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Friction-induced uniaxial orientation of a liquid crystalline *N*-substituted polypyrrole

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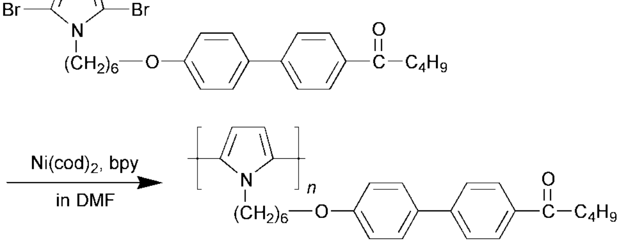
Uniaxial orientation of a liquid crystalline *N*-substituted polypyrrole by a friction technique resulted in the alignment of the polymer main chain in the direction of friction while the mesogenic side chains orientated vertically to the main chain.

There has been a growing demand for the synthesis of aligned conjugated polymers in order to elucidate their electrical, optical and optoelectronic anisotropies. Soluble and/or fusible conjugated polymers have a great advantage in conventional polymer processing, therefore the production of soluble rigid conjugated polymers by the introduction of liquid crystalline side chains into the conjugated main chains has received much attention. For example, liquid crystalline polyacetylenes[1,2] and polythiophenes[3,4] have been studied.

Syntheses of soluble polypyrrole derivatives have also been attempted by introducing a liquid crystalline substituent at the *N*- or 3-position of the pyrrole ring.[5–10] However, even in successful cases, the liquid crystalline state formed only very small domains and poor reproducibility made it difficult to align the polymers macroscopically. In order to synthesise polypyrrole derivatives with a stable mesophase, we have studied symmetrical *N*-substituted polypyrroles that should have no head-to-tail structural defects.[10] Recently, we have successfully synthesised a liquid crystalline biphenyl ketone type *N*-substituted polypyrrole (BPK-PPy) with a stable mesophase with large domains by dehalogenative polycondensation of the corresponding monomer using $Ni(cod)_2$[11] as shown in Scheme 1.

In this paper, we report uniaxial orientation of BPK-PPy by a friction-transfer technique[12,13] and its optical anisotropic properties. BPK-PPy was synthesised according to the reported method.[11] The polymer was soluble in common organic solvents such as $CHCl_3$ and THF, and the number average molecular weight (M_n) determined by gel permeation chromatography was about 7000 *vs.* polystyrene standard ($M_w/M_n = 1.4$). A stable enantiotropic smectic phase was observed by polarising optical microscopy (POM) in the range of 116 °C to 154 °C with a good fan-shaped texture. The phase was identified as an intricate smectic A (S_A) from a X-ray diffraction (XRD) pattern with a sharp peak at small angle due to a layer distance of 29 Å and a broad halo at wide angle due to an intermolecular distance of the mesogenic side chains of about 4 Å. Below 116 °C, the phase changed first to another mesophase and then to solid state. Usually liquid crystalline polymers retain the structure of the liquid crystalline state after cooling to a glassy state. The mesophase was identified as an intricate smectic E (S_E) phase with approximate lattice constants $a = 9.2$, $b = 4.5$ and $c = 29$ Å determined by XRD in a glassy state and by molecular mechanics calculations[14] with Cerius^2.



Scheme 1

Uniaxial alignment of BPK-PPy sandwiched between two pre-treated substrates[15] was carried out by sliding the substrates over each other. The polymer was frictionally treated in a liquid crystalline state at 131 °C. The texture changed to an aggregate of vertically aligned thin domains as shown in Fig. 1 after the frictional processing. In most of the liquid crystalline side-chain type polymers studied so far, liquid crystalline domains tend to align in the direction of rubbing or frictional treatment. However, BPK-PPy gives an opposite result, *i.e.*, the domains align perpendicular to the direction of friction. The frictionally treated sample was allowed to stand at rt and was analysed by XRD. The XRD patterns suggested that the peak intensity corresponding to interlayer distance was largely enhanced in the direction perpendicular to the friction in the S_E state.

Characterisation of the aligned structure in the glassy state was carried out by following polarising optical measurements. Polarising parallel and perpendicular IR spectra of the aligned BPK-PPy on a KBr substrate and difference spectrum are shown in Fig. 2. Dichroic ratios ($R = A_\parallel/A_\perp$) of IR absorptions at 1601 cm^{-1} (ν_{ring} of phenylene, $R = 0.46$), and at 1254, 1193 cm^{-1} ($\nu_{as,\ C\text{–}O\text{–}C}$, $R = 0.55$) are smaller than unity. These results suggest that the biphenyl ether mesogenic substituents

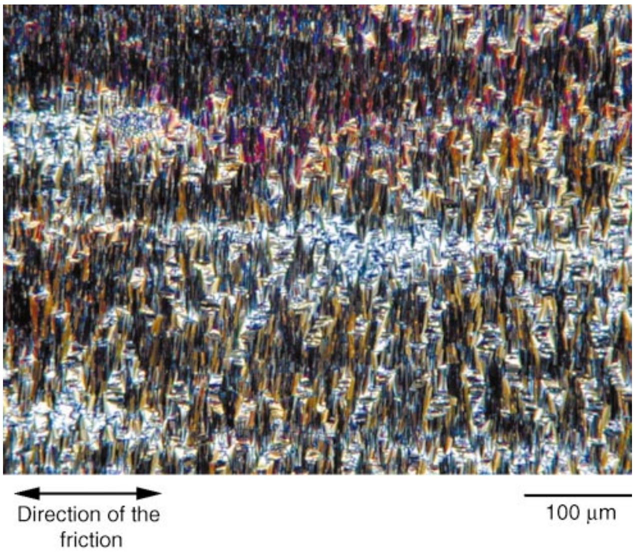


Fig. 1 POM texture of BPK-PPy after orientation at 131 °C.

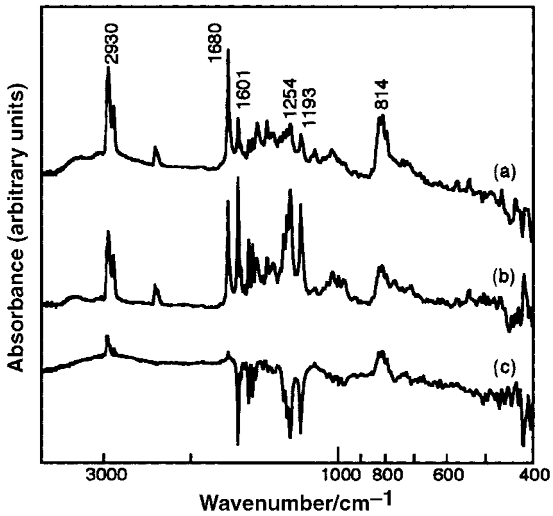


Fig. 2 Polarising parallel (a), perpendicular (b), and difference (c) IR spectra of the friction-treated BPK-PPy.

align perpendicular to the direction of friction. On the contrary, the R values of absorptions around 2900 cm^{-1} ($\nu_{\rm as,\,C–H}$ of methylene, $R = 1.3$) and around 820 cm^{-1} due to out-of-plane C–H bending of the biphenyl ring ($\nu_{\rm C–H}$, $R = 2.1$) show larger values than unity. These results support such an intramolecular arrangement as represented in Fig. 3. Thus, the side chain moiety extends perpendicular to the friction direction on the substrate. It is noteworthy that the carbonyl group is perpendicular to both the main chain and substrate plane because the close to unity value of the dichroic ratio of an absorption peak at 1680 cm^{-1} ($\nu_{\rm C=O}$, $R = 1.1$) suggests that the band is independent of the polarisation. In addition, the dichroic ratios of these IR peaks maximise at about 90-degree polarisation.

Orientation of the polypyrrole backbone was determined by polarising UV-VIS and fluorescence spectra that provide information on π-conjugation. UV-VIS spectra of BPK-PPy in parallel and perpendicular directions to the friction showed a broad shoulder absorption around 450 nm tailing to longer wavelength, which was assigned to a π→π* transition of the conjugated main chain. The dichroic ratio ($A_{\parallel}/A_{\perp}$) was 1.41 at 452 nm. This result suggests that the π-conjugated main chain of BPK-PPy aligns parallel to the direction of friction.

Additional results confirming the parallel orientation of the main chain were obtained by polarising fluorescence spectroscopy. Polarising fluorescence spectra of frictionally aligned BPK-PPy excited with 323 nm (a) and 396 nm (b) are shown in Fig. 4. The 323 nm excitation should stimulate a π→π* transition of the biphenylene moiety in the side chain. A dichroic ratio ($I_{\parallel}/I_{\perp}$) of emission intensity at the maximum of 397 nm ($R = 0.80$) corresponds with the results from polarising IR that the side chains orientate perpendicular to the frictional direction. On the other hand, an excitation with 396 nm, which contributes to a π→π* transition of the polypyrrole backbone, exhibits an emission spectrum with a maximum of 539 nm ($R = 2.2$), indicating that the conjugated polymer backbone is forced to align in the direction of the frictional treatment. Like the IR results, the dichroic ratios of the UV-VIS absorption and the fluorescence emissions maximise at about 90-degree polarisation.

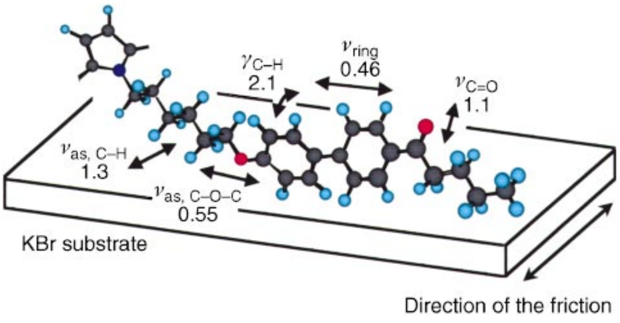


Fig. 3 A schematic representation of the intramolecular arrangement of BPK-PPy.

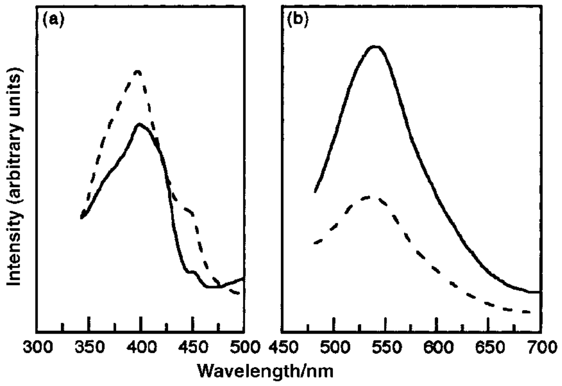


Fig. 4 Polarising fluorescence spectra excited with 323 nm (a) and 396 nm (b) in a direction parallel (solid line) and perpendicular (broken line) to the friction.

In conclusion, we have achieved macroscopic orientation of BPK-PPy by using a convenient friction-transfer technique. From POM and polarising spectroscopic analyses, an unusual orientation was confirmed, that is, the polypyrrole main chain aligned parallel to the friction while the mesogenic side chain oriented to the perpendicular. Similar uniaxially orientation has been recognised by stretching flexible fibres of smectic polymers such as polyacrylates and polysiloxanes.[16,17] In this case, it is postulated that the most rigid moiety in the domains are forced by mechanical stress of the friction. Thus, at first a friction-transfer force selectively aligns the rigid rod-like polypyrrole main chain, which successively induces the vertical order of the flexible mesogenic side chain by a spontaneous alignment.

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