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# Oriented Thin Layer Crystalline Films of Poly(1,4-phenylene)

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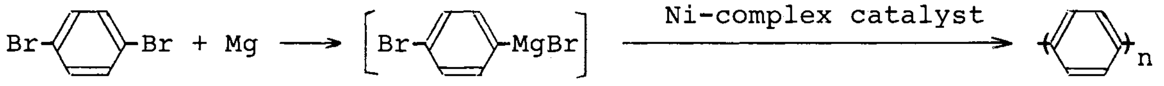
Evaporation of poly(1,4-phenylene) on heated carbon and gold substrates under vacuum affords oriented thin layer crystalline film of the polymer with its c-axis (the polymer chain axis) essentially perpendicular to the surface of the substrates as revealed by electron diffraction method.

$\pi$-Conjugated poly(arylene)s such as poly(1,4-phenylene) and poly(2,5-thienylene) exhibit electrically conducting properties,[1-7] and for further development of science and use of the electrically conducting polymers, more detailed characterization of their structural and electrical properties (e.g., inherent mobility of carrier along the polymer chain) in solid is desired. In order to obtain clear-cut information on the structural and electrical properties, it is desired to obtain oriented crystals or single crystals of poly(arylene)s, if possible. However, their general low solubility has prevented preparation of their single crystal.

We now report preparation of oriented thin layer crystalline films of poly(1,4-phenylene) (PPP) by vacuum evaporation of the sample on substrates and characterization of the crystal structure of PPP in the state of a crystalline thin layer. The source material for the vacuum evaporation was prepared by the following method.[8)]



(1)

As for the preparation method for PPP, there have been reported several methods, however, the method described by Eq. 1 affords the polymer with well-defined linkage between the monomer units. This PPP shows very sharp diffraction peaks in its powder X-ray diffraction pattern and seems to have rigid rod-like structure; similar rigid rod-like structure has been confirmed for poly(2,5-pyridinediyl) prepared by analogous organometallic process.[9)]

Vaporization of PPP from tantalum boat at 250 °C at $10^{-4}$ Pa on KBr, carbon, and gold substrates afforded thin layer film with high mechanical strength. The IR spectrum of PPP deposited on the KBr substrate was essentially the same as that of source PPP. It is reported that PPP (the one prepared according to Eq. 1) with a molecular weight of about 2 000 corresponding to a degree of polymerization of about 26 is sublimable under vacuum.10)

Figure 1 shows the electron diffraction pattern of the PPP film (thickness = ca. 100 nm as determined by multiple beam interfering method) formed on the carbon substrate. If we assume that one 1,4-phenylene unit has 0.43 nm spacing along the polymer chain as roughly estimated from the structure of biphenyl,11) the chain length of PPP with 26 monomer units is calculated as 11.4 nm and the thickness of 100 nm of the PPP thin film corresponds to piling of about 9 layers of molecular PPP if the PPP film is oriented perpendicularly to the substrate.

The electron diffraction pattern shown in Fig. 1 was taken by using electron beam (60 keV corresponding to $\lambda$ of 0.0050 nm) irradiated perpendicularly to the carbon substrate. The PPP thin film on the gold substrate gave rise to essentially the same diffraction pattern. As shown in Fig. 1, the diffraction pattern shows distinct and clear diffraction spots, indicating that the film is constituted of oriented crystals of PPP. All of the observed 86 spots were able to be indexed by assuming orthorhombic crystal system with abc parameters of 0.782 nm, 0.560 nm, and 0.420 nm, respectively.12) Similar abc parameters (a = 0.781 nm, b = 0.553 nm, c = 0.420 nm) have been proposed by several research groups13) based mainly on powder X-ray diffraction method.

Table 1 summarizes the indexation of the spots obtained in Fig. 1.

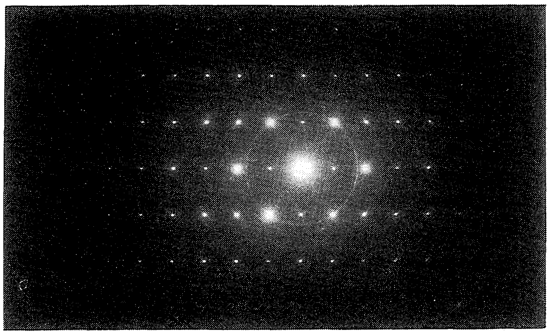


Fig. 1. Electron diffraction pattern of PPP evaporated on carbon substrate. Substrate temperature = 150 °C. Under $10^{-4}$ Pa.

As shown in Table 1, all of 26 observed plane distances calculated from the 86 spots coincide with the calculated values based on the assumed abc parameters in experimental errors, and all the spots are reasonably assigned to the diffraction related to the ab plane of PPP, indicating that the polymer molecules are arranged perpendicularly to the surface of the substrate. No diffraction related to the c-axis (the direction of polymer chain) was observed.

These data shown above not only indicate the formation of oriented crystalline film with the c-axis perpendicular to the surface of the substrate, but also support the crystal data of PPP proposed by other research groups mainly based on powder X-ray diffraction method.13,14) It is interesting that not only the first PPP molecular layer directly contacted with the surface of the substrate but also the PPP molecules in the upper layers are oriented perpendicularly to the surface of the substrate. The PPP film with the good crystallinity and orientation was obtained at the substrate temperature of 150 °C, but at lower temperatures the orientation and crystallinity were not so excellent and at 20 °C only a diffused 5 diffraction spots and three Debye-Scherrer rings were observed. A preliminary study on electron diffraction for poly(2,5-thienylene) (PTh) also showed that evaporated PTh on the surface of carbon and gold substrates formed crystalline thin film with the polymer chain axis perpendicularly to the surface of the substrate, although evaporation of PTh on glass substrate at room temperature seems to afford its thin film with the polymer chain axis rather parallel with the surface of the glass plate due to dipole-dipole interaction between PTh and hydroxy groups of glass.

Table 1. Plane distances estimated from the electron diffraction pattern of the PPP film

| No. | Plane distance/nm | | hkl$^{a)}$ |
|---|---|---|---|
| | observed | calculated$^{a)}$ | |
| 1 | 0.782 | 0.782 | 100 |
| 2 | 0.560 | 0.560 | 010 |
| 3 | 0.455 | 0.455 | 110 |
| 4 | 0.391 | 0.391 | 200 |
| 5 | 0.320 | 0.321 | 210 |
| 6 | 0.280 | 0.280 | 020 |
| 7 | 0.266 | 0.261 | 300 |
| 8 | 0.262 | 0.264 | 120 |
| 9 | 0.241 | 0.237 | 310 |
| 10 | 0.229 | 0.228 | 220 |
| 11 | 0.201 | 0.196 | 400 |
| 12 | 0.194 | 0.191 | 320 |
| 13 | 0.187 | 0.187 | 030 |
| 14 | 0.185 | 0.185 | 410 |
| 15 | 0.180 | 0.182 | 130 |
| 16 | 0.168 | 0.169 | 230 |
| 17 | 0.162 | 0.160 | 420 |
| 18 | 0.161 | 0.156 | 500 |
| 19 | 0.155 | 0.150 | 510 |
| 20 | 0.151 | 0.152 | 330 |
| 21 | 0.139 | 0.136 | 520 |
| 22 | 0.137 | 0.135 | 430 |
| 23 | 0.134 | 0.130 | 600 |
| 24 | 0.130 | 0.127 | 610 |
| 25 | 0.123 | 0.120 | 530 |
| 26 | 0.120 | 0.118 | 620 |

a) Calculated by assuming orthorhombic crystal system with a = 0.782 nm, b = 0.560 nm, and c = 0.420 nm.11)

The oriented thin layer crystalline film of PPP is expected to have interesting electrical properties, and we are now studying chemical, physical, and electrical properties of the PPP film.

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12) As described in the text, the PPP molecule is considered to be oriented perpendicularly to the surface of the substrate and no diffraction spot related to the c-axis (the direction of polymer chain) was observed. Therefore, we did not obtained the information about the c-axis from the electron diffraction data, and we tentatively use the c-axis parameter previously given in literature.13) Moreover, we have assume the orthorhombic crystal system. However, the possibility for monoclinic crystal system with $\beta$ angle of near 90° can not be excluded, since at the moment we have not observed diffraction spot related to the c-axis.
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