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π-Conjugated Charge Transfer Polymer Constituted of Electron-donating Thiophene and Electron-withdrawing Quinoxaline

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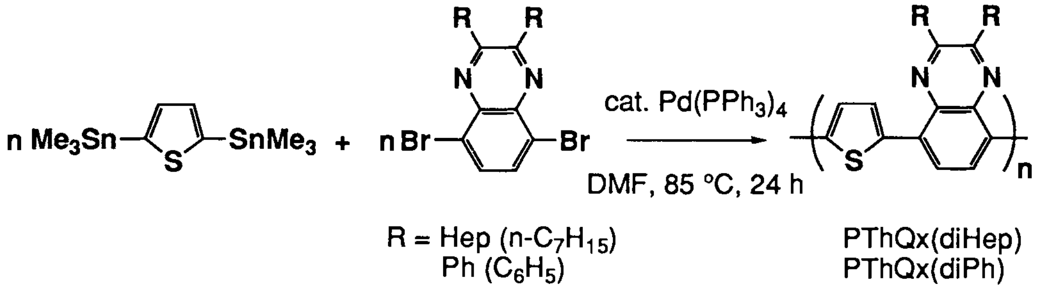
Palladium-catalyzed polycondensation between 2,5-bis(trimethylstannyl)thiophene and 5,8-dibromoquinoxaline derivatives gives soluble new π-conjugated polymers, which exhibit absorption bands at 575 ± 30 nm assignable to intramolecular charge transfer bands and show the three-photon resonant third-order nonlinear optical susceptibility $\chi^{(3)}$ of about 5×10^{-11} esu.

Electronic and optical properties of π-conjugated polymers have been the subject of recent interest, and numerous papers have been published on the preparation and properties of various types of π-conjugated polymers. However, π-conjugated polymers with charge transfer structure constituted of electron-donating unit and electron-withdrawing unit have received less attention.[1,2] Previously it was reported that such π-conjugated charge transfer type polymers constituted of electron-donating thiophene and electron-withdrawing pyridine rings show interesting electronic and optical properties including their showing charge transfer band and considerably larger $\chi^{(3)}$ values compared with usual poly(arylene)s.[1,3] In order to obtain further information about such π-conjugated charge transfer polymers, we have prepared new polymers constituted of thiophene and quinoxaline rings, the latter of which has higher electron-withdrawing ability than the pyridine ring due to its having two π-electron-withdrawing imine nitrogens,[4] and report the results.



(1)

Application of an organometallic polycondensation[5)] between 2,5-bis(trimethylstannyl)thiophene and 5,8-dibromoquinoxaline derivatives gives the following alternative π-conjugated polymers PThQx's.

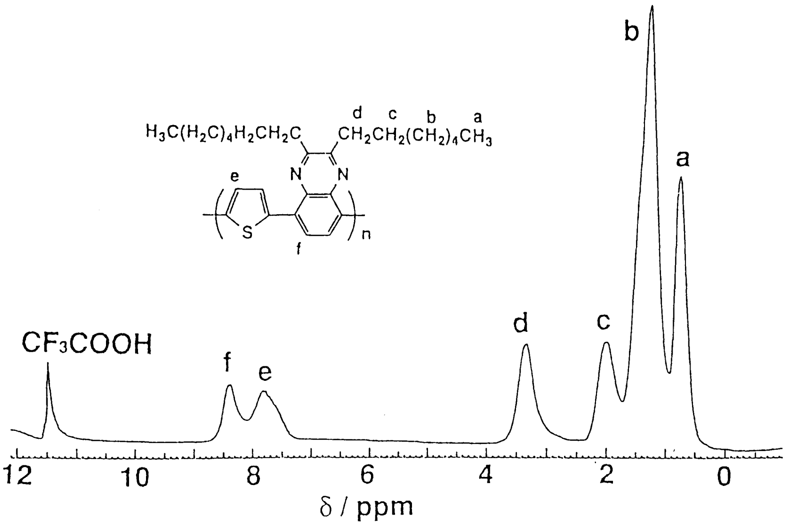
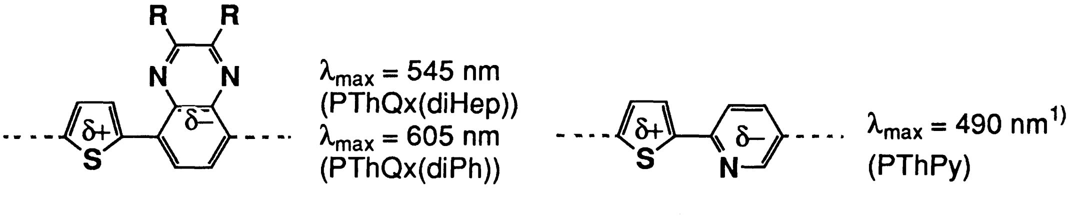


Fig. 1. ^{1}H-NMR (100 MHz) of PThQx(diHep) in CF_3COOD.

Data from elemental analysis[6)] of PThQx(diHep) and PThQx(diPh) as well as IR and NMR (Fig. 1) spectra agree with the formulae shown above. PThQx(diHep) is soluble in CF_3COOH and $CHCl_2COOH$ and give the [η] value of 0.47 dLg^{-1} (dL = 100 cm^3) at 30 °C in $CHCl_2COOH$. PThQx(diPh) is also soluble in CF_3COOH, and drying up the CF_3COOH solutions of PThQx's under vacuum affords original PThQx's as proved by IR spectroscopy. UV-visible spectra of the CF_3COOH solutions of PThQx(diHep) and PThQx(diPh) (Fig. 2) exhibit absorption bands at λ_{max} = 545 and 605 nm (ε = ca. 5000 M^{-1} cm^{-1}; M is based on the repeating unit). The absorption bands locate at longer wavelength compared with those of poly(thiophene-2,5-diyl) PTh (λ_{max} = 420-480 nm)[1a)] and the corresponding poly(2,3-diheptylquinoxaline-5,8-diyl) PQx(diHep) (λ_{max} = 374 nm) and poly(2,3-diphenylquinoxaline-5,8-diyl) PQx(diPh) (λ_{max} = 420 nm).[4c)] These results support the occurrence of the charge transfer between the thiophene and quinoxaline rings similar to that previously postulated for the π-conjugated copolymer constituted of the thiophene and pyridine units.[1)]

The charge transfer (CT) absorption is generally considered to originate from the



Scheme 1.

interaction between occupied orbital(s) of donor and unoccupied orbital(s) of acceptor, and the CT band is to appear at longer wavelength when the energy difference between the ionization potential of the donor and the electron affinity of the acceptor is smaller.$^{7)}$ Polarographic reduction potentials ($E_{1/2}$) of pyridine and quinoxaline are reported to be -2.15 and -1.09 V (vs. a mercury pool),$^{4a)}$ respectively, indicating that quinoxaline has stronger electron-accepting properties than pyridine. Thus, the appearance of the CT bands of PThQx's at longer wavelength (545-605 nm, Scheme 1) than those of PThPy (490 nm) is reasonably accounted for by the stronger electron-accepting properties of the quinoxaline ring than the pyridine ring. The difference in the λ_{max} position between PThQx(diHep) and PThQx(diPh) is explained by the difference in the inductive effect between the heptyl and phenyl groups and/or larger π-conjugation system of the 2,3-diphenyl-quinoxaline unit than that of 2,3-diheptylquinoxaline unit.

Casting of the CF_3COOH solutions of PThQx's on glass plates and removal of CF_3COOH under vacuum gives films with good optical quality. The films of PThQx(diHep) and PThQx(diPh) on the glass substrate show the absorption bands at 570 and 600 nm, respectively, which are also assigned to the CT band. Both the PThQx(diHep) and PThQx(diPh) films give the third-order nonlinear optical susceptibility $\chi^{(3)}$ of about 5 x 10^{-11} esu at three photon resonance region (fundamental wavelength (λ_f) = 1.7 µm; $\lambda_f/3$ = 567 nm) and 1 x 10^{-11} esu in nonresonant region (λ_f = 2.2 µm) of the polymers, as shown in Fig. 2 for the PThQx(diHep) film (thickness = 0.079 µm). The $\chi^{(3)}$ values are considerably larger than those of usual poly(arylene)s$^{8)}$ without the CT structure (e.g., poly(thiophene-2,5-diyl) and poly(pyridine-2,5-diyl)) and comparable to those of PThPy and poly(phenylenevinylene).

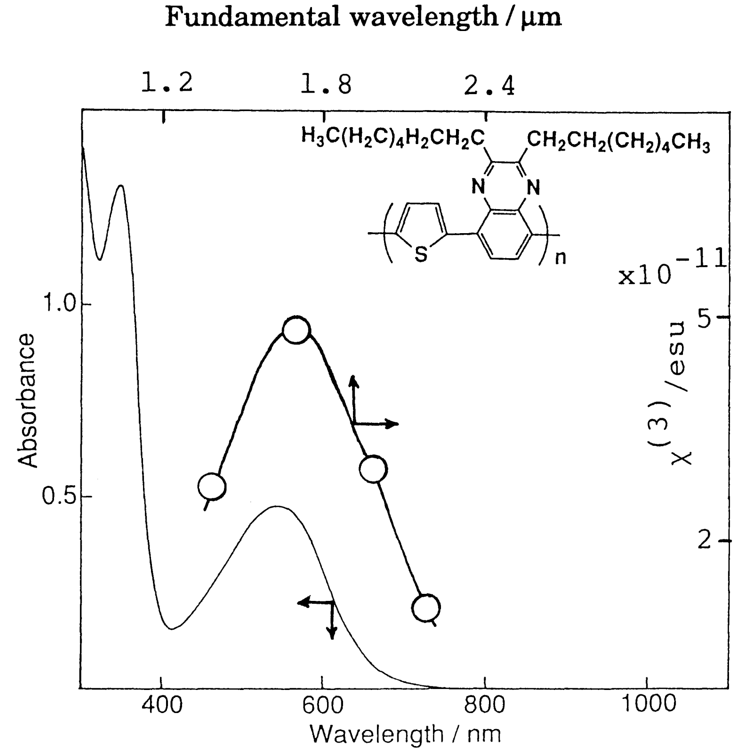


Fig. 2. UV-visible spectrum of PThQx(diHep) in CF_3COOH and the $\chi^{(3)}$ data.

The results shown above, together with the previously reported examples,$^{1,2)}$ indicate that the π-conjugated polymers constituted of electron-donating aromatic unit and electron-withdrawing aromatic units, in general, exhibit absorption bands which are accounted for by the charge-transferred structure and they give large $\chi^{(3)}$ values. Since PThQx's are soluble in organic solvents, they may serve as materials to make interesting optical devices utilizing their large $\chi^{(3)}$ values.

References

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6) PThQx(diHep): Found: C, 75.3; H, 8.3; N,6.3; Br, 0.6%. Calcd for $(C_{26}H_{34}N_2S)_n$: C, 76.8; H, 8.4; N. 6.9%. PThQx(diPh): Found: C, 78.3; H, 4.1; N, 7.2; Br, 1.1%. Calcd for $(C_{24}H_{14}N_2S)_n$: C, 79.5; H, 3.9; N, 7.7%. Determination of the molecular weight of PThQx(diHep) and PThQx(diPh) by a light scattering method was not possible due to the absorption band in the visible region. If the polymers have mono-brominated quinoxaline units at both the ends of the polymers, the molecular weights of PThQx(diHep) and PThQx(diPh) are calculated as 27000 and 15000, respectively, from the content of Br. Experimental conditions for the preparation of PThQx(diHep): a mixture of 2,5- bis(trimethylstannyl)thiophene (0.41 g, 1.0 mmol), 5,8-dibromo-2,3-diheptylquinoxaline (0.48 g, 1.0 mmol), and $Pd(PPh_3)_4$ (0.12 g, 0.1 mmol) was stirred in 25 cm^3 of DMF. Yield = 96%. PThQx(diPh) was prepared analogously. Yield = 95%.

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