# Dichroism of $\pi$-Conjugated Poly(quinoxaline-5,8-diyl)s in Stretched Poly(vinyl alcohol) Film and Photoluminescence of the Polymer

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Poly(quinoxaline-5,8-diyl)s exhibit two $\pi$-$\pi^*$ absorption bands, and one of the two absorption bands is assigned to a $\pi$-$\pi^*$ transition occurred along the direction of the polymer main chain from their dichroism. Photoluminescence of the polymer suggests intramolecular energy transfer.

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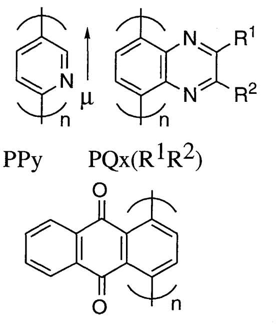
Optical properties of $\pi$-conjugated polymers are the subject of recent interest.[1] It has recently been reported that a strong dichroism is observed for $\pi$-$\pi^*$ transition of $\pi$-conjugated poly(pyridine-2,5-diyl) PPy molecules in a stretched poly(vinyl alcohol) PVA film.[2] In the case of PPy, the $\pi$-$\pi^*$ absorption band of the pyridine unit at 248 nm[3] completely disappears in the polymer, and its UV-visible spectrum exhibits only one absorption band at 375 nm originated from the $\pi$-$\pi^*$ transition occurred along the polymer chain; the absorption band is considered to have a transition moment $\mu$ along the direction of the linear rod-like polymer chain to show the strong dichroism in the stretched PVA film.



PPy PQx($R^1R^2$)

P(1,4-AQ)

$R^1 = R^2$ = H: PQx
$R^1 = R^2$ = *p*-tolyl: PQx(diTol)
$R^1 = R^2$ = 2-pyridyl: PQx(diPy)
$R^1$ = n-butyl; $R^2$ = phenyl: PQx(BuPh)

However, in cases of poly(arylene)s constituted of repeating units having a larger $\pi$-system, e.g., poly(quinoxaline-5,8-diyl) PQx,[4] poly(anthraquinone-1,4-diyl) P(1,4-AQ),[5] and their derivatives, their UV-visible spectra show several $\pi$-$\pi^*$ absorption bands (presumably one with along the polymer chain and others related to the $\pi$-$\pi^*$ transitions in the repeating monomer unit), and assignment of the $\pi$-$\pi^*$ absorption occurred along the polymer chain is considered of importance for comprehension of basic optical properties of the $\pi$-conjugated polymers. We report here that such assignment is possible with PQx's shown above.

PQx's give two UV-visible absorption bands in a region of 300-500 nm under various conditions: (i) in $CHCl_3$,[6] (ii) as cast film on a quartz plate, and (iii) in the surface region of a PVA film, the last sample being prepared by painting a PVA film with a formic acid solution of the polymer and drying under vacuum. Figure la exhibits the UV-visible absorption spectrum of a PQx(diTol) cast film on a quartz plate, which shows two absorption bands, Band A and Band B; essentially the same spectrum is observed in $CHCl_3$.

When a PVA film containing PQx(diTol) is stretched, the PQx(diTol) molecules are considered to be aligned along the direction of the stretching as in the case of PPy molecules in the stretched PVA film, and the aligned PQx(diTol) is expected to

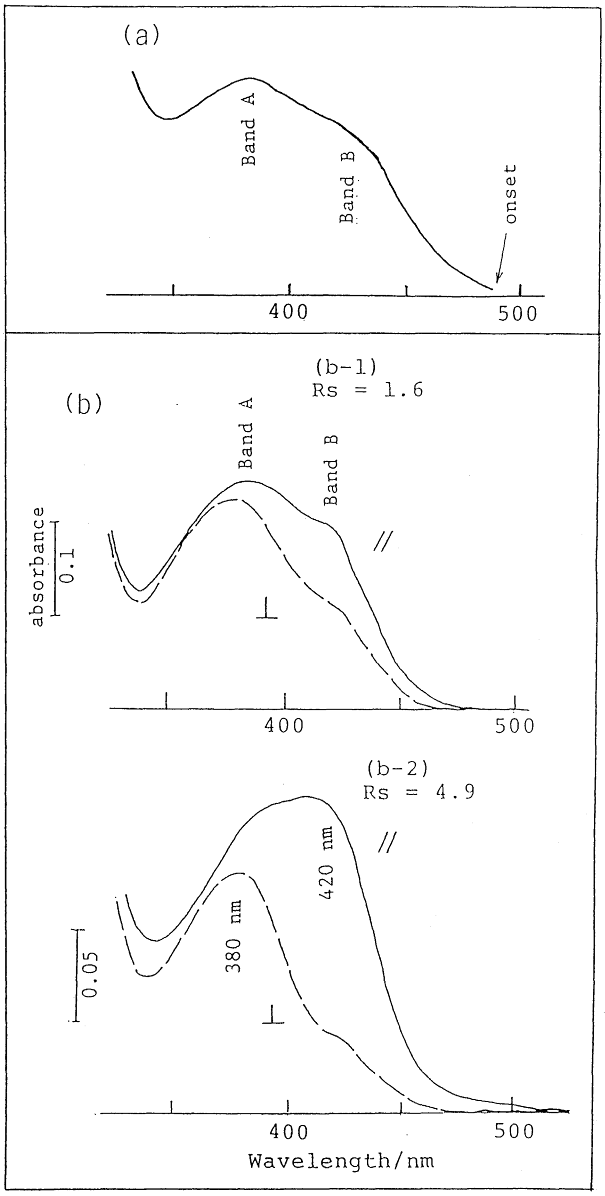


**Figure 1**. UV-visible spectra of (a) PQx(diTol) film on a quartz plate and (b) stretched PVA film containing PQx(diTol) at stretching ratio $Rs^2$ of (b-1) 1.6 and (b-2) 4.9. In Figure 1b, the solid and broken lines are observed by irradiation with polarized light at // and ⊥ modes (Figure 2), respectively.

exhibit dichroism on irradiation with polarized light (Figure 2) and make it possible to assign the π-π* absorption band having the transition moment along the polymer chain.

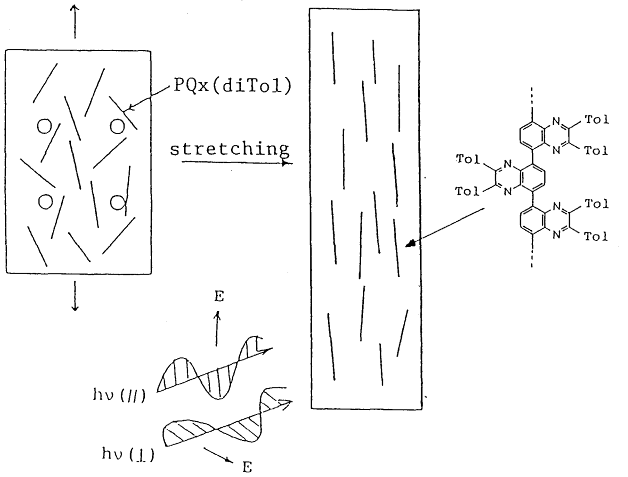


**Figure 2.** Stretching of PVA film containing PQx(diTol) and irradiation with polarized light, hν(//) and hν(⊥).

As shown in Figure 1b,[7] Band B shows high intensity on irradiation with polarized light with its oscillating electric field in the direction of the stretching of the PVA film (Figure 2, hν(//)), whereas its intensity considerably decreases on irradiation with polarized light with its oscillating electric field perpendicular to the direction of the stretching. These results clearly indicate that the π-π* transition of Band B takes place along the polymer main chain or the direction of the stretching.

On the contrary, intensity of Band A receives only a minor effect[8] from the direction of the oscillating electric field of the light. This suggests that Band A arises mainly from the π-π* in the repeating monomer unit. Actually all of PQx's and quinoxaline derivatives give an absorption band near Band A, although the position of Band A shifts to somewhat longer wavelength by introducing the aromatic substituent(s) as the $R^1$ and $R^2$ groups. The dichroic ratio Rd (e.g., ca. 5 at a stretching ratio Rs of 4.9) observed with PQx (diTol) is smaller than that observed with PPy (Rd = ca. 10 at Rs = 4.9) presumably due to less rigidly linear structure of PQx(diTol). Other PQx's depicted above also show dichroism similar to that observed with PQx(diTol). However, a PQx with two ($R^1$ and $R^2$) *p*-methoxyphenyl substituents did not exhibit the dichroism; its reason is not clear at the moment.

One of other interesting optical properties of PQx's is that they show strong photoluminescence when they have at least one aromatic substituest.[4] The peak position (e.g., 492 nm for PQx(diTol)) of the photoluminescence generally appears at onset position of Band B (Figure 1), revealing that the photoluminescence takes place by migration of electron in an excitated state related to Band B to its corresponding ground state. Such agreement between the onset position of the π-π* transition band and the peak position of the photoluminescence is generally observed with various π-conjugated compounds including π-conjugated poly(arylene)s.

Irradiation with 420 nm light corresponding to Band B actually causes the photoluminescence of PQx(diTol) with the peak at 492 nm. However, irradiation with 380 nm light corresponding to Band A also leads to the photoluminescence with the same peak pattern. In addition, an excitation spectrum monitored at the peak position of the photoluminescence (492 nm) gives two peaks which agree with the peak positions of Band A and Band B, respectively. PQx(diPy) and PQx(BuPh) give analogous results, and these results indicate that energy of photoactivated monomer unit (Band A) is transferred to the main chain of the polymers and light is emitted from the activated main chain π-conjugation system. Energy transfer (or internal conversion) from a photoactivated molecular unit to another molecular unit is the subject of recent interest.

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## References and Notes

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6 PQx(BuPh) was fully soluble in $CHCl_3$, howeve, other PQx's were only partly soluble in $CHCl_3$; in the latter case, the UV-visible absorption data in $CHCl_3$ were obtained with the $CHCl_3$-soluble fraction.

7 Absorption by the PVA film is corrected.

8 The decrease in the intensity of Band B at the ⊥ mode in Figure 1b-2 will leads to decrease in its tail absorption at 380 nm (the position of Band A). It one takes into account of this, the intensity of Band A seems to be increased at the ⊥ mode compared with that at the // mode.