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Strong Dichroism of π-Conjugated Poly(2,2'-bipyridine-5,5'-diyl) and Poly(pyridine-5,2-diyl-thiophene-2,5-diyl) in Stretched Poly(vinyl alcohol) Film

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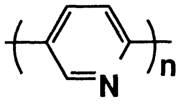
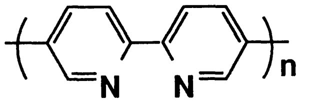
Stretching of poly(vinyl alcohol) PVA film containing poly(2,2'-bipyridine-5,5'-diyl) PBPy or poly(pyridine-5,2-diyl-thiophene-2,5-diyl) PTPy in the surface region of PVA leads to alignment of the π-conjugated polymers along the stretching direction. The stretched PVA-PBPy and PVA-PTPy aduct films showed a strong dichroism and polarizing effect at 350 nm and 450 nm, respectively.

Electrical and optical properties of π-conjugated polymers are subjects of recent interest. It is previously reported that poly(pyridine-2,5-diyl) PPy takes a linear rod-like structure in a solution and a good polarizing film can be obtained by stretching poly(vinyl alcohol) PVA film containing PPy molecules in the surface region of PVA.1) Poly(2,2'-bipyridine-5,5'-diyl) PBPy also takes similar rigidly linear structure both in a solution2) and in a vacuum deposited film on a carbon substrate.3) The linearity of PBPy in the vacuum deposited film is higher than that of PPy.3)

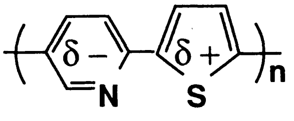
On the other hand, poly(pyridine-5,2-diyl-thiophene-2,5-diyl) PTPy shows interesting electrochemical4) and optical (absorption, luminescence, and non-linear property)4,5) properties due to its intramolecular charge transfer structure. However, PTPy adopts a rather random conformation in contrast to the rigid linear rod-like structure of PPy, as proved by much smaller value of degree of depolarization, ρ_V ,6) of PTPy (ρ_V = 0.093)4) compared with that of PPy (ρ_V =0.33).1) This seems to be attributed to some bending at the bonding between the aromatic nuclei.



PPy
n = 25 and 49



PBPy
n = 21



PTPy
n = 40

In order to obtain further information on the dichroic properties of oriented π-conjugated polymers and to align the optically interesting PTPy, we have prepared stretched poly(vinyl alcohol) films containing PBPy or PTPy, and now report the dichroic properties of the aligned π-conjugated polymers. The polymers were prepared by dehalogenation polycondensation 7) of the corresponding dihaloaromatic compounds based on organonickel chemistry.8)

Painting a PVA film with a formic acid solution of PBPy and evaporating the formic acid affords a PVA film containing PBPy in a surface region of PVA as shown in Fig. 1a. When this film is stretched as shown in Fig. 1b, the linear PBPy molecules will be aligned along the direction of the stretching. When polarized light is irradiated as shown in Fig. 2, the dichroism is expected if the PBPy molecules are aligned.

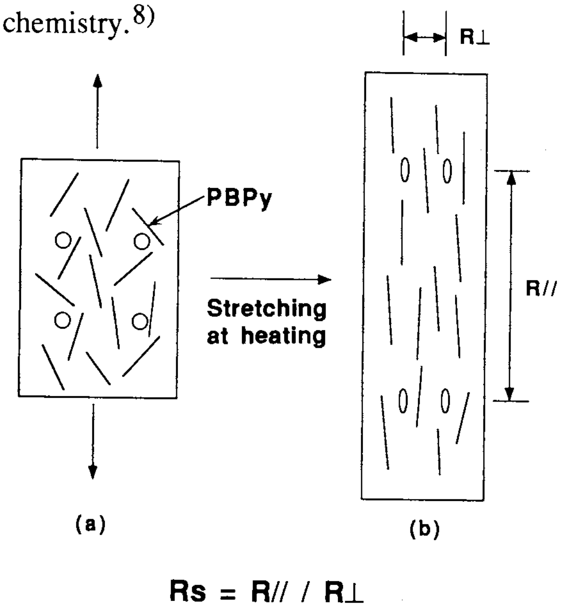


Fig. 1. Stretching of PVA film containing linear PBPy molecules in its surface region and definition of Rs. The four ○ marks are made at the corners of a square (Fig. 1a) to determine the Rs value (Fig. 1b).

The strong dichroism of the stretched film as shown in Fig.3 indicates that the expected alignment actually takes place in the surface region of PVA film; a much larger value of absorbance (A) is observed at $\theta = 0°$ (A_0) (Fig. 3) than at $\theta = 90°$ (A_{90}). The A_0/A_{90} ratio (R_d, cf. Fig. 3) is plotted against the stretching ratio (cf. Fig. 1) of the PVA film to give Fig. 4, which also includes similar data for PPy's with degree of polymerization (n) of 49.1) The data shown in Fig. 4 clearly indicate that PBPy, which has higher order of linearity than PPy due to its more highly regular structure (PPy contains not only the head-to-tail configuration but also the head-to-head configuration), also shows dichroism similar to PPy. The R_d value is considerably larger than the R_d value($R_d < 5$) shown by aligned low molecular weight aromatic compounds in stretched PVA

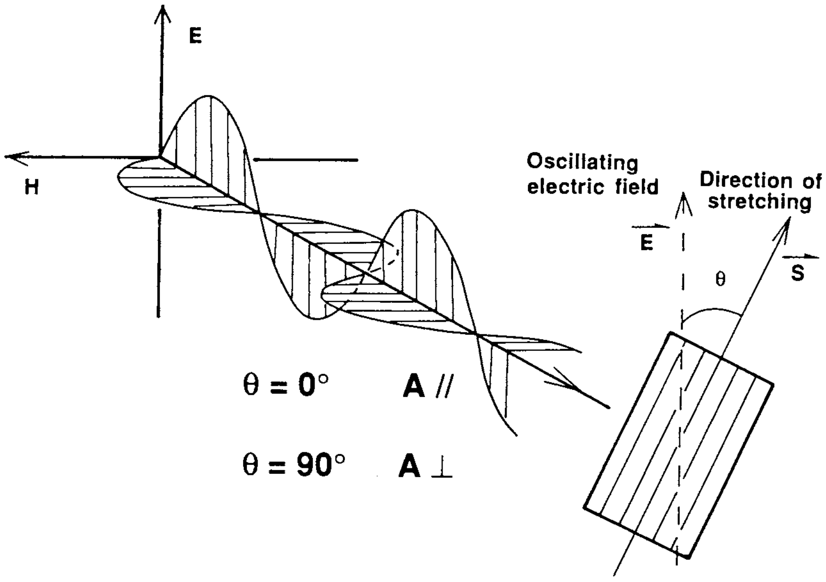


Fig. 2. Irradiation of polarized light on the stretched film.

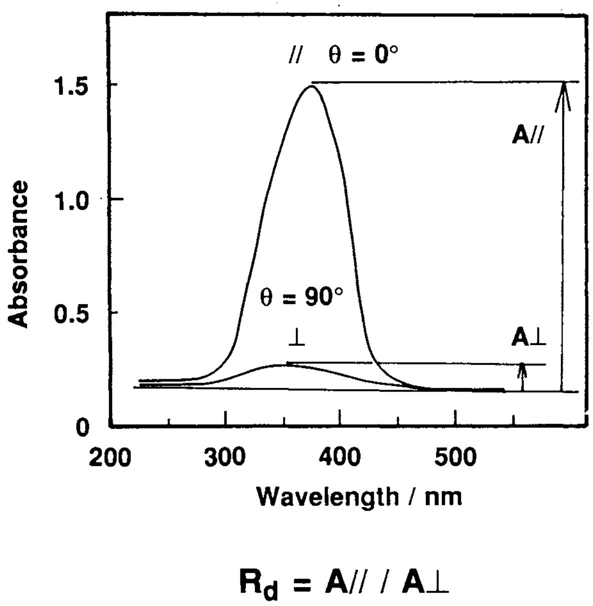


Fig. 3. Dichroism of the stretched PVA-PBPy film observed by the irradiation of the polarized light (Fig. 2) and definition of Rd.

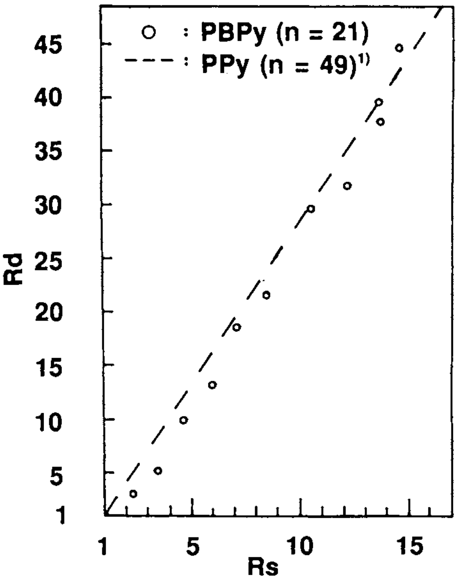


Fig. 4. Plot of Rd *vs.* Rs for the PVA-PBPy film (○) and comparison with the data for the PVA-PPy (n=49) film.[1]

films,[9] and such large R_d values shown in Fig. 4 may be taken as a kind of a limiting or ideal value for the dichroism.

Painting the PVA film with a formic acid solution of PTPy and removing the formic acid by evaporation also affords a PVA film containing PTPy in the surface region of PVA. Since PTPy takes the rather random conformation in the formic acid solution, the PTPy molecules in the surface region of non-stretched PVA film are considered to take a rather random conformation as shown in Fig. 5a. However, when the PVA film is stretched, the PTPy molecules may be expected to be stretched and aligned along the direction of the stretching of the PVA film to take a rather linear structure as shown in Fig. 5b. A strong dichroism shown in Fig. 6 strongly suggests that the expected stretching and alignment actually take place, and a R_d-R_s relation for PTPy in the surface region of PVA is shown in Fig. 7. The R_d value is smaller than that

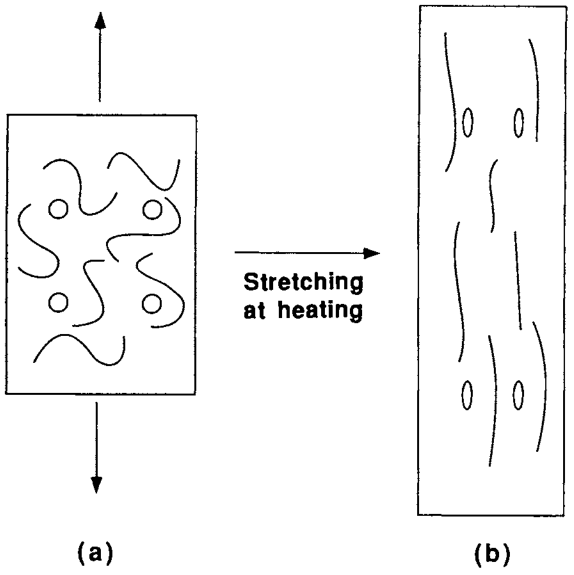


Fig. 5. Stretching of PVA film containing PTPy with rather a random conformation and alignment of the PTPy molecules along the direction of the stretching.

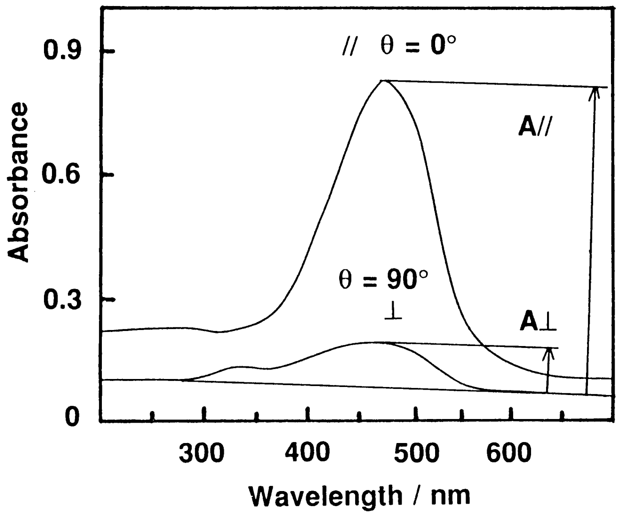


Fig. 6. Dichroism of the stretched PVA-PTPy film observed as shown in Fig. 2.

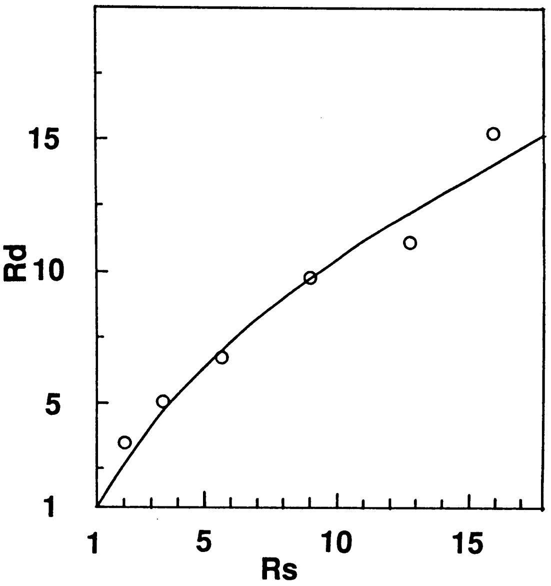


Fig. 7. Dependence of Rd on Rs for the stretched PVA-PTPy film.

of PBPy, because transition moment of the π-π* absorption of the non-linear PTPy molecules will not be completely aligned along the direction of the stretching. The R_d value for the PVA-PTPy film is stable and unvaried even after leaving the film at room temperature for 2 years.

Thus, not only PBPy, the highly linear molecules, but also a rather randomly coiled PTPy are aligned along the direction of the stretching of the PVA film, and the present results are expected to render bases for further usage of the optically interesting PTPy molecules for making optical devices.

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