SHORT COMMUNICATIONS

Colloidal Solution of Poly(3-hexylthiophene-2,5-diyl) in Mixtures of Chloroform and Methanol and Alignment of the Polymer in Stretched Poly(ethylene terephthalate) Film. Investigation for Intermolecular Interaction and Alignment of the Polymer

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Preparation and properties of π-conjugated poly(arylene)s such as polyphenylenes, polypyrroles, and polythiophenes are the subject of recent many papers.[1,2] Recently it has been reported that regioregular 5-membered ring poly(arylene)s such as HT (head-to-tail) type poly(3-alkylthiophene-2,5-diyl)[3] (P3RTh) and HH (head-to-head) type poly(4,4'-dialkyl-2,2'-bithiazole-5,5'-diyl)[4] (PRBTz) form stacked structures in the solid state.

P3RTh   PRBTz
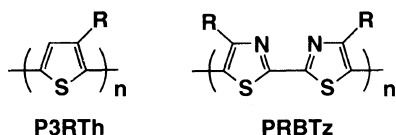
The π–π* absorption peak of the film of regioregular polymer appears at a longer wavelength by about 80—130 nm, compared with that of the corresponding regio-irregular polymer, presumably due to π–π intermolecular interaction between the regioregular polymer molecules in the film.
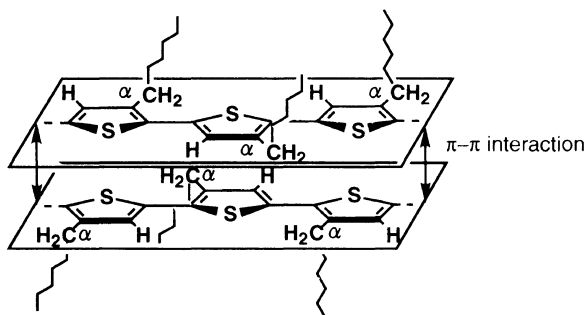
In the course of our investigation on P3RTh, we have noticed that (a) the polymer forms stable colloidal solutions in mixtures of $CHCl_3$ and CH_3OH and (b) the polymer is aligned in stretched poly(ethylene terephthalate) PET film to show dichroism. Results obtained from these findings give further interesting information on the polymer, and here we report the results.

EXPERIMENTAL

P3HexTh (Zn/Ni) [poly(3-hexylthiophene-2,5-diyl)

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obtained by using zinc and a nickel complex][3b] with HT/HH = 10/0 and M_n (GPC, polystyrene standard) of 16×10^3 was purchased from Rieke Metals, Inc. P3HexTh (Fe) with HT/HH = 6.3/3.7 and M_n of 33×10^3 and P3HexTh (Ni) with HT/HH = 3/7 and M_n of 7.6×10^3 were prepared according to the literature by using $FeCl_3$[5] and a zerovalent nickel complex,[6] respectively.

UV-visible spectra and photoluminescence spectra were recorded on Shimadzu UV-3100 PC and Hitachi 4010 spectrometers, respectively. Unstretched PET film was kindly donated from Toyobo Co., Ltd.

RESULTS AND DISCUSSION

$CHCl_3$ is a good solvent for P3HexTh,[7] whereas the polymer is insoluble in CH_3OH. However, addition of CH_3OH to a reddish yellow solution of P3HexTh in $CHCl_3$ gives a stable red colloidal solution over a wide range of the $CHCl_3/CH_3OH$ ratio. The colloidal solution is stable over several weeks at the concentration of P3HexTh below about 15 mg per 1 liter; at a higher concentration of P3HexTh, gradual precipitation of red P3HexTh is observed.

Figure 1A exhibits changes of the UV-visible spectrum of P3HexTh (Zn/Ni) on addition of CH_3OH to the $CHCl_3$ solution of the polymer. As shown in Figure 1A, by addition of CH_3OH, the peak of P3HexTh (Zn/Ni) at 450 nm is decreased, whereas the peaks characteristic of P3HexTh (Zn/Ni) in the solid state (the inset in Figure 1A) at 520, 560, and 610 nm increase. Although these data suggest aggregation of the polymer due to the above described stacking, the minor effect of added CH_3OH on the base line in a range of 700—800 nm indicates that the size of the aggregated particle is smaller than an order of 10^3 nm (1 μm). However, the aggregated particle does not pass through a membrane with a pore size of 0.02 μm. After the filtration by the membrane, the solution corresponding to c (CH_3OH content = 20%) in Figure 1A shows only an absorption band at 450 nm (a in Figure 1A) due to single molecule of P3HexTh (Zn/Ni), and the absorption bands assigned to the stacked unit almost completely disappear; the absorbance of the filtrate reveals that about half of P3HexTh (Zn/Ni) exists as the non-stacked molecule in the solution c shown in Figure 1A. All of the P3HexTh (Zn/Ni) molecules in $CHCl_3$ pass through the membrane with the pore size
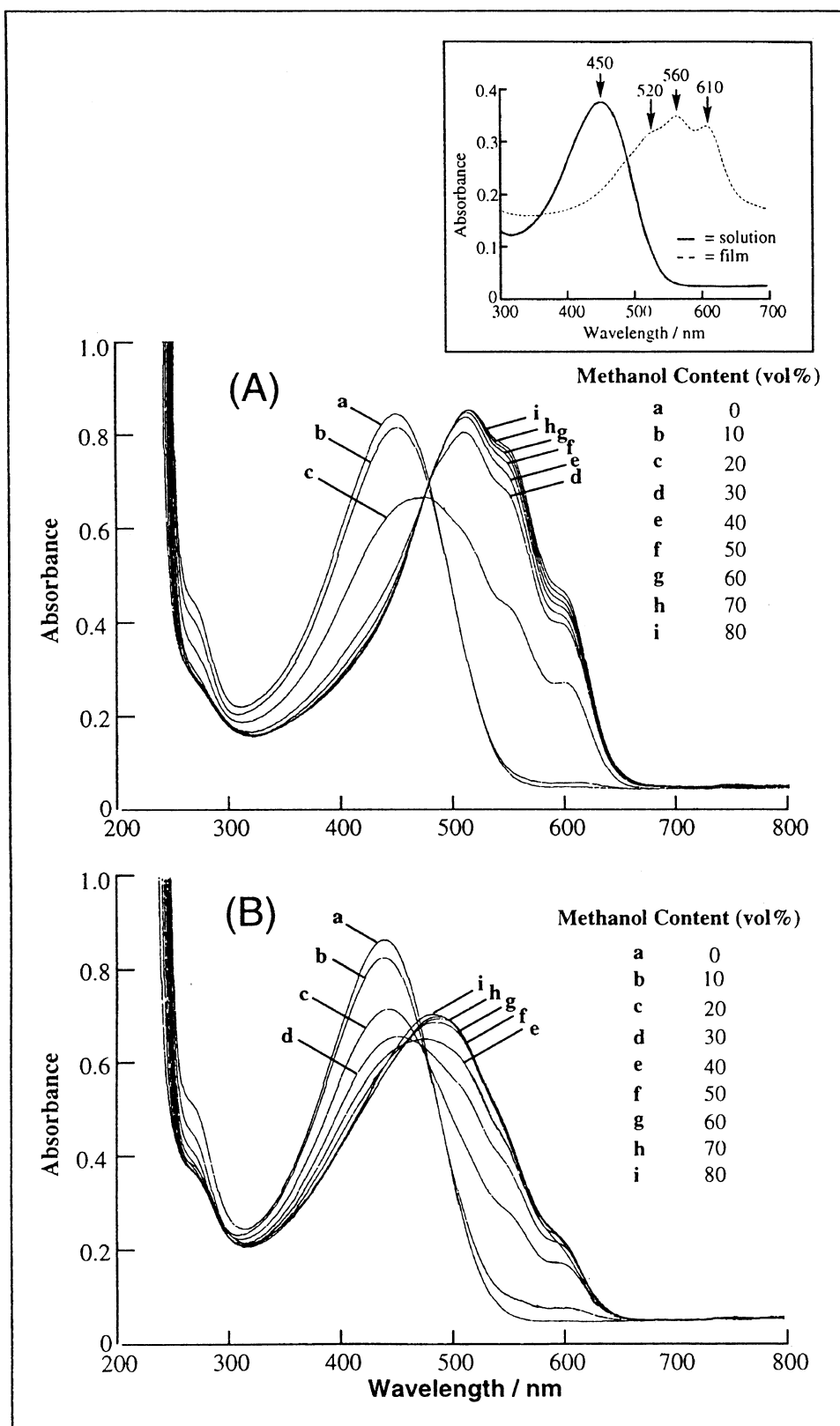
Figure 1. Change of the UV-visible spectrum of (A) P3HexTh (Zn/Ni) and (B) P3HexTh (Fe) on addition of CH_3OH to the $CHCl_3$ solution. The inset in Figure 1A compares the UV-visible spectrum of P3HexTh (Zn/Ni) in $CHCl_3$ and that in the solid state (film).[3b] At room temperature (about 20°C). [P3HexTh] $= 15\,mg\,l^{-1}$.

of 0.02 μm.

Light scattering analysis[8] of the colloidal solution with He–Ne laser (632.8 nm) suggests aggregation of about 1000 linear P3HexTh (Zn/Ni) molecules; the degree

of aggregation roughly corresponds to a diameter of 0.02—0.03 μm if the 1000 molecules form a columnar aggregate. Detailed results of the light scattering analysis will be reported in future.
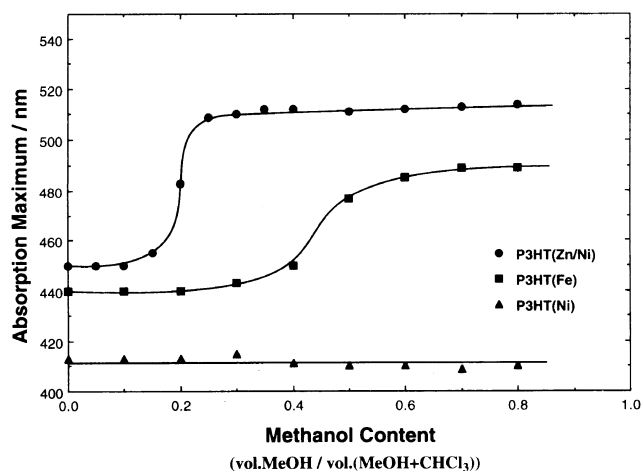
Figure 2. Change of absorption peak on addition of CH_3OH to the $CHCl_3$ solution of P3HexTh.
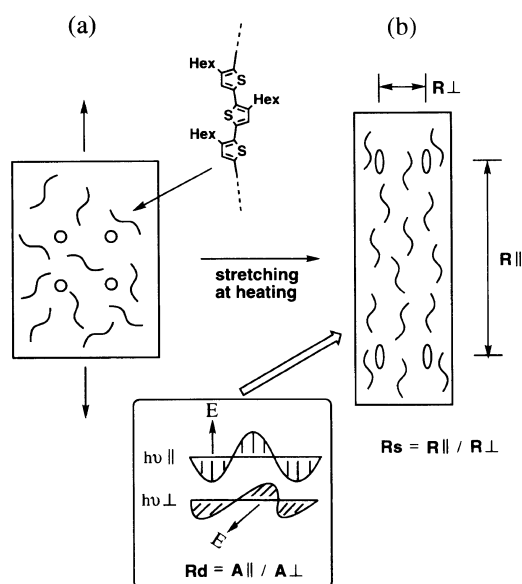

Figure 3. Procedure for measurement of dichroism of stretched PET film containing P3HexTh.

Figure 4. Dichroism of the stretched PET film containing (a) P3HexTh (Zn/Ni) and (b) P3HexTh (Fe). Charts with the ∥ and ⊥ marks are obtained with $hv_∥$ and $hv_⊥$ (Figure 3b).

P3HexTh (Fe) containing the HT unit in a high content (63%) also show an analogous change in the UV-visible spectrum on addition of CH_3OH as shown in Figure 1B, however, addition of CH_3OH to the $CHCl_3$ solution of P3HexTh (Ni) causes no observable shift of the absorption peak, indicating that it is difficult for P3HexTh(Ni) with a low content of the HT unit (30%) to form the stacked structure. Changes of the absorption peak of various P3HexThs on addition of CH_3OH are depicted in Figure 2, and the results clearly indicate a strong tendency of the regioregular P3HexTh (Zn/Ni) to form the stacked structure, in accordance with the previous results observed with P3HexThs in $CHCl_3$ at low temperatures.[3c] At low temperatures below 0°C, P3HexTh (Zn/Ni) seems to have lower solubility than P3HexTh (Fe) and P3HexTh (Ni).

All the UV-visible spectra shown in Figures 1A, 1B, and the inset in Figure 1A have substructures with peaks at 520, 560, and 610 nm. Two reasons are conceivable for the substructure; one is related to vibronic coupling, and another is separation of the peak according to the
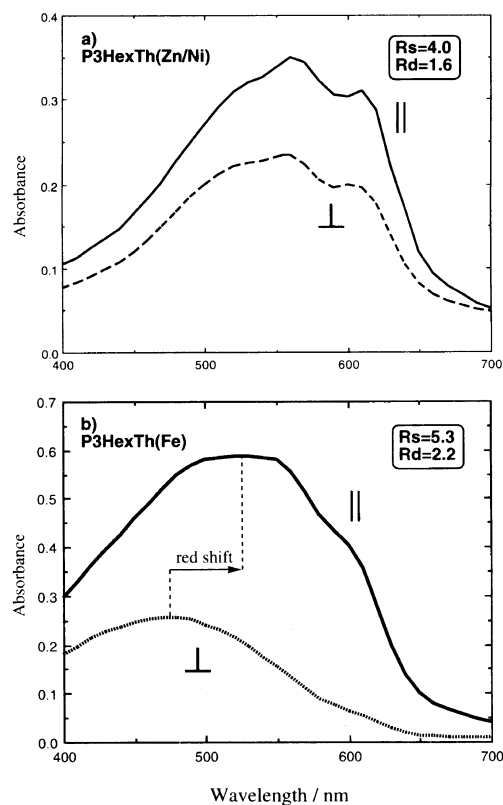
degree of stacking. The energy difference between the peaks (ca. $1400 cm^{-1}$) roughly agrees with the ring vibration frequency of the thiophene ring. However, the relative intensity of the peaks varies with the sample as shown in Figure 1. This suggests that the 3 absorption peaks rather corresponds to the stacked units with different degrees of stacking, although there still is a possibility that the peak separation originates from the vibronic coupling and the relative intensity of the peaks is affected by the state of the P3HexTh (Zn/Ni) molecule in the aggregate or in the solid. If the peak separation reflects the different degrees of stacking, the peak at 610 nm is associated with a highly stacked state. Photoluminescence study indicates that irradiation of the solution c (in Figure 1A; $CHCl_3/CH_3OH = 80/20$) with any of light at 460 nm (near absorption band by single P3HexTh (Zn/Ni) molecule), 480 nm, 550 nm, and 600 nm leads to emission of light only at 583 nm and 624 nm, which seem to correspond to onsets of the absorption bands at 560 nm and 610 nm. These data suggest occurrence of energy migration from the photoactivated non-stacked unit or the photoactivated stacked unit with a lower degree of stacking to the stacked unit with a higher degree of stacking. Photoluminescence usually occurs at the onset of the absorption band of the corresponding chromophore.[1,2,9]

Stretching of polymer film containing linear π-conjugated polymer sometimes gives valuable information about the structure of the polymer.[9] Painting PET film with the $CHCl_3$ solution of P3HexTh and drying gives the PET film containing P3HexTh in a surface region (Figure 3a) and stretching of the PET film will lead to
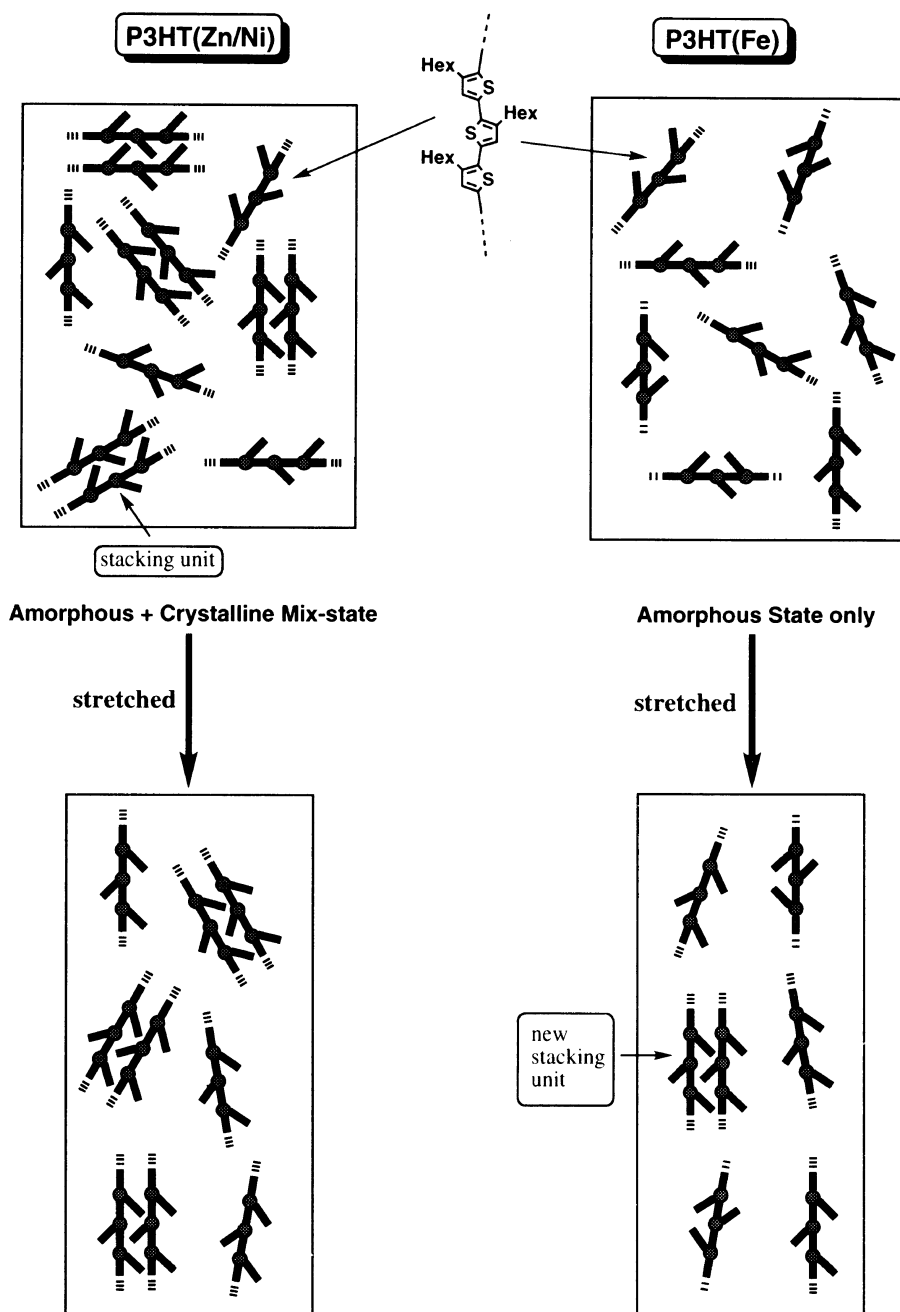
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Figure 5. Models for the alignment of P3HexTh (Zn/Ni) and P3HexTh (Fe) in the stretched PET film.

alignment of the P3HexTh molecules (Figure 3b), which is expected to show dichroism when irradiated with polarized light ($hv_\parallel$ and $hv_\perp$ in Figure 3b).

The stretched PET film containing P3HexTh (Zn/Ni), whose absorption pattern essentially agrees with that of stacked P3HexTh (Zn/Ni) in the solid state, actually show such dichroism with a dichroic ratio R_d ($A_\parallel/A_\perp$; $A_\parallel$ = absorbance observed with $hv_\parallel$, $A_\perp$ = absorbance with $hv_\perp$) of 1.6 at the stretching ratio R_s (Figure 3b)[9] of 4.0, as shown in Figure 4a. However, the R_d value is smaller than that observed with linear polypyridine.[9] Less stiff structure of P3HexTh (Zn/Ni) as well as difficulty for the stacked unit to move along the streching direction accounts for the smaller R_d.

On the other hand, P3HexTh (Fe) gives larger dichroism as shown in Figure 4b. P3HexTh (Fe) in the non-stretched PET film gives the peak at about 500 nm

(*cf.* chart i in Figure 1B) and is considered to form only a loosely stacked structure and movement along the direction of streching will be easier thus to give the higher R_d value. As shown in Figure 4b, the UV-visible spectrum observed with $hv_\parallel$ resembles the UV-visible spectrum of stacked P3HexTh (Zn/Ni) (Figure 1A) whereas that observed with $hv_\perp$ corresponds to the UV-visible spectrum of non-stacked P3HexThs in the $CHCl_3$ solution. These data indicate that the alignment of P3HexTh (Fe) along the stretching direction causes the formation of the stacked unit and that the stacked unit has the transition moment along the direction of the stretching (presumably the direction of polymer main chain) whereas the absorption by single polymer molecule rather has the transition moment perpendicularly to the direction of the stretching. Figure 5 exhibits models for the alignment of P3HexThs in the stretched PET film.

P3HexTh (Ni) does not show such dichroism probably due to the low tendency to form the stacked unit and its less stick structure.

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