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Anomalous Molecular Alignment of Liquid Crystalline Conducting Conjugated Polymer, Poly(2,5-dialkoxy -*p*-phenylenebutadiynylene), using Conventional Rubbing Process

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Liquid crystalline materials have large anisotropy of optical, electrical, magnetic and physical properties due to the anisotropic molecular structure and molecular alignment, which shows a variety of characteristic behaviors upon the application of electric and magnetic fields. In order to realize macroscopic anisotropy, mesogenic molecules must be aligned using molecular alignment techniques such as rubbing on the substrates, SiO evaporation, shear stress application and magnetic field application. Among such alignment techniques, a conventional rubbing method has been adopted in the display application because of its simplicity. Regarding liquid crystalline polymers, however, molecular alignment by the simple rubbing technique is difficult even in the nematic phase because of their extremely high viscosity, and only few studies on the molecular alignment of the liquid crystalline polymer has been carried out except for a shearing technique.

On the other hand, conducting polymers having highly extended π -conjugated systems in their main chain have attracted considerable attention from both fundamental and practical points of view, because various novel physical behaviors have been observed and also various functional applications have been proposed. In particular, the liquid crystalline conducting polymers having a mesogenic part in their side chain^[1-5] or long alkoxy chains as a substituent^[6,7] have attracted much interests in terms of the molecular alignment, which is expected for the realization of the polarized electroluminescence devices. However, uniform molecular alignment utilizing their liquid crystalline characteristics has never been performed previously.

In this study, we have realized, by a conventional simple rubbing procedure, a uniform molecular alignment with high quality in a sandwich cell of liquid crystalline conducting polymer, poly (2,5-dialkoxy -*p*-phenylenebutadiynylene) (PDAPB), including triple bonds in the main chain. We also report anomalous molecular alignment in which the alkoxy side chain aligns in parallel with the rubbing direction and the

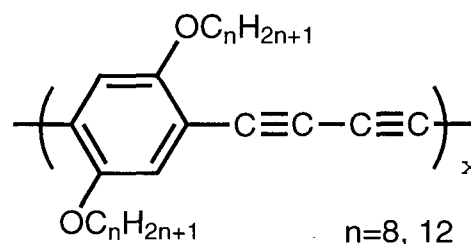


Fig.1. Molecular structure of PDAPB.

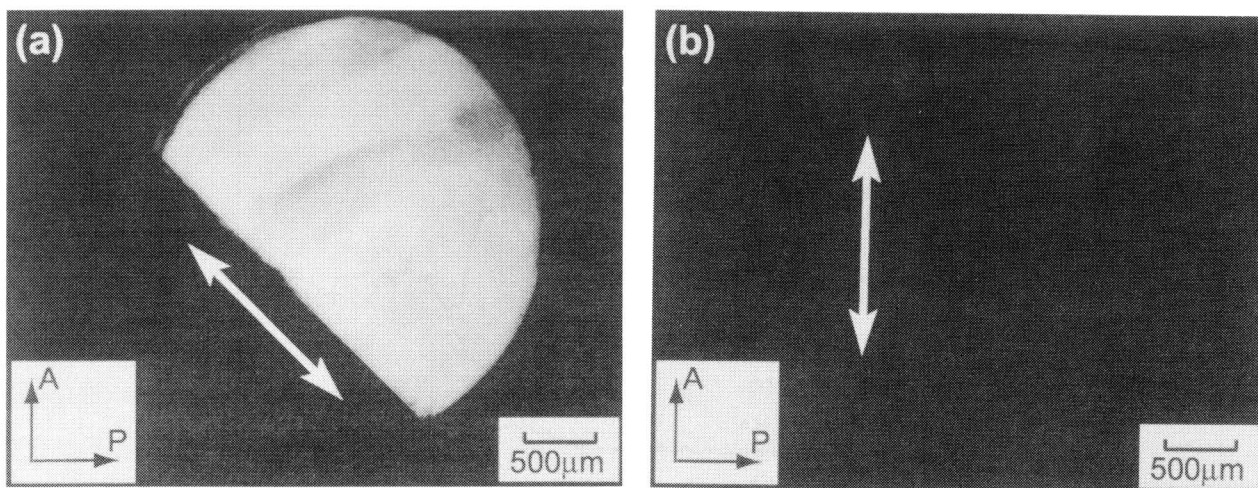


Fig.2. Polarizing microphotographs of PDAPB in a sandwich cell with rubbing treatment. (a) Bright state in which the rubbing direction shown as arrows makes an angle of 45° with respect to the polarizers. (b) Complete extinction state in which the rubbing direction is parallel to the analyzer.

mesogenic main chain aligns in perpendicular to the rubbing axis. This anomalous molecular alignment has been confirmed using polarizing spectroscopic measurements such as Raman, absorption and photoluminescence spectroscopies.

The molecular structure of the liquid crystalline conducting polymer, PDAPB, used in this study is shown in Fig.1. The elemental properties have been previously reported.^[8,9] The sample was sandwiched between two glass plates whose surfaces were rubbed by a nylon cloth. Any alignment layer such as polyimide did not covered on the glass surfaces. The polymer was filled into the cell by a capillary action.

PDAPB can be filled even into a thin sandwich cell of $1\mu\text{m}$ -thickness by a capillary action. Generally speaking, conducting polymers have high viscosity because they have rigid π -conjugated main chain in their structure. Even the liquid crystalline polymers including a polyacrylate or polysiloxysane main chain can be hardly filled into a such thin sandwich cell. However, the viscosity of PDAPB is relatively low compared with the conventional conducting polymers. This might be due to flexibility of the conjugated systems in terms of a free rotation of the triple bonds in their main chain.

Figure 2 shows polarizing microphotographs of PDAPB in a sandwich cell of $1\mu\text{m}$ -thickness. As is evident from this photograph that uniform alignment can be realized in the entire area of the cell. A complete extinction can be realized in a crossed polarizer geometry by rotating the sample cell as the rubbing direction is parallel to the polarizers, as shown in Fig. 2(b). This is a characteristic of liquid-crystalline material. It should also be noted that, even at room temperature, the texture is still maintained, which is common in the polymeric liquid crystal.

The color in the bright state as in Fig.2(a), in which the rubbing axis is not parallel to the polarizers, depends on the temperature. In other words, the transmission spectrum through the sandwich cell placed between the crossed polarizers changes upon the temperature. In general, color of a uniaxial

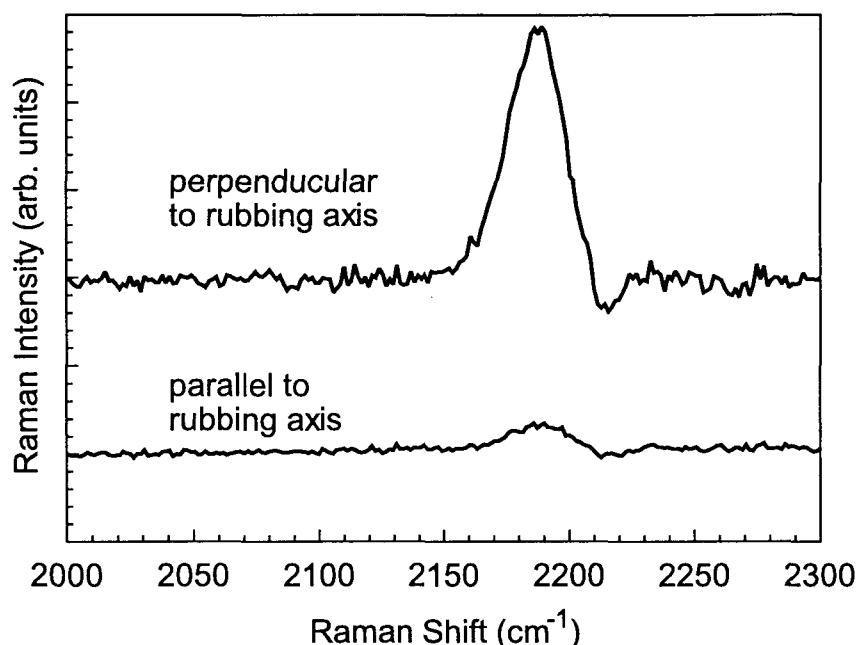


Fig.3. Polarizing Raman spectrum of PDAPB in a sandwich cell with rubbing treatment. Polarization directions of excitation light and Raman signal are perpendicular and parallel to the rubbing direction.

anisotropic material placed between crossed polarizers is determined by a retardation $\Delta n d$, where Δn is the birefringence and d is the thickness. In this case, because of a constant cell thickness d , the change in retardation should reflect that in the birefringence Δn , which may originate from the change in the effective conjugation length of the polymer main chain or the change in the distance between the main chains due to the conformation change of side chain alkoxy units.

In order to directly clarify the molecular alignment, polarizing Raman spectrum was investigated. Figure 3 shows polarizing Raman spectrum of PDAPB in the aligned sandwich cell. The excitation wavelength is 488 nm. A clear peak appears around 2100 cm^{-1} , which is associated with the C-C stretching vibration of the butadiynylene in the polymer main chain. As evident from the figure, it should be noted that the Raman intensity of the peak strongly depends on the polarization direction. Namely, the Raman signal for the light perpendicular to the rubbing direction is much stronger than the parallel component. This result clearly indicates that the C-C triple bond extends along the direction perpendicular to the rubbing treatment. In other words, the polymer main chain along which the C-C triple bond extends is perpendicular to the rubbing axis. The average direction of the substituted alkoxy side chain is perpendicular to the polymer main chain. In this case, therefore, instead of the mesogenic part in the main chain, the alkoxy side chains align in the rubbing direction.

The polarizing absorption and photoluminescence (PL) measurements of the aligned PDAPB cell support the Raman results. Namely, the optical absorption corresponding to the excitation of the π -conjugated electron system in the polymer main chain, is large for the light polarized perpendicular to the rubbing axis compared with that parallel to the rubbing direction. Also in the PL spectrum from the

π -conjugated main chain, the PL intensity polarized perpendicular to the rubbing axis is stronger than the parallel one. These results also mean that the mesogenic main chain lies in the direction perpendicular to the rubbing treatment. The anisotropy in these spectra is observed both in the liquid crystalline and solid phases, while that disappears in the isotropic phase.

Generally speaking, the rod-like mesogenic molecules align with its long axis parallel to the rubbing direction. Also in the case of the polymeric liquid crystal having mesogens in their side chain, the mesogenic part in the side chain aligns in the direction of the rubbing treatment. Originally, therefore, the mesogenic chain of the main chain type polymeric liquid crystal was expected to align along the rubbing direction. However, PDAPB used in this study aligns in the unexpected manner, that is, as the π -conjugated main chain aligns perpendicular to the rubbing direction.

In conclusions, molecular alignment characteristics of liquid crystalline conducting polymer, poly(2,5-dialkoxy -*p*-phenylenebutadiynylene), was studied. Although this polymer has a π -conjugated main chain, a uniform molecular alignment in a sandwich cell whose surfaces were treated with a conventional rubbing technique was realized by cooling down from the isotropic phase. In this aligned sandwich cell, alkoxy side chain of the polymer aligned parallel to the rubbing direction. This molecular alignment behavior was quite different from that of a conventional rod-like liquid crystal with low molecular weight or side-chain type polymeric liquid crystal having a polyacrylate or polysiloxane skeletons.

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