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PREPARATION OF A VARIETY OF POLYMERIC CONDUCTORS FROM DIACETYLENES

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Several different structures of conducting polymers have been synthesized from diacetylenes including non-substituted one, i.e. butadiyne (BDy). Semiconducting polymer single crystals were obtained by thermally or γ-ray induced doping-polymerization of diacetylenes, where chemical doping had been made before rigid polymer crystal lattice was formed. Conductivities attained were in the range of $10^{-4\sim-7}$ S/cm, depending on compounds (2,4-hexadiyne-1,6-diol p-toluenesulfonate, 1,6-dicarbazoyl-2,4-hexadiyne etc.) and dopants (I_2, SbF_5, $AgClO_4$, $FeCl_3$, SO_3, etc.). The doping-polymerization method was found to be applicable also for semiconducting thin layer formation. γ-Ray induced post-polymerization of BDy in the solid-state explosively produced a carbon-like polymer with the conductivity of 10^{-2} S/cm, whereas spontaneous polymerization of BDy in solution gave a soluble brownish polymer whose conductivity increased upto 10^{-4} S/cm upon I_2 doping. Oxidative coupling of BDy in solution resulted in a black powdery polymer formation. Conductivity of the poly-yne was improved from $10^{-11}$to 10^{-4}S/cm by I_2 doping. Two kinds of metal containing polymers were obtained by the reaction of BDy with metal halides in basic solution. Upon I_2 doping, conductivities of the peletized BDy-Cu polymers were enhanced upto the order of 10^{1} S/cm. Temperature dependence verified metallic conduction and no metal-insulator transition was observed downto 7K.

INTRODUCTION

Since the dramatic appearance of highly conducting polyacetylene in 1977 (1,2), there has been much effort to find conjugated organic polymers that can be made conducting upon doping with electron donors and acceptors. Highly conducting polymers so far found, however, principally contain double bond character in their conjugation scheme,such as those in polyacetylene, polyphenylene (3), and polypyrrole (4). Only a little has been known for polymers containing triple bond character. Rare example includes a kind of metal coordination polymer, i.e. phenylethynyl copper which has been reported to become highly conducting upon I_2 doping (5). We also have been studying the latter type of conducting polymers, all of which can be obtained from diacetylenes.

Diacetylenes are interesting compounds which take place various types of polymerization. A class of substituted diacetylenes (DA) are well known to give a large single crystals of conjugated polymers by a topochemical polymerization in the solid-state (6) (Fig. 1(a)). The single crystals of poly-DAs are insulators (7) and have not yet been doped successfuly. The reason why they are resistant to chemical doping must be the rigidity of the nearly perfect crystal lattice of the polymers. In fact, poly-DAs with a less perfect crystalline lattice, such as those in multilayers (8), bilayers (9), and some soluble films (10), have been doped with I_2 upto a conductivity of ca. 10^{-6} S/cm. So, in order to get conducting polymer single crystals, we have

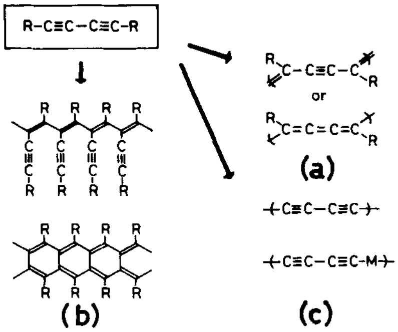

Fig. 1. Polymers of intesests from diacetylenes

tried a doping-polymerization where chemical doping has been made before rigid a polymer crystal lattice is formed.

Non-substituted diacetylene, say butadiyne (BDy) is a especially interesting compound, since it has possibilities to give three different types of interesting polymers shown in Fig. 1. For the structure (b) (11), we might be able to expect stability and metallic conduction (12), and for (c) the heaviest intermolecular interaction of π-electrons. We have investigated the possibilities of the schemes (a) and (c), and obtained highly conducting metal-ynes, together with some other semiconducting polymers.

This report concerns with the successful preparation of semiconducting large polymer single crystals from substituted DAs and a variety of conducting polymers from BDy.

EXPERIMENTAL

DOPING-POLYMERIZATION OF SUBSTITUTED DIACETYLENS

Monomer

2,4-Hexadiyne-1,6-diol p-toluene sulfonate (PTS), dipheylurethane (HDPU), and 1,6-dicarbozoyl-2,4-hexadiyne (DCHD) were synthesized according to the methods in the literatures (13~15). Curde materials were purified by three times of recrystallization. Hexagonal plate-shaped crystals of PTS, larger than 5 mm in size, were grown from acetone solution by slow evaporation at room temperature. Doped single cryst-

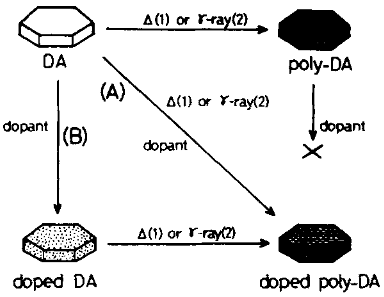

Fig. 2. Doping-polymerization of diacetylenes

als of PTS were grown from the acetone solution which contained definite amounts of dopant and PTS. Since some dopants are humidity sensitive, the solution was kept under Ar atomosphere during crystal growth until dry. The doped crystals had nearly the same shape but were smaller than pure crystals.

Doping-polymerization

In this study, doping during polymerization (A), as well as before polymerization (B), was examined. In the case of A, pure crystals were sealed in a glass tube together with definite amounts of dopant under Ar atomosphere and were subjected to thermal polymerization (1) or γ-ray-induced polymerization (2). In the case of B, doped PTS crystals were sealed and polymerized. Thus, four different paths of doping polymerization, A-1, A-2, B-1, and B-2, have been investigated, as shown in Fig. 2.

Conductivity Measurement

Conductivity of polymer crystals was measured with single crystals unless otherwise stated: Resistivity along the polymer chain axis was measured by the four-point probe method and was converted into conductivity. Since the resistivity value was found to be affected by humidity and temperature, measurements were taken with the specimen under Ar atomosphere at ca. 20°C. Carbon-filled conductive resins was used for electrical contacts between the Pd wire and the crystals.

CONDUCTING POLYMERS FROM BUTADIYNE

Monomer

BDy was prepared by heating the xylene solution of 2,7-

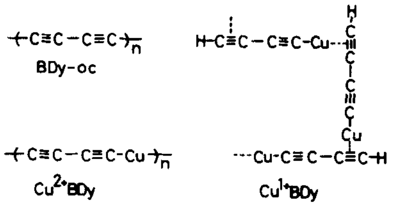

Fig. 3. Basic structures of polymers from butadiyne.

dimethylocta-3,5-diyne-2,7-diol with catalytic amounts of sodium hydroxide (16). The gas evolved was collected in a glass tube with Ar flow, and was stored at -30°C.

Polymerization

Poly-yne (BDy-oc in Fig. 3) was prepared by oxidative coupling of BDy: Into the blue-colored solution of cuprous chloride and tetramethylethylenediamine in dimethylacetamide (DMAc), butadiyne and oxygen were bubbled at room temperature. Immediately after starting of the bubbling, color changed into dark blue and dark brownish powder started to precipitate. The precipitation continued as long as the bubbling continued.

In contrast, when BDy was bubbled into the solution of cuprous chloride in DMAc under Ar atmosphere, the color of the solution changed from pale yellow to red and further to dark brown, and thereafter black precipitate, i.e. Cu^{1+}BDy in Fig. 3, was produced. The precipitation was saturated within the time depending on the amount of cuprous chloride. Cu^{2+}BDy in Fig. 3, also as a black powder, was obtained by bubbling BDy into the ammoniacal methanol solution of cupric chloride. The precipitation was saturated just as in the case of Cu^{1+}BDy. All the precipitates of these three polymers were filtered, washed with aquaous hydrogen chloride, water, aceton, and then dried in vacuo. They were neither soluble (even in strong acids and bases) nor fusible.

Solid-State Polymerization

About one grams of BDy crystals in a glass tube were irradiated by γ-ray at -78°C. After 22.5 Mrad of the irradition, the crystals became dark-brown. When kept at -40°C for post-polymerization, the crystals explosively changed into fine black powders. One the other hand, when BDy crystals with a fourth of molar ratio of iodine was treated under the same condition, dark-brown powders were obtained almost quantitatively without any explosion.

Conductivity Measurements

Conductivity measurements were done with disked samples (12.5 mm in diameter and ca. 0.1 mm in thickness), being made under 60 kg/cm^2 by use of an IR pelletizer. The van der Pauw's method was adopted in a vacuum cell, using gold paste and Pd wire for electrical contacts.

RESULTS AND DISCUSSION

DOPING-POLYMERIZATION OF SUBSTITUTED DIACETYLENES

Using combination of PTS and I_2, feasibility of the above-mentioned four paths of doping-polymerization were first examined. The results are listed in Table 1, where conductivity values are those measured on the original surfaces of single crystals. Quantitative formation of the polymer with the same structure as that in the literature (13) was estimated by its characteristic color, decompositon temperature, and insolubility against the usual organic solvents, and was confirmed by resonance raman spectroscopy (17). All the polymers obtained were the pseudomorphs of their parent monomer crystals and showed golden metallic luster, though they became blackened as the dopants concentration increased.

It is noteworthy that by any of the present four paths, the conductivity of poly-PTS single crystals (originally 2.9×10^{-13} S/cm (7)) is enhanced by 6~9 orders of magnitude upto semiconductor levels. The highest values, on the order of 10^{-4} S/cm, were attained by the path B. In the cases of both the B-1 and B-2, however, conductivities on cleaved surfaces were about one order less than those on the original surfaces, suggesting that the doping and/or dopant distribution is heterogeneous. The heterogeneous distribution of

Table 1 Doping-polymerization of PTS with I_2 via four different paths.

doping method	polymerization type	temp. (°C)	time(hr)	molar ratio (I_2/PTS)	conductivity (S cm^{-1})
A	1	50	72	excess	2.6×10^{-7}
A	1	RT	2400	excess	2.6×10^{-7}
A	2*	RT	120	excess	4.3×10^{-7}
B	1	50	72	0.5	2.2×10^{-10}
B	1	RT	1440	0.5	1.2×10^{-4}
B	2*	RT	120	0.3	5.6×10^{-5}
B	2*	RT	120	0.8	1.6×10^{-4}

* Co^{60} at the dose rate of 1.87×10^{5} rad/hr.

dopants, rich near the surface and less in the middle of crystal was confirmed by X-ray microanalysis.

Fig. 4 shows the effect of the molar ratio of dopants on conductivity. Here, the molar ratio shows the effect of the original solution from which doped monomer crystals were grown. The conductivity increases sharply with increase of the molar ratio until it reaches a plateau at about a ratio of 0.1 and, therafter, the dopant does not affect the conductivity. Because of heterogeneity of doping, it is, at present, difficult to define what precentage of the dopants is actually working in the crystalline lattice.

Some other dopants such as Br_2, SbF_5, $AgClO_4$, $FeCl_3$, and SO_3 were also examined for PTS. The results are listed in Table 2, Br_2 was not suitable since it reacted with the PTS monomer. As far as the path B-2 is concerned, $AgClO_4$ is the best dopant. It caused the increase in conductivity upto 10^{-4} S/cm, and the doped crystal did not change its conduc-

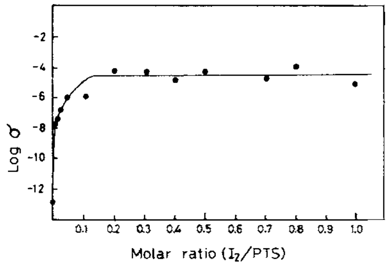

Fig. 4. Effect of molar ratio (I_2/PTS) on conductivity

Table 2. Doping polymerization of PTS with some dopants.

doping·poly-merization*	dopant	molar ratio (dopant/PTS)	conductivity (S cm^{-1})
B-2	SbF_5	0.3	5.6×10^{-6}
B-2	SbF_5	0.5	5.0×10^{-5}
B-2	$AgClO_4$	0.3	1.6×10^{-5}
B-2	$AgClO_4$	0.5	3.3×10^{-4}
B-2	$FeCl_3$	0.2	1.5×10^{-5}
A-2	SO_3	excess	1.9×10^{-4}

* Co^{60} (1.87×10^5 rad/hr) for 120 hr at room temperature.

tivity after six months even under air atmosphere. Only for SO_3 was rather high conductivity attained by the path A. This is because the SO_3 gas has strong power to immerse into PTS crystals.

The present doping-polymerization method used to prepare conducting single crystals has been found to be effective for some other diacetylenes such as DCHD and HDPU. As an example the results for DCHD are listed in Table 3. Conductivity for DCHD did not exceed those for PTS. The present method was also applicable to prepare semiconducting thin layers. For instance, thin layers of doped-DCHD has been obtained as follows. DCHD solutions containg 0.5 molar ratio of I_2 or $AgClO_4$ were spreaded onto glass plate and spinnered to form thin films of crystallites. The plates were irradiated by γ-ray under the same conditions as in Table 3. Conductivities of the polymer films thus obtained were 2.3×10^{-6} and 2.2×10^{-6} S/cm for I_2 and $AgClO_4$, respectively.

CONDUCTING POLYMERS FROM BUTADIYNE

Since Cu^{1+}BDy and Cu^{2+}BDy decomposed explosively by heat-shock or mechanical shock, elementary analysis of the polymers were not reliable. The basic structures of these polymers in Fig. 3 have been estimated from the results of electron spectroscopy for chemical analysis (ESCA) and fourier

Table 3. Doping polymerization of DCHD with some dopants.

doping·poly-merization*	dopant	molar ratio (dopant/ DCHD)	conductivity (S cm^{-1})
undoped	-	-	2.4×10^{-12}
B-2	I_2	0.3	4.0×10^{-8}
B-2	I_2	0.5	5.9×10^{-7}
B-2	SbF_5	0.3	6.6×10^{-6}
B-2	SbF_5	0.5	7.7×10^{-5}
B-2	$AgClO_4$	0.3	2.4×10^{-7}
B-2	$AgClO_4$	0.5	6.7×10^{-6}
B-2	TCNQ	0.5	1.1×10^{-7}
B-2	TCNQ	0.5	1.4×10^{-7}

* Co^{60} (1.87×10^5 rad/hr) for 120 hr at room temperature.

transforming infrared spectroscopy (FTIR). ESCA measurements showed that BDy-oc consisted of only carbon, and Cu^{1+}BDy and Cu^{2+}BDy of carbon and copper in the ratio of 4 : 1. Electron binding energy spectra and Auger trasition spectra of Cu^{1+}BDy and Cu^{2+}BDy revealed that in both polymers copper atoms exist in its monovalent state (double peaks at 931 and 951 eV for the binding energies, and single peak at 388 eV for the Auger transition). It is interesting that even in the polymer Cu^{2+} BDy obtained by use of cupric chloride, copper atoms are in the monovalent state. Although the reason is not clear at present, donation of an electron from diyne orbital to copper orbital may take place. FTIR absorption of triple bonds of these three polymers occured in three different ways; that is, a strong and broad peak at 2180 cm^{-1} for BDy-oc, very shallow diffused peaks between 2200 and 1900 $cm^{-1}$for Cu^{1+}BDy, and clear double peaks at 2100 and 1950 $cm^{-1}$for Cu^{2+}BDy. This means that the electronic state of the triple bonds in these three polymers differs from the polymer to the polymer. In the disk-making process using an IR pelletizer, it was found that when the pressure greater than 100 kg/cm^2 was applied and reduced upto the normal atmosphere, resulting disks of BDy-oc and Cu^{2+}BDy expanded like an elastomer, whereas that of Cu^{1+}BDy did not. The result implies that molecular structures of BDy-oc and Cu^{2+}BDy are similar so that they probably cause some crosslinking under such pressure. The similarity of the structures of the polymers BDy-oc and Cu^{2+}BDy was also supported by the doping behavior mentioned later. By considering these results together with the reported structure of phenylethynyl copper (5), the structures in Fig. 3 are proposed.

When these polymers were kept under air atmosphere at

Table 4. Change in conductivities of the polymers from BDy upon iodine doping

	conductivity ($S\ cm^{-1}$)		I_2(wt%)
	undoped	iodine doped	
BDy-oc	10^{-11}	2.1×10^{-4}	63
Cu^{1+}BDy	10^{-9}	6.3	20
Cu^{2+}BDy	10^{-9}	10.2	42

room temperature, they gradually degradated. IR spectra suggested the formation of small amounts of aromatic rings and carbonyl group as a quinone type. X-ray powder diffraction patterns showed that all these polymers were nearly amorphous.

The conductivity of these polymers, originally in the range of insulators, were largely improved upon iodine doping, as listed in Table 4. It should be noted that the conductivities of Cu^{1+}BDy and Cu^{2+}BDy are enhanced by about 10 orders of magnitude upto metallic conductor level (6.3 and 10.2 S/cm, respectively). Close similarity in the doping behavior of BDy-oc and Cu^{2+}BDy was observed as follows. Amounts of iodine uptake of BDy-oc and Cu^{2+}BDy are greater

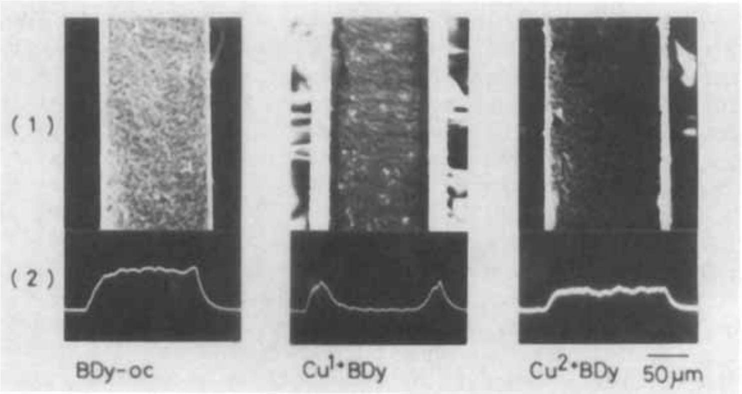

Fig. 5. Distribution of dopants along the cross section of pelletized specimen; (1) scanning electron micrographs, (2) X-ray microanalysis of I_2.

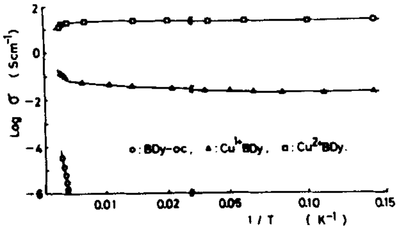

Fig. 6. Temperature dependence of the conductivities of I_2-doped polymers.

than that of Cu^{1+}BDy. Dopant distribution along the cross section of pelletized specimen, examined by X-ray microanalysis, was homogeneous for BDy-oc and Cu^{2+}BDy, whereas heterogeneous for Cu^{1+}BDy (Fig. 5).

Fig. 6 shows the temperature dependence of the conductivity of I_2-doped polymers. It is clear that BDy-oc behaves like a semiconductor with large activation energy of ca. 0.65 eV. Because of reduced pressure in measuring cell, the conductivity of Cu^{1+}BDy at room temperature is already lowered to a tenth of the original value in Table 4. With falling temperature, the conductivity decreases monotonously to ca. 35K and thereafter remains nearly constant downto 7K. Log $[\sigma(T)-\sigma(7K)]$ vs. $T^{-1/4}$ plot of Cu^{1+}BDy become a straight line (Fig. 7), indicating that the temperature dependence is due to the granular disorder (18), and the nature of the I_2 doped Cu^{1+}BDy is metallic. Cu^{2+}BDy behaves like a metal with small negative value of activation energy. It should be emphasized that Cu^{1+}BDy and Cu^{2+}BDy do not undergo a metal-insulator transition downto 7K. Highly conducting polymers containing acetylene moieties and transition metals may suggest the new direction of polymeric conductors.

Fine black powders obtained by solid-state post-polymerization of BDy showed the conductivity of 10^{-2}S/cm in its pelletized state. Doping of I_2 and SO_3 to the pellets hardly improved the conductivity. Dark-brown solids obtained by solid-state doping-polymerization of BDy were like a solid-lubricant so that pellet-making for conductivity measurement was impossible. Both polymers were neither soluble nor crystalline. Further details will be published elsewhere.

When BDy in DMAc was kept at room temperature for a week, spontaneous polymerization occured; the solution became orange-brown and thin brownish films were obtained by slow evaporation. Conductivity of the films was improved from ca. 10^{-13}S/cm to 10^{-4}S/cm by I_2 doping.

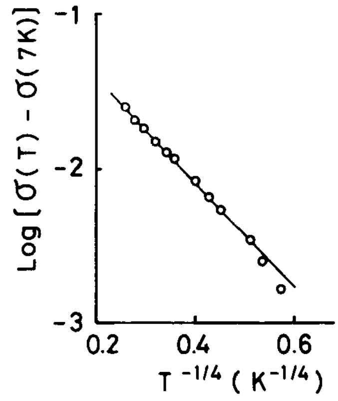

Fig. 7. Log $[\sigma(T)-\sigma(7K)]$ vs. $T^{-1/4}$ plot for the I_2 doped Cu^{1+}BDy.

In conclusion, a variety of conductive polymers have been obtained from DAs and BDy.

REFERENCES

1) H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chiang, and A. J. Heeger, J. Chem. Soc. Chem. Commun., 578 (1977).

2) C. K. Chiang, C. R. Fincher, Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, and A. G. MacDiarmid, Phys. Rev. Lett., 39, 1098 (1977).

3) D. M. Ivory, G. G. Miller, J. M. Sowa, L. W. Shacklette, R. R. Chance, and R. H. Baughman, J. Chem. Phys., 71, 1056 (1979).

4) A. F. Diag, K. K. Kanazawa, and G. P. Gardini, J. Chem. Soc. Chem. Commun., 635 (1979).

5) Y. Okamoto and M. C. Wang, J. Polym. Sci. Polym. Lett. Ed., 18, 249(1980).

6) G. Wegner, "Molecular Metals", E. W. Hatfield Ed., Plenum, New York, 1979, p209.

7) G. Wegner and W. Scherman, Colloid Polym. Sci., 252, 655 (1974).

8) D. Bloor, C. L. Hubble, and D. J. Ando, "Molecular Metals", E. W. Hatfield Ed., Plenum, New York, 1979, p243.

9) D. R. Day and J. B. Lando, J. Appl. Polym. Sci., 26, 1605 (1981).

10) K. Se, H. Ohnuma. and T. Kotaka, Polym. Prepr. Jpn., 31(4), 710 (1982), and references cited therein.

11) a) A. A. Berlin, M. I. Cherkashin, M. G. Chauser, and R. R. Shifrina, Vysokomolek. Soedin., A9, 2219 (1967).
b) R. H. Wiley and J. Y. Lee, J. Macromol. Sci. Chem., A5, 513 (1971).
c) A. W. Snow, Nature, 292, 40 (1981).
d) P. J. Russo and M. M. Labes, J. Chem. Soc. Chem. Commun., 53 (1982).

12) J. L. Bredas, R. R. Chance, and R. H. Baughman, J. Chem. Phys., 76, 3673 (1982).

13) G. Wegner, Makromol. Chem., 145, 85 (1971).

14) G. Wegner, Z. Naturforsch., 24b, 824 (1969).

15) K. C. Yee and R. R. Chance, J. Polym. Sci. Polym. Phys. Ed., 16, 431 (1978).

16) R. J. Tedeschi and A. E. Brown, J. Org. Chem., 29, 2051 (1964).

17) A. J. Melveger and R. H. Baughman, J. Polym. Sci. Polym. Phys. Ed., 11, 603 (1973).

18) P. Sheng and J. Klafter, Phys. Rev., B27, 2583 (1983).