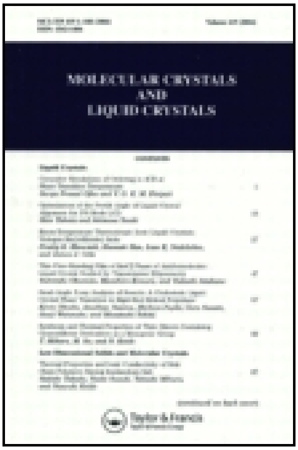

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Orientation of Liquid Crystalline N-Substituted Polypyrroles

Shota Abe [a], Masashi Kijima [a] & Hideki Shirakawa [a]

[a] Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki, 305-8573, Japan

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Orientation of Liquid Crystalline N-Substituted Polypyrroles

SHOTA ABE*, MASASHI KIJIMA† and HIDEKI SHIRAKAWA

Institute of Materials Science, University of Tsukuba, Tsukuba,
Ibaraki 305–8573, Japan

Liquid crystalline polypyrroles having a mesogenic substituent with oxobiphenyl and cyanobiphenyl mesogenic cores at the *N*-position were synthesized by Ni(cod)$_2$ method. The polymers showing stable enantiotropic smectic phases with large domains and good reproducibility were macroscopically oriented by mechanical alignment techniques of rubbing and friction-transfer, respectively. The ordered structure was characterized from dichroic ratio of polarizing IR and PL spectra. In case of orientation by the rubbing method, arranged mesogenic side chains on the rubbed substrate induced a vertical alignment of polymer backbone to the rubbing direction. In contrast, the friction-transfer method selectively aligned rigid polymer backbone parallel to the friction direction, which successively induced a vertical arrangement of mesogenic side chains.

Keywords: liquid crystalline polypyrrole; orientation; rubbing alignment; friction-transfer

INTRODUCTION

Uniaxial alignment of π-conjugated main chain is essential to realize conjugated polymer materials with electrical, optical, and optoelectronic anisotropies. Introduction of a liquid crystalline (LC) side chains into

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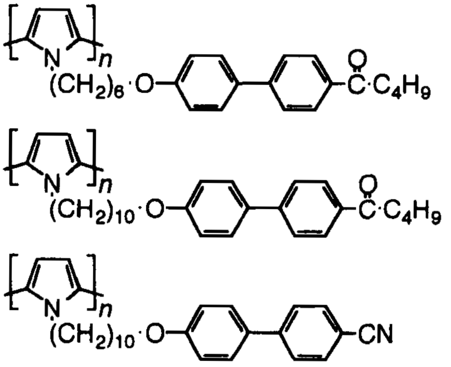
* Also corresponding author: email: sabe@ims.tsukuba.ac.jp.

† Corresponding author: email: kijima@ims.tsukuba.ac.jp.

conjugated polymers is a probable method to align the conjugated main chain. Moreover, the method has a great advantage of making the rigid polymers soluble and fusible. Along the line, polypyrroles having a LC substituent have been synthesized by oxidative manners [1-6]. However, LC states of those polymers showed only very small domains with poor reproducibility. Recently, LC *N*-substituted polypyrroles showing stable mesophases have successfully synthesized by dehalogenative polycondensation with $Ni(cod)_2$ [5, 6]. The *N*-substituted polypyrroles have merits of 2,5-regio selective linkage without head-to-tail structural defects.

In this paper, we report orientation of LC *N*-substituted polypyrroles having an oxobiphenyl mesogenic core and a cyanobiphenyl core (Chart 1), by a conventional rubbing technique and a friction-transfer technique.



OB6

OB10

CB10

Chart 1

EXPERIMENTAL

Properties of the polymers

In this study, LC polypyrroles (**OB6**, **OB10**, **CB10**) were synthesized according to the reported method [7]. The polymers were soluble in common organic solvents such as $CHCl_3$ and THF. The number average molecular weights (M_n) of the polymers were about 10000, which was determined by gel permeation chromatography vs. polystylene standard [7]. All the polymers showed stable enantiotropic LC phases with good fan-shaped textures observed by thermo-controlled polarizing optical microscopy (POM). Phase transition temperatures and identifications of the phases were determined by POM, DSC, and XRD. The phase transition behaviors of the polymers were summarized as follows; **OB6**: (G) S_E • 116 • S_A (131) • 154 • I; **OB10**: G • 111 • S_E • 130 • S_A (152) • 166 • I; **CB10**: (G) S_A (91) • 99 • I.

Alignment procedures of the polymers by rubbing and friction-transfer methods

Glass substrates pre-treated by rubbing with polyimide were purchased from EHC jpn Co., Ltd. KBr substrates for IR measurement were rubbed with teflon in advance.

Rubbing treatment of the polymers was carried out by following process. First, a thin film of the polymer was prepared on the substrate by a casting method, which was succesively heated up to its isotropic state. After the sample was kept at the temperature for 1hour (**OB6**: 160 °C, **OB10**: 170 °C, **CB10**: 105 °C), it cooled to a temperature in its LC state at a rate of 0.2 °C/min. The sample was kept for another 1 hour at the temperature (**OB6**: 150 °C, **OB10**: 152 °C, **CB10**: 91 °C), then it cooled to r.t..

In case of frictional alignment, the polymers sandwiched between two pre-treated substrates was forced by sliding the substrates each other in one direction at a temperature in the LC state (**OB6**: 131 °C, **OB10**: 145 °C, **CB10**: 95 °C).

RESULTS AND DISCUSSION

Alignment of the polymers by rubbing method

Firstly, macroscopic alignment of the polymers was attempted by a typical method of rubbing technique. Among LC *N*-substituted polypyrroles synthesized so far [5,7], polypyrroles having an oxobiphenyl mesogenic core, **OB**s show most grown LC domains that may be appropriate for macroscopic alignment. However, in case of **OB6**, only partial orientation is achieved by the rubbing treatment as shown in Figure 1. Similar partial orientation is observed for **OB10**. These results of **OB**s can be elucidated that an intermolecular force between mesogenic side chains is stronger than interaction between the polymer and the rubbed substrates. In case of **CB10**, LC domains observed by

POM (Figure 2) are apparently smaller than those of **OBs**. Contrary to the results for **OBs**, the texture of **CB10** changes to an aggregate of aligned thin domains as shown in Figure 3. Since LC side chains are usually forced to align in the rubbing direction on substrates, domains arrange parallel to the rubbing direction. The aligned **CB10** was investigated by polarizing UV-Vis and PL spectra. Both UV-Vis absorption and PL emission bands derived from a π-conjugation of polypyrrole main chain enhance in perpendicular to the rubbing direction. The dichroic ratio is about 1.5 estimated from PL emissions ($I_{//}/I_{\perp}$). These results suggest that parallel alignment of LC side chains on the rubbed substrate induces vertical order of the polymer main chains to the rubbing direction.

Alignment of the polymers by friction method

Friction-transfer method has been recognized as a useful method for uniaxial alignment of polymer main chain [8]. In our recent work, LC domains of **OB6** aligned vertical to the direction of friction. In this case, the polymer main chain aligned parallel with a perpendicular arrangement of the LC side chains to the friction direction [6]. However, the frictional orientation is not successful for **OB10** having larger domains than **OB6**, that is, aligned domains immediately return to an original multidomain state with a fan-shaped texture. This may be due to a strong intermolecular force between the LC side chains with much fluidity.

In case of **CB10**, a fan-shaped texture of LC state changes to an aligned texture as shown in Figure 4. Likewise the cese of **OB6**, domains arrange vertical to the direction of treatment, which is opposite to the results of rubbing treatment. XRD analyses of the aligned sample shows that a peak intensity due to interlayer distance is largely enhanced in perpendicular to the friction direction, which means that the smectic layer structures extend perpendicular to the direction of friction.

Moreover, the aligned structure of **CB10** was confirmed from polarizing IR, UV-Vis, and PL spectroscopies. Polarizing parallel and perpendicular IR spectra of frictionally treated **CB10** on a KBr substrate are shown in Figure 4 with a difference spectrum. Dichroic ratios ($R = A_{//}/A_{\perp}$) of IR absorptions due to stretching of cyano group (2222 cm^{-1}, R = 0.41), phenyl ring (1600 cm^{-1}, R = 0.49), and ether linkage (1250 cm^{-1}, R = 0.51) are smaller than unity. On the other hand, ratios of absorptions due to C-H stretching of methylene spacer (2925 cm^{-1}, R = 1.25) and out-of-plane bending of C-H at the biphenyl ring (820 cm^{-1}, R = 1.76) show larger values than unity. These results suggest that the side chain

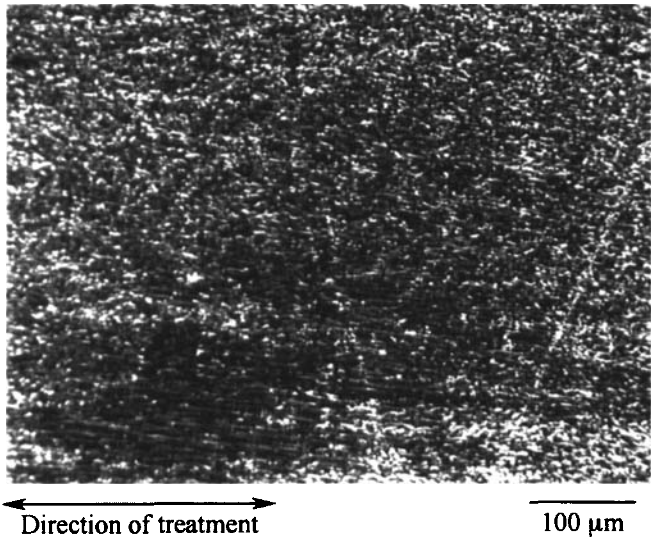


FIGURE 3 Polarizing optical micrograph of **CB10** after rubbing treatment See Color Plate IX at the back of this issue.

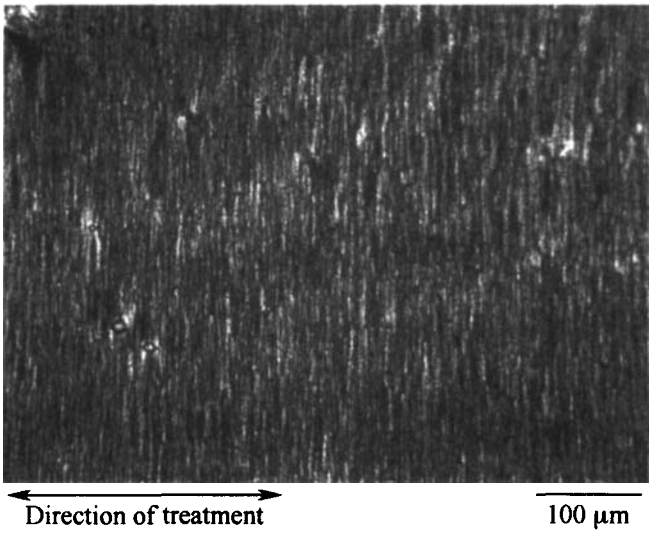


FIGURE 4 Polarizing optical micrograph of **CB10** after frictional treatment See Color Plate X at the back of this issue.

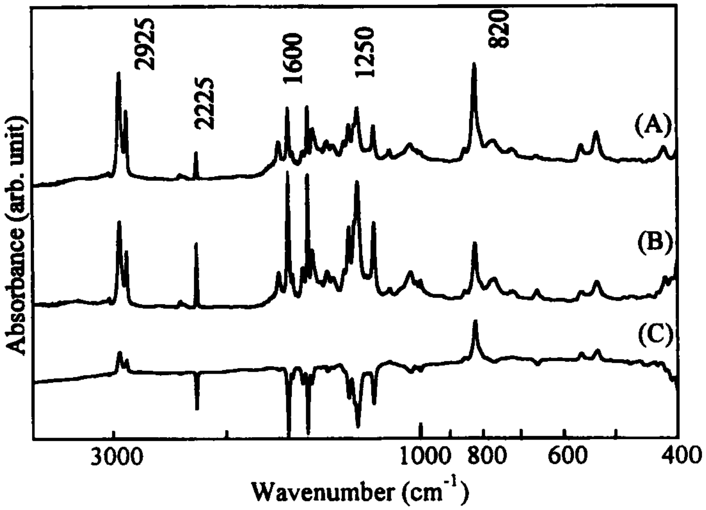


FIGURE 4 IR spectra of frictional treated **CB10** polarized parallel (A) and perpendicular (B) with difference spectrum (C).

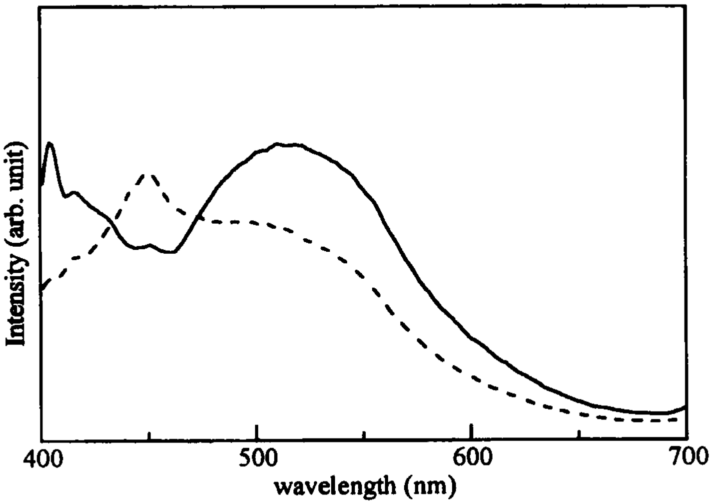


FIGURE 5 PL spectra of frictional treated **CB10** polarized parallel (solid line) and perpendicular (dashed line).

places perpendicular to the direction of friction on the substrate. In addition, the dichroic ratios of these IR peaks maximize about 90° polarization.

Both UV-Vis absorption and PL emission bands due to the π-conjugation of polypyrrole main chain enhance in parallel to the friction. A dichroic ratio of aligned main chain is determined by polarizing PL emission band (Em_{max} = 510 nm, Figure 4) to be R ($I_{//}/I_{\perp}$) = 1.4 with excitation of 370 nm. These results indicate that the conjugated main chains align in the friction direction.

Thus, a mechanical stress of frictional force selectively aligns conjugated main chain at first, which successively induces the vertical order of the mesogenic side chain by a spontaneous alignment.

CONCLUSION

Macroscopic orientations of LC *N*-substituted polypyroles **OB6**, **OB10**, and **CB10** were attempted by rubbing and friction-transfer techniques, respectively. In the case of rubbing alignment, parallel alignment of LC side chains placed polymer main chains perpendicular to the rubbing direction. On the contrary, friction alignment realized a parallel orientation of rigid polypyrrole backbones with a perpendicular alignment of LC side chains to the friction direction. Alignment by rubbing method was applicable to **CB10** but inappropriate for **OBs**, while friction method was effective for **OB6** and **CB10**. Choice of alignment techniques with the suitable polymers especially about fluidity was key factor to achieve macroscopic orientation of LC conjugated polymers.

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