Intermolecular π-π Interaction of Poly(4,4'-dialkyl-2,2'-bithiazole-5,5'-diyl)s and Photoluminescence of the Polymers

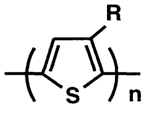
Takakazu Yamamoto,* Tsukasa Maruyama, Hajime Suganuma, Minoru Arai, Dharma Komarudin, and Shintaro Sasaki†
Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226
†Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Tatsunokuchi, Ishikawa 923-12

(Received October 15, 1996)

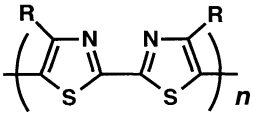
UV-vis. absorption spectra of films of regioregular poly(4,4'-dialkyl-2,2'-bithiazole-5,5'-diyl)s PRBTz's show bathochromic shifts from those of PRBTz's in solutions and their corresponding regio-irregular polymers. This bathchromic shift is considered to originate from stacking of the polymer, and powder X-ray diffraction and photoluminescence data support this view.

Compounds with large π-conjugation systems (e.g., phthalocyanines) often form a stacked structure in the solid, and UV-visible absorption peaks of such compounds in the stacked solid state are usually shifted to a longer wavelength from those in solutions due to an intermoleular π-π interaction in the solid.[1] Recently it has been reported that π-conjugated and regioregular (head-to-tail HT type) poly(3-alkylthiophene-2,5-diyl) P3RTh also forms a face-to-face stacked structure in the solid state (in film) and the stacked polymer molecules give an absorption band at a longer wavelength than that observed in solutions.[2,3]

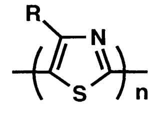
On the other hand, recently preparation of another type of π-conjugated polymers, poly(4,4'-dialkyl-2,2'-bithiazole-5,5'-diyl)s PRBTz's, constituted of similar 5-membered rings and having a head-to-head HH type regular structure, has been reported.[4]



P3RTh



PRBTz



PRTz

In order to expand the scope of stacking of π-conjugated polymers, we have investigated optical properties of PRBTz in comparison with those of P3RTh and here report the results.

As described in the previous paper, a crystallin film of HT type P3HexTh (R = hexyl) shows a π-π^* absorption band at a longer wavelength than an amorphous film of random type (HT/HH ratio = 3/7) P3HexTh,[2,3]

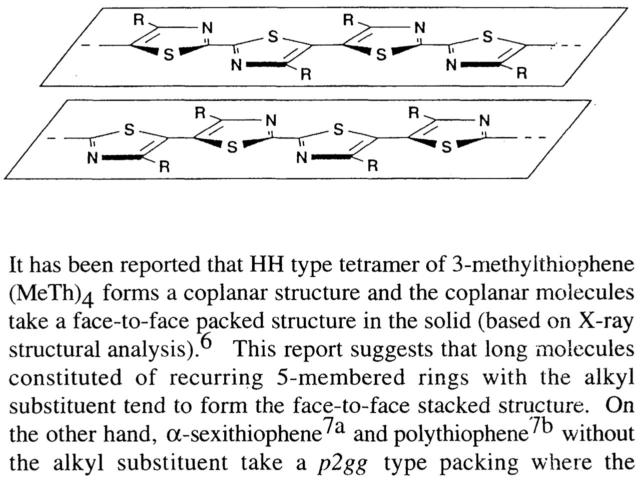
P3HexTh: film HT type: 560 nm } difference =
random type: 430 nm } 5400 cm^{-1}
in solution: both types: 430 ± 15 nm

although, in solutions (e.g., in CH_2Cl_2), both the polymers give the absorption peak at almost the same position (λ_{max} = 430 ± 15 nm) near the absorption peak of the amorphous P3HexTh (HT/HH = 3/7) film.[5] A similar difference is observed between solvent-free films (cast from trifluoroacetic acid and dried under vacuum) of PMeBTz (R = CH_3) and its corresponding random type polymer PMeTz (R = CH_3: see the above shown structural formula) with a HT/HH ratio of 3/7.[4b]

PMeBTz: film: 498 nm } difference =
PMeTz: film: 420 nm } 3700 cm^{-1}
PMeBTz and PMeTz in solution: 420 nm

In solutions (e.g., in trifluoroacetic acid), both the polymers show the absorption peak at almost the same position (λ_{max} = 420 nm) near the λ_{max} position of the film of regio-irregular PMeTz, similarly to the case of P3HexTh.

Although regio-irregular PMeTz forms amorphous solid, powder X-ray diffraction pattern of the regioregular PMeBTz shows several distinct peaks at scattering angle $2\theta(CuK_\alpha)$ = 12.6, 25.2, ca. 39, and ca. 51°. The molecules are stacked with a separation of b in the C-centered orthorhombic unit cell with dimensions a = 14.1 Å, b = 3.64 Å, c = 7.61 Å, γ = 90 °. The following proposed stacking mode of PMeBTz in view of the atomic van der Waals contact is similar to those proposed for HT type P3RTh.[2,3]



It has been reported that HH type tetramer of 3-methylthiophene $(MeTh)_4$ forms a coplanar structure and the coplanar molecules take a face-to-face packed structure in the solid (based on X-ray structural analysis).[6] This report suggests that long molecules constituted of recurring 5-membered rings with the alkyl substituent tend to form the face-to-face stacked structure. On the other hand, α-sexithiophene[7a] and polythiophene[7b] without the alkyl substituent take a *p2gg* type packing where the molecules are packed with their molecular planes tilted from each other.

A UV-visible spectrum (Figure 1a) of a solvent-free film of PBuBTz (R = butyl) also shows a bathochromic shift of the π-π^* absorption peak compared with that of PBuBTz in a solution (in trifluoroacetic acid).

PBuBTz: film: 550 nm } difference =
in solution: 422 nm } 5520 cm^{-1}

Although the corresponding regio-irregular PBuTz has not been prepared, the results also suggest the presence of intermolecular π-π interaction in the film of PBuBTz. The UV-visible spectrum of the film of PBuBTz exhibits a shoulder absorption band at about 450 nm besides the main absorption band at 550 nm. The film of regioregular HT type P3HexTh also exhibits a shoulder absorption band (Figure 1b), although the shoulder absorption band is not so distinct. These results suggest that the films of PBuBTz and regioregular P3HexTh partly contain amorphous part in addition to the main face-to-face stacked crystalline part.

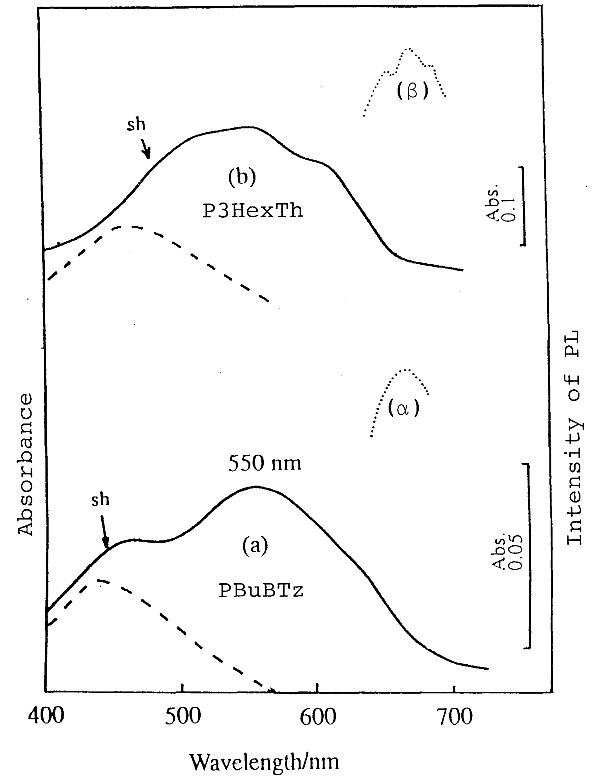


Figure 1. UV-vis. spectra of (a) PBuBTz and (b) P3HexTh (HT/HH = 10/0). Solid and broken lines indicate the spectra of film and solution (solvent = trifluoroacetic acid for (a) and chloroform for (b)[2]), respectively. Dotted lines (α) and (β) indicate PL spectra (irradiated with λ_{max} light) of PBuBTz and P3HexTh films, respectively.

Relative strength of the shoulder peak varies with preparative conditions (temperature, solvent, etc.) of the film, presumably due to a change in a relative amount of the amorphous part. As for PBuBTz, the polymer with a higher molecular weight ($[\eta] = 0.85\ dLg^{-1}$; $dL = 100\ cm^3$) usually gives a stronger shoulder peak than that with lower molecular weight ($[\eta] = 0.39\ dLg^{-1}$). A thinner film generally show a relatively stronger shoulder peak. The PMeBTz film does not exhibit such a shoulder peak, probably due to a well-stacked structure.

All of the above shown polymers exhibit photoluminescence PL both in solutions and films. In solutions, their photoluminescence spectra show peaks at onset positions[2,4] of the UV-absorption bands as usually observed with fluorescent aromatic compounds, suggesting that the photoluminescence in solution involves essentially a unimolecular process.

Photoluminescence peak (λ_p) in solution:
PMeBTz: 562 nm PMeTz: 572 nm
P3HexTh (HT/HH = 10/0): 570 nm
P3HexTh (HT/HH = 3/7): 555 nm
PBuBTz: 570 nm

In the case of film, irradiation with light at the λ_{max} position ($\lambda_{ex} = \lambda_{max}$ of main peak) causes emission of light with the following peak positions.

Photoluminescence peak (λ_p) in film:
PMeBTz: 670 nm PMeTz: 540 nm
P3HexTh (HT/HH = 10/0): 670 nm
P3HexTh (HT/HH = 3/7): 590 nm
PBuBTz: 670 nm

The λ_p positions also agree with onsets of the absorption bands of the films, revealing that the photoluminescence takes place by involving the interchain π-π interaction.

On the other hand, irradiation of the PBuBTz film with light at the wavelength of the shoulder peak (λ_p = 460 nm) gives the photoluminescence with λ_p of 590 nm, near the λ_p positions of PBuBTz in the solution (Fig. 1);[8] these results support the above described assumption that the shoulder peak originates from amorphous part of the PMeBTz film. However, irradiation of the light (λ_p = 455 nm) also leads to weak emission of light at 690 nm. These results indicate that (i) a photo-activated single PBuBTz molecule in the amorphous part transfers its absorbed energy to the PBuBTz molecules in the crystalline part or (ii) the photo-activated PBuBTz molecule forms an excimer-type adduct with neighboring PBuBTz molecule(s). Such a molecule-to-molecule energy transfer and formation of excimer-type adduct are subjects of recent interest. Irradiation of the film of P3HexTh (HT/HH = 10/0) with light at the shoulder peak gives analogous results. Thus, the above described data reveal a general trend that π-conjugated five-membered ring polymers form the stacked structure in the solid state, and their films show unique optical properties.

References and Notes

1 C. C. Leznoff and A. B. P. Lever, ed., "Phthalocyanines," VCH Publisher, New York, (1989) Vol. 1 and (1993) Vol. 3; Z. Z. Ho, C. Y. Ju, and W. M. Hetherington III, J. Appl. Phys., **62**, 716 (1996).
2 T. -A. Chen, X. Wu, and R. D. Rieke, *J. Am. Chem. Soc.*, **117**, 233 (1995).
3 T. Yamamoto, *Chem. Lett..*, **1996**, 703.
4 a) T. Yamamoto, H. Suganuma, T. Maruyama, and K. Kubota, *J. Chem. Soc., Chem. Commun.*, **1995**, 1613. b) T. Maruyama, H. Sugiyama, and T. Yamamoto, *Synth. Met.*, **74**, 183 (1995).
5 The HT type P3HexTh is considered to be partly coagulated through the stacking even in solutions to show λ_{max} at a somewhat longer wavelength than that of random type P3HexTh.[3]
6 G. Barbarella, M. Zambianchi, A. Mongini, and L. Antolini, *Adv. Mater.* **4**, 282 (1992).
7 a) G. Horowitz, B. Bachet, A. Yassar, P. Lang, F. Demanze, J. -L. Fave, and F. Garnier, *Chem. Mater.*, **7**, 1337 (1995); b) S. Bruckner and W. Porzio, *Makromol. Chem.*, **189**, 961 (1988).
8 Background PL was reduced.