried out by mixing the polymer with iodine in $CHCl_3$, followed by evaporating the solvent to obtain doped films. This doping technique is referred to as the solution method. The amount of dopant in the film was calculated from the initial amounts of the two components and was corrected for sublimation during casting by comparing the difference in weights of the film and the polymer plus iodine in the initial solution. The dopant concentration Y was expressed as the number of moles of I_3^- ion per 1 mol of the diacetylene monomer unit because I_3^- appeared to be the most likely dopant species.[18] Doped films are designated as poly[xACMU$(I_3)_Y$].

Methods. Dynamic mechanical measurements were made on a Rheovibron DDV-II (Toyo-Baldwin Co.) at 110 Hz. Differential scanning calorimetry was carried out on a DSC apparatus (Rigaku Denki Co., Model 8055) with a heating rate of 10 K min^{-1}.

The direct current (dc) conductivity, σ_{dc}, was measured by a four-terminal method usually with a film of 20 × 5 × 0.2 mm^3 size or a parallel-plate electrode with guarding (the area of electrode was 1–2 cm^2 and the film thickness was 0.2 mm). Electrodes were made on each film by painting carbon-black conductive paste (Dotite XC-12, Fujikura Kasei Co.), and by connecting platinum wires to them. In each measurement, a specimen with the electrodes was sealed in a glass cell or a brass container[21] filled with helium. The temperature was measured with a copper–constantan thermocouple placed close to the specimen. Currents were measured under an applied voltage between 1 and 130 V with a Keithley 640 electrometer. The procedures are described elsewhere.[18,19]

Table I
Molecular Characteristics of Poly(*x*ACMU) Powders Prepared at 45-Mrd Dose[a]

samples	$10^{-6}M_n$	$10^{-6}M_w$	M_w/M_n
poly(3BCMU)	0.077	0.97	12
poly(3ECMU)	0.10	1.00	10
poly(2BCMU)	0.066	0.89	13

[a] Molecular weights based on polystyrene standards.

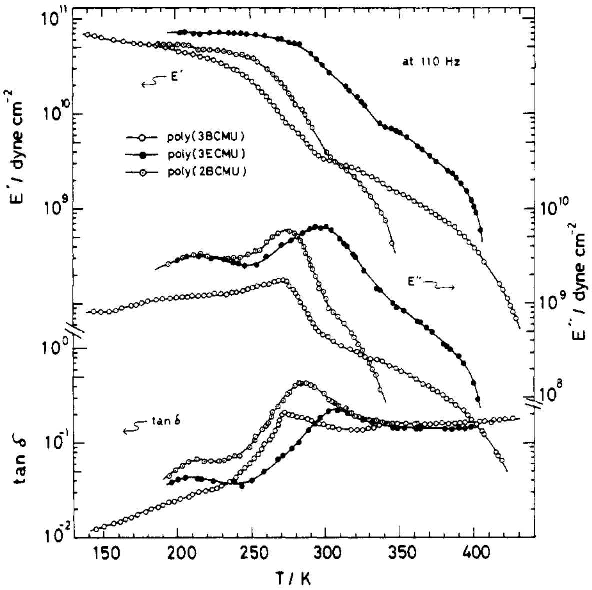

Figure 1. Temperature dependence of storage Young's moduli E', loss moduli E'', and tan δ at 110 Hz for $CHCl_3$-cast films of poly(*x*ACMUs).

Results and Discussion

Dynamic Mechanical Properties and Differential Scanning Calorimetry (DSC). Table I shows molecular characteristics of poly(*x*ACMU) samples obtained by irradiating the monomers with ^{60}Co γ-rays at about 45-Mrd dose. Dynamic mechanical measurements were carried out on $CHCl_3$-cast films of these samples. Figure 1 shows temperature dependences of storage Young's moduli, E', loss moduli, E'', and tan δ of the three poly(*x*ACMU) samples. These results resemble those of common semicrystalline polymers. The loss maximum temperatures T_{max} corresponding to the glass transition temperatures T_g for poly(3BCMU), poly(3ECMU), and poly(2BCMU) are about 270, 295, and 273 K, respectively. Poly(3BCMU) and poly(3ECMU) films began to flow at about 420 K and poly(2BCMU) film at about 360 K. For poly(3BCMU)[18] and poly(4BCMU),[19] the DSC thermograms of as-polymerized powder and/or single-crystal specimens usually exhibited two endothermic peaks, while those of the $CHCl_3$-cast specimens exhibited only one peak corresponding to the high-temperature peak of the former. Figure 2 shows DSC thermograms of $CHCl_3$-cast films of poly(3BCMU), poly(3ECMU), and poly(2BCMU). Only one endothermic peak, tailing to lower temperature, is observed for all the films. The melting temperatures determined from the endothermic peaks of the thermograms were 440, 445, and 398 K for poly(3BCMU), poly(3ECMU), and poly(2BCMU), respectively. These values correspond to those of the high-temperature peaks of the powder form or single-crystal specimens. Figure 2 also shows the enthalpy of fusion, ΔH_f, calculated from the areas under the

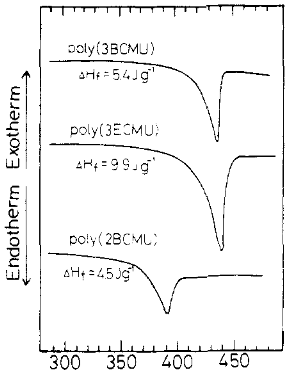

Figure 2. DSC thermograms of $CHCl_3$-cast films of poly(xACMUs).

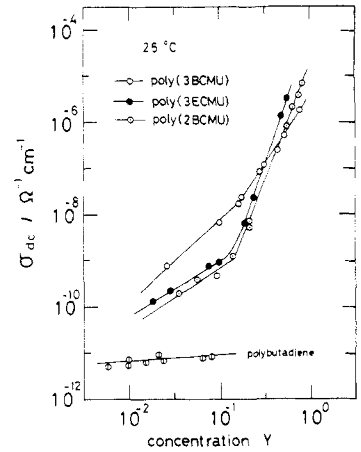

Figure 3. Dc conductivity of poly(xACMU) and polybutadiene films as a function of dopant concentration Y.

melting peaks. These values are very small in comparison with ΔH_f = 28.5 J g^{-1} of the corresponding peak of poly(3BCMU) powder specimens.[18]

Patel and Miller[22] assigned the two endothermic peaks of powder and/or single-crystal specimens to the destruction of intermolecular and intramolecular ordering (from the low-temperature side). They also suggested that the intramolecular ordering is reinforced by the intramolecular hydrogen bonding between the C=O and N—H groups of the adjacent side chains, and that poly(xACMU) chains assume a planar flat ribbonlike conformation in the solid state. The flat ribbons are stacked to form intermolecular ordering. Then, the absence of the low-temperature peak and the small ΔH_f value of the high-temperature peak for the $CHCl_3$-cast specimens imply that the degrees of the inter- and intramolecular orderings are very low. These results coincide with the previous result[18] that the degrees of crystallinity (in terms of both inter- and intramolecular ordering) of $CHCl_3$-cast films of poly(3BCMU) and poly(4BCMU) are usually very low.

Electrical Conductivity of Poly(xACMUs). Figure 3 shows the dependence of dc conductivity, σ_{dc}, at 25 °C on dopant concentration Y for iodine-doped poly(xACMU) and polybutadiene films. The doping was carried out by the vapor method. The σ_{dc} of poly(xACMUs) increases with increasing Y and finally reaches the value of the semiconductive region of 10^{-5}–10^{-6} Ω^{-1} cm^{-1} at Y of about 0.7. The σ_{dc} of polybutadiene is almost constant in the range of Y from 10^{-2} to 10^{-1}. These results suggest that the conjugated main chains of poly(xACMUs) strongly contribute to their high σ_{dc}. As reported previously for a doped poly(3BCMU) sample,[18] the current through a doped film under constant voltage did not change over more than 200 h, and the total amount of the transported charge during the period was 100 times larger than that of iodine (assumed in the form of I_3^-) absorbed by the film. Probably, iodine ions are not acting merely as ionic carriers but also as electron acceptors, thereby producing holes along the conjugated chains.

As seen in Figure 3, the log σ_{dc} vs. log Y curves comprise two straight lines with a break at a characteristic dopant concentration, Y_c, for each poly(xACMU). The Y_c appears to be nearly the same for the three poly(xACMUs). The two lines may be represented approximately by $\sigma_{dc}(Y) = AY^a$ with A and a being empirical parameters depending on the polymer species. The values of a for poly(3BCMU), poly(3ECMU), and poly(2BCMU) films are 1.8, 1.3, and 1.2 in the region of $Y < Y_c$, and 3.9, 4.8, and 5.7 in the region of $Y > Y_c$, respectively. If iodine molecules were acting merely as ionic carriers, a should be directly proportional to Y. However, since the values of a are always greater than 1, the iodine dopant must be interacting with the conjugated main chains of poly(xACMU) to produce charge carriers along the chains.

A possible explanation for Y_c is that vapor-phase doping is inhomogeneous at low dopant concentrations, leading to a heterophase structure composed of doped conducting and undoped insulating domains. In the region $Y > Y_c$, the doped domains may join to make a continuous semiconductive phase.

Another possibility is that iodine molecules diffusing into the film are absorbed first by urethane groups and only a fraction of them act as effective dopants at low dopant concentrations. These speculations are consistent with the result that the values of Y_c are roughly the same for all the samples.

Table II
Dc Conductivities of Poly(3BCMU) Films Doped by the Solution Method

specimen	$\sigma_{dc}^S/(\Omega^{-1}\ cm^{-1})$	$\sigma_{dc}^S/\sigma_{dc}^V$
poly[3BCMU$(I_3)_{0.032}$]	5.2×10^{-7}	1×10^3
poly[3BCMU$(I_3)_{0.23}$]	2.9×10^{-6}	2×10
poly[3BCMU$(I_3)_{0.81}$]	2.6×10^{-6}	2×10^{-1}

Table II shows the conductivity, σ_{dc}^S, of poly(3BCMU)/0.09 Mrd A films doped by the solution method, and the ratio, $\sigma_{dc}^S/\sigma_{dc}^V$, to that of the vapor-doped films, σ_{dc}^V. At $Y = 0.032$, σ_{dc}^S is larger than σ_{dc}^V by three orders of magnitude, and at $Y = 0.23$ by a factor of 20. This result implies that solution doping proceeds rather inhomogeneously even at low dopant concentrations. On the other hand, at $Y = 0.81$ σ_{dc}^S is smaller than σ_{dc}^V by one order of magnitude. At this high dopant concentration, we observed that iodine molecules separated from the polymer during solvent evaporation and deposited on the surface of the film. Obviously, the conductivity of doped poly(xACMU) films depends on the effective concentration of iodine complexed with conjugated backbones and not on the overall quantity absorbed by the specimen. Our attempts to determine the concentration and the distribution of effective dopants have not yet succeeded and are continuing.

Figure 4 shows the temperature dependence of σ_{dc} for iodine-doped poly(xACMU) films. For comparison, the data for undoped poly(3BCMU) are also shown. The values of σ_{dc} first decrease rapidly with decreasing temperature and then become constant or decrease only slightly below certain characteristic temperatures, T_c.

Such a sharp break in the temperature-dependence curves may possibly be an artifact in the equipment due to its incapability of dealing with high-impedance samples.

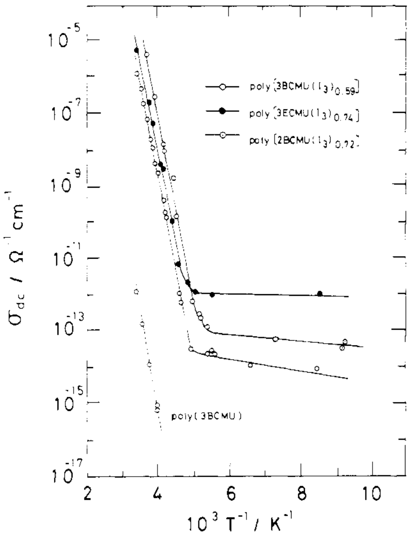

Figure 4. Temperature dependence of dc conductivity σ_{dc} for iodine-doped poly(*x*ACMU) and undoped poly(3BCMU) films.

However, this possibility is unlikely for the following reasons. In our typical low-temperature experiments, we employed specimens (with a conductivity of roughly 10^{-14} Ω^{-1} cm^{-1}) with about 1-cm^2 electrode area and 0.2 mm thick and confirmed that the Ohm's law was obeyed under the applied voltage of 1–130 V. The current through the specimen was approximately 10^{-12}–10^{-10} A. These values are certainly above the sensitivity limit (about 10^{-15} A) of the high-performance electrometer employed in this study.

Additional evidence is that similar changes in the temperature dependence have been observed in the alternating current (ac) conduction σ_{ac} of doped poly(3BCMU) films measured with a transformer bridge at four frequencies of 0.1, 1, 10, and 100 kHz. The values of σ_{ac} at fixed temperatures extrapolated to zero frequency reached those of σ_{dc}.[18]

A common feature of ionic conduction in polymers is a change in temperature dependence of conduction as the temperature is decreased through the glass transition temperature T_g.[23,24] However, this is not the case for the poly(*x*ACMU) films. The values of T_c for the doped poly(*x*ACMUs) are much lower than the values of T_g estimated from dynamic mechanical measurements.

From the slope of the plots of log σ_{dc} vs. $1/T$ above T_c, we estimated the thermal activation energy E_a as 1.07 eV for poly(3BCMU), 0.98 eV for poly(3ECMU), and 0.99 eV for poly(2BCMU). The values of E_a are not significantly different among the different polymer species. The values of E_a for the undoped films are also nearly the same as those of the doped films, although the conductivities of the former are much smaller than those of the latter. The dopant appears to have a significant effect on σ_{dc}, but little on E_a.

In the low-temperature region, the E_a is 0.33, 0.0085, and 0.019 eV for the iodine-doped poly(3BCMU), poly(3ECMU), and poly(2BCMU) specimens, respectively. The σ_{dc} of undoped films in the low-temperature region was too small to be measured accurately. Thus, the data are not shown in Figure 4.

The temperature dependence of σ_{dc} for poly(*x*ACMUs) suggests that two independent conduction regimes might exist above and below T_c. In the high-temperature region, the conduction mechanism might be governed by a thermally activated process in which both the number and the mobility of charge carriers increase with temperature. In the low-temperature region, an electronic process such as tunneling or variable-range hopping over low barriers close to the Fermi level might be prevailing. A similar temperature-dependence behavior of σ_{dc} has been reported for poly(phenylacetylene) films by Bhatt et al.[25] They also showed that T_c is independent of the dopant concentration Y within experimental error.

Table III
Molecular Characteristics and Heat of Fusion, ΔH_f, for $CHCl_3$-Cast Poly(3BCMU) Films

poly(3BCMU)[a]	$10^{-6}M_n$	$10^{-6}M_w$	M_w/M_n	ΔH_f/(J g^{-1})
0.09 Mrd A	0.23	1.38	5.8	11.5
0.09 Mrd B	0.15	0.87	5.6	
0.09 Mrd C	0.071	0.63	8.8	10.9
0.6 Mrd[b]	0.10	0.58	5.6	12.1
15 Mrd[b]	0.044	0.73	16	10.9
45 Mrd A	0.039	2.3	58	10.9
45 Mrd B	0.020	0.41	20	5.0

[a] A, B, and C for poly(3BCMU) polymerized at the same total dose designate samples of different polymerization batches and/or different casting history. [b] These two samples are the polymer listed in Table I.

The temperature dependence of σ_{dc} for the various poly(*x*ACMU) films is qualitatively similar. This result suggests that the electrical conduction is mainly due to the conjugated main chains of poly(*x*ACMU), and the substituent side groups affect the conductivity relatively little, presumably through their influence on the planarity of the chain backbones.

Molecular Weight Dependence of Conductivity. The conductivity of doped poly(*x*ACMU) films may also depend in a complicated manner on various structural parameters of the films, including the degree of crystallinity and the molecular weight and its distribution.

In order to study the effects of molecular weight on electrical conductivity, we prepared poly(3BCMU) powder samples with different molecular weights by adjusting the total dose of ^{60}Co γ-rays in the solid-state polymerization because the total dose has been found to affect not only the conversion to polymer but also the molecular weight and its distribution.[18]

We also found that the molecular weights of $CHCl_3$-cast films are always lower than those of the corresponding powder specimens, and the molecular weights of powder and solvent-cast specimens decrease rather slowly on aging. The observed decrease in molecular weight on aging may have resulted from UV-induced chain scission and/or degradation due to oxygen or impurities in the $CHCl_3$. In fact, photoinduced random scission of poly(diacetylene) chains in solution has been reported for poly[5,7-dodecadiyne-1,12-diol bis(*p*-toluenesulfonate)] by Wenz and Wegner.[26] Recently, Patel et al.[27] reported that the blue-colored poly(3BCMU) on filter paper decolorized in seconds on exposure to ozone at 2 ppm concentration. This result was attributed to destruction of the conjugated backbones, and the authors suggested the use of poly(*x*ACMUs) as ozone indicators and dosimeters.[27] Therefore, when some previously made solvent-cast films were used for conductivity measurements, we redissolved them in $CHCl_3$ and redetermined the molecular weights by GPC. Table III shows molecular weight data including these redetermined values, together with the values of ΔH_f estimated from DSC measurements on these films. The values of ΔH_f are almost the same except for that of poly(3BCMU)/45 Mrd B film. Therefore, it can be concluded that there is little difference in the degree of molecular ordering in the films.

Figure 5 shows the dependence of σ_{dc} on Y at 18 °C for iodine-doped films of the seven poly(3BCMU) samples. Doping was carried out by the vapor method. Obviously, the values of σ_{dc} at a given Y are different for samples of

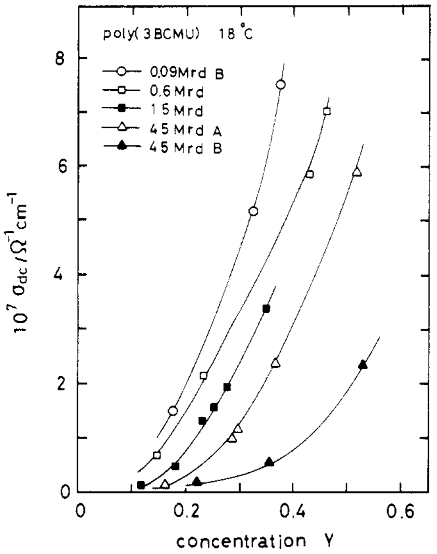

Figure 5. Dopant concentration dependence of dc conductivity for typical iodine-doped poly(3BCMU) films with different molecular weights and molecular weight distribution at 18 °C.

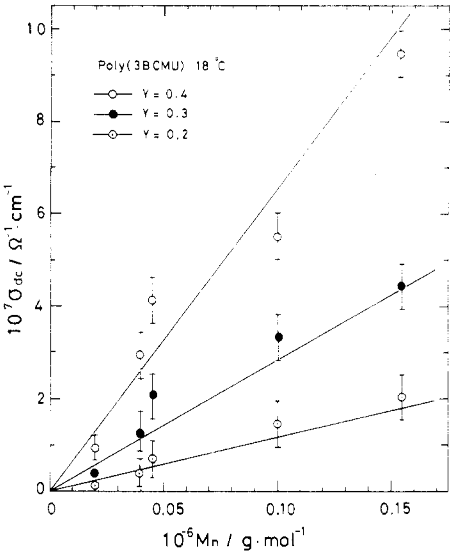

Figure 6. Dependence of dc conductivity on M_n for poly(3BCMU) films at three different dopant concentrations of $Y = 0.2$, 0.3, and 0.4.

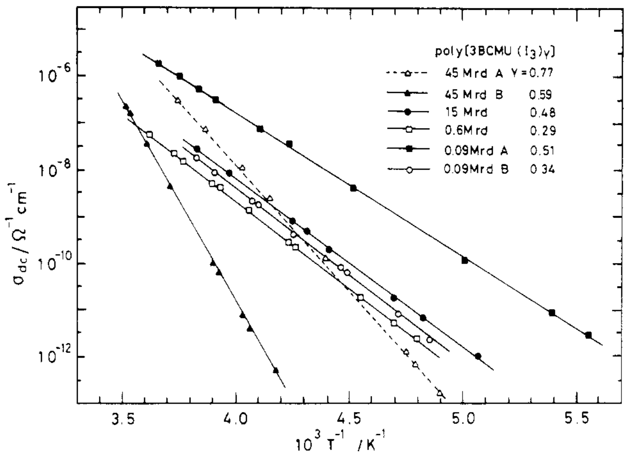

Figure 7. Temperature dependence of dc conductivity for iodine-doped poly(3BCMU) films.

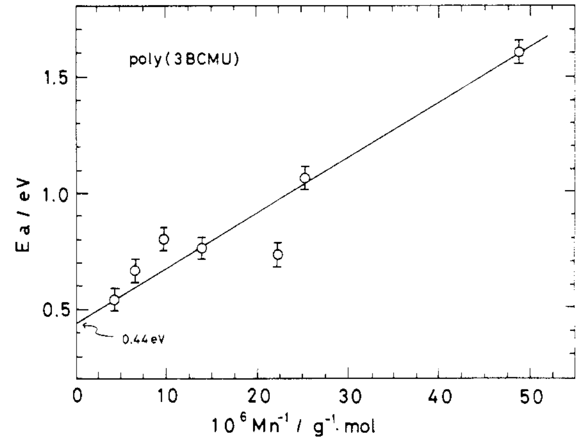

Figure 8. Dependence of activation energy E_a on number-average molecular weight M_n of poly(3BCMU) films.

different molecular weights. This result may be the first evidence that demonstrates the molecular weight dependence of σ_{dc} in conducting polymers. No correlation was found between σ_{dc} and M_w at a given Y, but a good correlation was found between σ_{dc} and M_n. Figure 6 shows that σ_{dc} increases linearly with increasing M_n for each value of Y. The σ_{dc} appears to extrapolate to zero at $M_n = 0$. If the migration of dopant ions is the main cause of the conduction, σ_{dc} cannot depend on the molecular weight. Presumably, electrons or holes in the conjugated backbones are dominant charge carriers. The migration of electrons and/or holes may be delayed at the chain ends. Therefore, the resistivity is proportional to the number of chain ends, and σ_{dc} is directly proportional to M_n rather than to M_w.

Figure 7 shows the temperature dependence of σ_{dc} for iodine-doped films of poly(3BCMUs) in the region $T > T_c$. All the films showed the same temperature dependence before and after doping, although the curves for undoped specimens are not shown. A typical example is shown for undoped and doped films of poly(3BCMU) in Figure 4. The activation energy E_a, determined from the Arrhenius plots, does not depend on Y but depends on the molecular weight of the films.

Figure 8 shows the activation energy E_a plotted against M_n^{-1}. The value of E_a decreases with decreasing M_n^{-1}, and extrapolates to 0.44 eV for infinitely large M_n. This value might correspond to the energy needed to produce an electron or a hole in the conjugated backbone of the polymer from the dopant iodine and for transporting it along a chain of infinite molecular weight. In a chain with a finite molecular weight, presumably the chain ends act as localized trap sites and provide a barrier for hopping of charge carriers to another chain.

Acknowledgment. This work was supported in part by a Grant from the Naoji Iwatani Memorial Foundation.

Registry No. Poly(3BCMU), 68777-87-7; poly(3ECMU), 68777-88-8; poly(2BCMU), 75240-46-9; I_2, 7553-56-2.

References and Notes

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

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

(3) Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, CO, 1982, Aug 9–14 (*Mol. Cryst. Liq. Cryst.* **1981**, 77; **1982**, 83).

(4) Baughman, R. H.; Brédas, J. L.; Chance, R. R.; Elsenbaumer, R. L.; Shacklette, L. W. *Chem. Rev.* **1982**, *82*, 209.

(5) Chance, R. R.; Baughman, R. H.; Muller, H.; Eckhardt, C. J. *J. Chem. Phys.* **1977**, *67*, 3616. Chance, R. R.; Patel, G. N.; Witt, J. D. *J. Chem. Phys.* **1979**, *71*, 206.

(6) Bloor, D. In "Recent Advances in the Quantum Theory of Polymers"; André, J.-M., Brédas, J.-L., Delhalle, J., Ladik, J., Leroy, G., Moser, C., Eds.; Springer-Verlag: Berlin, 1980; p 14.

(7) Wegner, G. *Pure Appl. Chem.* **1977**, *49*, 443.

(8) Baughman, R. H.; Yee, K. C. *J. Polym. Sci., Macromol. Rev.* **1978**, *13*, 219.

(9) Enkelman, V. In "Recent Advances in the Quantum Theory of Polymers"; André, J.-M., Brédas, J.-L., Delhalle, J., Ladik, J., Leroy, G., Moser, C., Eds.; Springer-Verlag: Berlin, 1980; p 1.

(10) Baughman, R. H. In "Contemporary Topics in Polymer Science"; Pearce, E. M., Schaefgen, J. R., Eds.; Plenum Press: New York, 1977; Vol. 2, p 205.

(11) Schermann, W.; Wegner, G. *Makromol. Chem.* **1974**, *175*, 667. Wegner, G.; Schermann, W. *Colloid Polym. Sci.* **1974**, *252*, 655.

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

(13) Siddiqui, A. S.; Wilson, E. G. *J. Phys. C* **1979**, *12*, 4237.

(14) Bloor, D.; Hubble, C. L.; Ando, D. J. In "Molecular Metals", NATO Conference Series IV; Hatfield, W., Ed.; Plenum Press: New York, 1979; p 243.

(15) Seiferheld, U.; Bassler, H. *Solid State Commun.* **1983**, *47*, 391.

(16) Patel, G. N. *Polym. Prep. (Am. Chem. Soc., Div. Polym. Chem.)* **1978**, *19*, 154; Patel, G. N.; Walsh, E. K. *J. Polym. Sci., Lett. Ed.* **1979**, *17*, 203. Patel, G. N. *J. Chem. Phys.* **1979**, *70*, 4387.

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

(18) Se, K.; Ohnuma, H.; Kotaka, T. *Macromolecules* **1983**, *16*, 1581.

(19) Ohnuma, H.; Inoue, K.; Se, K.; Kotaka, T. *Macromolecules* **1984**, *17*, 1285.

(20) Hay, A. S. *J. Org. Chem.* **1962**, *27*, 3320.

(21) Adachi, K.; Hirose, Y.; Ishida, Y. *J. Polym. Sci.* **1975**, *13*, 737.

(22) Patel, G. N.; Miller, G. G. *J. Macromol. Sci.-Phys.* **1981**, *B20*, 111.

(23) Saito, S.; Sasabe, H.; Nakajima, T.; Yada, K. *J. Polym. Sci., Part A-2* **1968**, *6*, 1297.

(24) Blythe, A. R. "Electrical Properties of Polymers"; Cambridge University Press: Cambridge, U.K., 1979.

(25) Bhatt, A. P.; Anderson, W. A.; Kang, E. T.; Ehrlich, P. *J. Appl. Phys.* **1983**, *54*, 3973.

(26) Wenz, G.; Wegner, G. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 231.

(27) Patel, G. N.; Lee, L. T. C. *J. Macromol. Sci.-Phys.* **1983**, *B22*, 259.

Local Conformation of Poly(methyl methacrylate) by Intermediate-Angle X-ray Scattering

Saburo Yamaguchi, Hisao Hayashi, Fumiyuki Hamada,* and Akio Nakajima

Department of Polymer Chemistry, Kyoto University, Kyoto 606, Japan.

Received December 15, 1983

ABSTRACT: Local conformations of poly(methyl methacrylate) (PMMA) chains in solution have been investigated by intermediate-angle X-ray scattering. Scattered intensity was measured for atactic and syndiotactic PMMA dissolved in benzene, acetone, and 3-heptanone (Θ-solvent) and placed on an absolute scale with reference to the primary beam intensity. The theoretical scattering functions were also calculated by use of the rotational isomeric state scheme based on the conformation energies calculated by Sundararajan and Flory. All atoms effective to X-ray scattering were incorporated in the calculations. The effect of the electron density of the solvent was also taken into account but found to have no major influence on the scattering curves. Although the theoretical scattering functions based on the ordinary two-state scheme can reproduce major features of the experimental scattering functions, quantitative agreement was inadequate. Adoption of an increased number of rotational isomeric states (14-state scheme) was found to fail in reducing this discrepancy. In an attempt at readjusting the molecular parameters in favor of the accordance between the theory and experiments, considerably better agreement was observed when a larger skeletal bond angle ($\theta' = 53°$) at the dyad was assumed. This readjusted angle, however, seems to be slightly beyond the uncertainty of the conformation energy calculations. Therefore we are led to suspect the existence of specific long-range interactions, which annihilate the simple statistical mechanical treatment, owing to specific characteristics of the chain.

Introduction

The methods[1] of determining overall conformations of polymer chains in solution have fully been established; e.g., the radius of gyration of the polymer chain can be determined by light scattering[2] with accuracy. A vast body of information thereby accumulated provides foundations for comprehensive theories of polymer solutions. On the other hand, little is known about local conformations, or conformations in short bond sequences within polymer chains, despite their importance for elucidating conformation-dependent properties on a molecular level. Scattering of X-rays and neutrons,[3] mean-square dipole moments, and optical anisotropy are known to depend on such local conformations.[4] In particular, intermediate-angle X-ray scattering (IAXS)[4] corresponding to a Bragg spacing of about 5–50 Å has been proven to be sensitive to correlations between the loci of atoms separated by short bond sequences and hence to the local conformations.

The conformation of poly(methyl methacrylate) (PMMA) in solution has been studied by many investigators. Kirste and co-workers[5–7] measured X-ray and neutron scattering from PMMA of different tacticities in solution and in bulk and observed oscillation in the scattering curve at intermediate angles for the syndiotactic chain. They attributed this peculiarity to a helical feature of the local chain conformation based on the calculations of the scattering functions of wormlike chains with persistence of curvature.[8] Yoon and Flory[9,10] also calculated the scattering function of syndiotactic PMMA using a more realistic model based on conformational energy calculations[11] and the rotational isomeric state (RIS) scheme.[12] Whereas their calculation[10] of the neutron scattering function was performed by treating methyl and methylene groups as scattering elements, the X-ray scattering function was calculated with α carbons regarded as the scattering loci. Since the choice of the scattering elements is of crucial importance in the precise calculations of the scattering functions at intermediate angles,[13] it is desirable to calculate the X-ray scattering functions by taking into account all effective atoms explicitly.

In this paper we performed absolute measurements of IAXS by syndiotactic and atactic PMMA in benzene,