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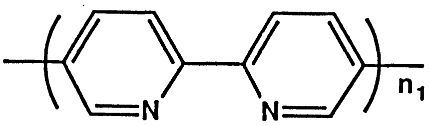
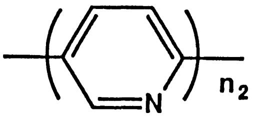
Orientation of Linear π-Conjugated Poly(2,2'-bipyridine-5,5'-diyl), Poly(2,5-thienylene) and Poly(pyridine-2,5-diyl) on Substrates

Takakazu YAMAMOTO,* Chiaki MORI, Hiroyuki WAKAYAMA, Zhen-hua ZHOU, Tsukasa MARUYAMA, Rokuro OHKI,† and Takaki KANBARA
Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227
†Research Cooperation Division, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro, Tokyo 152

Linear π-conjugated poly(2,2'-bipyridine-5,5'-diyl) and poly(pyridine-2,5-diyl) form oriented thin layer film with their c-axes (the polymer chain axes) essentially perpendicular to the surface of carbon and gold substrates when deposited under vacuum, whereas they and poly(2,5-thienylene) are arranged along the direction of rubbing on the surface of rubbed polyimide substrate.

π-Conjugated poly(2,2'-bipyridine-5,5'-diyl) (PBpy) and poly(pyridine-2,5-diyl) (Ppy) are reported to (1) take rigid rod-like linear structure both in solutions1) and in the surface region of polymer film (e.g., film of poly(vinyl alcohol)),2) (2) show excimer-like emmision due to strong interaction between the rigid linear molecules,3) and (3) are converted into an n-type electrical conductor1) due to π-deficient nature of the recurring pyridine ring.


PBpy


Ppy

On the other hand, it has been also reported that linear π-conjugated poly(2,5-thienylene), which is constituted of π-excessive thiophene rings and can be converted into p-type conductor, is oriented perpendicularly to carbon and gold substrates when deposited under vacuum.4) The interesting properties of PBpy and Ppy and the interesting orientation of poly(2,5-thienylene) (PTh) prompted us to investigate whether or not a similar orientation of PBpy and Ppy on the surface of substrates is also possible.

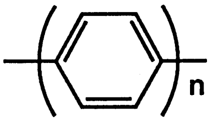
Our another interest was whether or not such linear π-conjugated polymers as PBpy, Ppy, and PTh can be arranged along the direction of rubbing of rubbed polyimide; such arrangement is known for liquid crystals.5) We now report results of the investigation in the two lines. PBpy (degree of polymerization (DP) = 20) and Ppy (DP = 50) were prepared as previously reported.1)

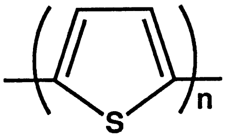
Vaporization of PBpy and Ppy from tantalum boat at 250 °C at 10^{-4} Pa on KBr pellet, carbon, gold, and In-Sn oxide (ITO) substrates afforded thin layer film with good mechanical strength. Thermogravimetric analysis of PBpy and Ppy indicated that they were thermally stable up to 300 °C. The IR spectra of the PBpy and Ppy films formed on the KBr pellet were identical to those of the source polymers, respectively, and cyclic voltammograms of the PBpy and Ppy films deposited on the ITO substrate (in anhydrous tetrahydrofuran containing 0.2 M of $[N(n\text{-}C_4H_9)_4]BF_4$) also showed the same pattern as those of the source polymers with n-doping peak at -2.15 V vs. Ag/Ag^+.1)

These results indicate that PBpy and Ppy having essentially the same structure as those of the original polymers were deposited on the substrates by the vacuum deposition. As for poly(p-phenylene), PPP, and PTh it is reported that these polymers with molecular weight of about 1500-2000 corresponding to DP of about 20-26 and length of about 8.6-11.4 nm can be vaporized under vacuum.4,6)

Figure 1a shows electron diffraction (ED) pattern of the PBpy film deposited on the carbon substrate at room temperature, in comparison with the ED patterns of oriented film of PPP and PTh with their c-axes (direction of polymer chain) perpendicularly to the carbon substrate (Fig. 1b and 1c).4)

Thickness of the PBpy film was about 60 nm as determined by multiple beam interferring method. If the PBpy molecule is oriented perpendicularly to the substrate and it has length of about 10-17 nm as roughly estimated from its DP and molecular weight of sublimable PPP,6) the thickness corresponds to stacking of about 4-6 layers of PBpy molecule.


PPP


PTh

The ED patterns shown in Fig. 1 were taken by using electron beam (60 keV corresponding to a wavelength of 0.0050 nm) irradiated perpendicularly to the carbon substrate. The observation of regular diffraction spots, similarly to the observation of the regular diffraction spots for PPP and PTh, is taken as an indication of orientation of the PBpy molecule essentially perpendicularly to the surface of the carbon substrate.

If the deposited PBpy has the packing similar to those of PPP and PTh, the ab crystallographical parameters (c axis is the direction of the polymer chain) are 0.81 nm (a) and 0.57 nm (b), respectively. The values are larger than the ab parameters of PPP (a = 0.78 nm, b = 0.56 nm),7) PTh (0.78 nm, 0.56 nm),8) poly(acetylene) (0.76 nm, 0.44 nm)9) and poly(ethylene) (0.76 nm, 0.49 nm),10) all of which have orthorhombic or similar crystal system. The spots shown in Fig. 1a disappeared by long irradiation and only Debye-Sherrer rings were observed. Use of gold substrate afforded analogous ED pattern.

Use of Ppy, instead to PBpy, in the vacuum deposition also gave similar film, whose ED pattern also showed some diffraction spots. However, the sharpness of the spots was lower and the number of the observed spots was smaller. It is reported that powdery Ppy has lower crystallinity than powdery PBpy presumably due to mixing of head-to-tail and head-to-head structures.1)

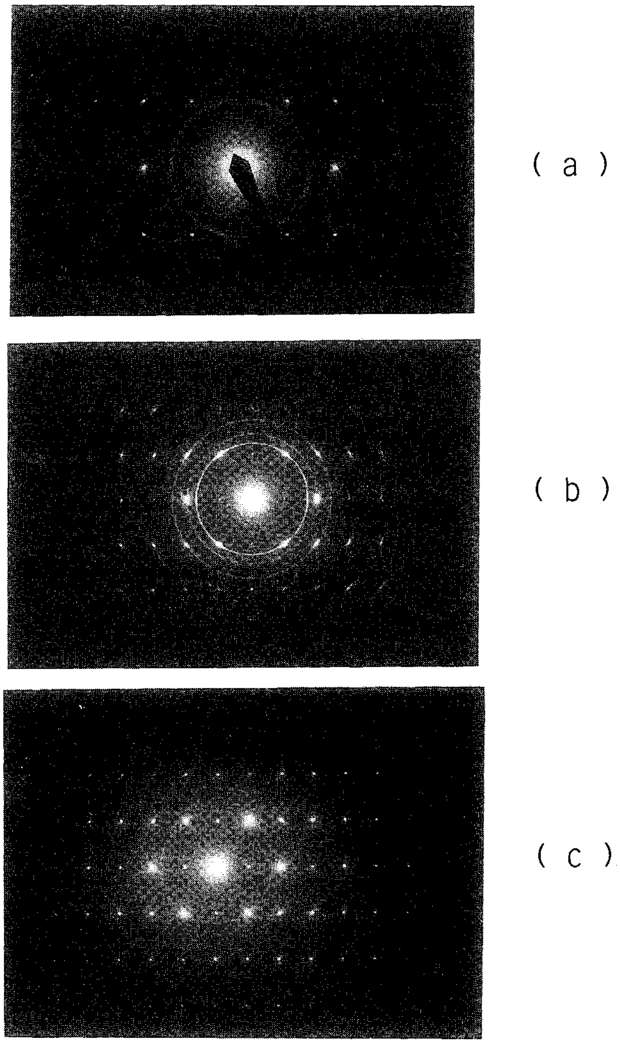


Fig. 1. ED pattern of (a) PBpy, (b) PTh, and (c) PPP deposited on carbon substrate.

The present finding that both the electron donating PTh and electron withdrawing PBpy and Ppy can be arranged perpendicularly to the surface of the substrates suggests the possibility for making interest electronic junctions (e.g., supper lattice) by stacking PBpy (or Ppy) and PTh alternatively. Revealing of inherent electrical properties of PBpy and Ppy (e.g., mobility of carrier along the polymer chain) may become possible by using the oriented crystalline thin films of PBpy and Ppy.

On the other hand, it is known that rod-like molecules (e.g., liquid crystalline molecules) can be oriented along the direction of rubbing of polyimide film and liquid crystal layer thus oriented is now widely used for display devices.5) Vapor deposition of the rod-like PBpy and PTh on the rubbed polyimide also leads to similar orientation of the polymer as revealed by measuring dichroism2) of polyimide film containing vacuum deposited PBpy and PTh.

Irradiation of polarized light to rubbed polyimide (#AL-1051 from Japan Synthetic Rubber Co. Ltd.) film containing the vacuum deposited PTh and PBpy in its surface region showed π-π^* absorption peaks of PTh and PBpy at 430 and 340 nm, respectively, and revealed dichroism2) for the absorption peaks. When the direction of the oscillating electric field of the polarized light coincided with the direction of the rubbing, the absorbance of the peak ($a_{/\!/}$) was larger than the absorbance ($a_{\perp}$) observed at 90° of angle between the two directions. These results indicate that the polymer chains are oriented along the direction of the rubbing. The $a_{/\!/}/a_{\perp}$ ratios were 1.5 and 1.2 for PTh and PBpy, respectively. The rubbed polyimide film itself did not show such dichroism.

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