Stacking of Poly(3-alkylthiophene)s and Poly(4-alkylthiazole)s in a Colloidal Solution and in the Solid

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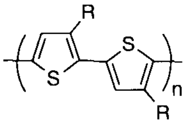
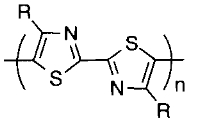
Regioregular poly(3-hexylthiophene-2,5-diyl) and poly(4-heptylthiazole-2,5-diyl) form colloidal solutions in $CHCl_3$-CH_3OH mixtures; light scattering analysis and filtration experiments reveal that about 10^3 molecules of stiff poly(3-hexylthiophene-2,5-diyl) aggregate in a side-to-side stacking mode. The two polymers and related polymers are stacked in an end-to-end or interdigitation mode in the solid.

π-Stacking of π-conjugated polymers is the subject of recent interest,[1-3] and formation of the π-stacked state is important for better perforormance (e.g., larger optical third-order nonlinear susceptibility[3a]) of the π-conjugated polymers. In this paper we report behaviors of head-to-tail type poly(3-alkylthiophene)s, HT-P3RThs, and head-to-head type poly(4-alkylthiazole)s, HH-P4RTzs, in solutions and their packing mode in the solid; the polymers having been prepared by the literature method:[2,3a]


HT-P3RTh


HH-P4RTz

R = butyl (Bu), hexyl (Hex), heptyl (Hep), etc.

Light scattering analysis[4] of HT-P3HexTh (R=Hex) with *M*n of 1.7 x 10^4 in $CHCl_3$ (one of the best solvent[5]) gives a ρ_v (degree of depolarization)[4,6,7] value of 0.26 and Rg (radius of gyration)[4] of 36 nm, indicating that HT-P3HexTh takes a stiff structure even in the good solvent. Addition of CH_3OH (non-solvent) to the $CHCl_3$ solution of HT-P3HexTh gives a stable colloidal solution at the concentration of HT-P3HexTh below 15 mg dm^{-3}. As shown in Figure 1, the colloidal solution gives rise to new absorption peaks in a region of a longer wavelength, and positions of the new peaks agree with those of film of HT-P3HexTh which has the π-stacked structure.[2] Light scattering analysis of the colloidal solution in a 70 : 30 $CHCl_3$-CH_3OH mixture gives about 10^3 times stronger light scattering, revealing that about 10^3 molecules of HT-P3HexTh are aggregated to form the colloidal particle.[6] The Rg value (42 nm), however, shows only a small increase, and this can be taken as an indication that HT-P3HexTh molecules are stacked along the main chain with the center of each molecule at almost the same position; if the molecules are stacked in a largely slipped style from each other, a larger increase in the Rg value will be observed. The colloidal particle gives a small ρ_v value of 0.021, which suggests that anisotropy of the polarizability[4,7] decreases in the particle due to the presence of mobile electron along directions perpendicular to the main chain in the aggregate.

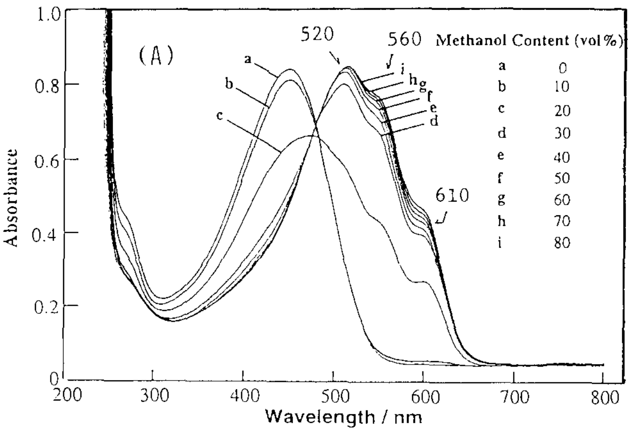


Figure 1. Changes of UV-visible spectra of the $CHCl_3$ solution of HT-P3HexTh on addition of CH_3OH at 25 °C.

Filtration of the colloidal solution through membranes with pore sizes of 0.2, 0.1, and 0.02 μm (Figure 2) indicate that most of the colloidal particles can pass through the pore of 0.2 μm whereas they can not pass through the pore of 0.02 μm, and these results agree with the degree of the aggregation estimated from the light scattering. Addition of CH_3OH to a $CHCl_3$ solution of HH-P4HepTz (R = Hep) gives analogous colloidal solutions, which also afford similar bathochromic shift of the absorption band and filtration results.

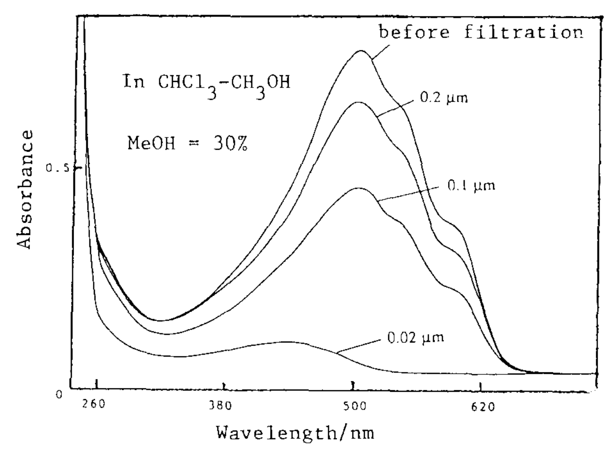
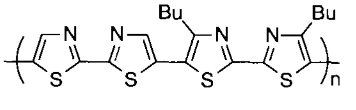


Figure 2. UV-visible spectra of the solutions of HT-P3HexTh after filtration through membrane filters with pore sizes of 0.2, 0.1, and 0.02 μm.

Figure 3 exhibits X-ray diffraction patterns of HH-P4RTzs and the following copolymer:[3a]


Copoly-1

The X-ray diffraction patterns are similar to those of reported HT-P3RThs,[2] and show two characteristic peaks at about $2\theta = 25$ ° and in a range of $2\theta = 4$-13 °. The former peak is assigned to the face-to-face stacking distance and the latter to the distance (d) between the neighboring main chain separated by the R chain.

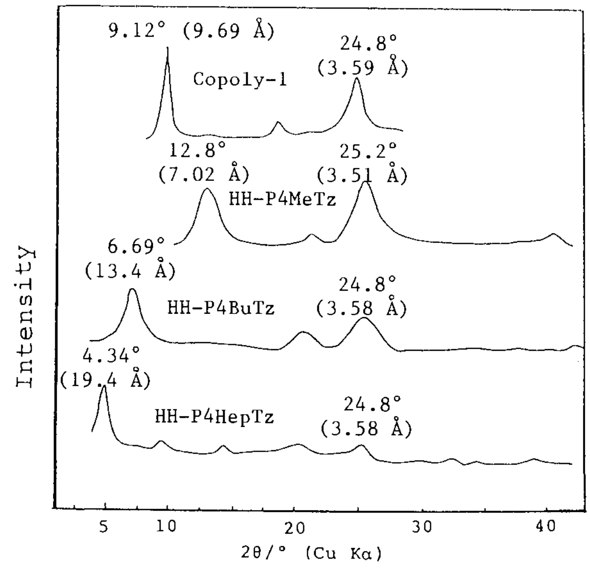
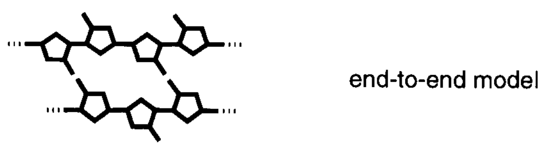
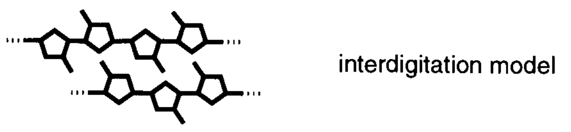


Figure 3. Powder X-ray diffraction pattern of HH-P4RTzs and Copoly-1

Rigid polymers with side R chain take an end-to-end stacking or interdigitation packing mode,[8] e.g., for HH-P4RTz:

Random type P3RTh[3b] gives no sharp X-ray diffraction peak. The number density of the R group and the effective radium (ca. 5 Å)[8,9] of R are the determining factor for the packing mode, and the end-to-end model is suggested for HH-P4RTz in view of these two factors. Actually plots of the distance d estimated from the X-ray diffraction peak against number m in $(CH_2)_{m-1}CH_3$ gives a straight line with a large slope of 2.0 Å per carbon. The slope is larger than the unit height (1.25 Å)[8,9] of the alkyl chain per carbon (the CH_2-CH_2 distance along the direction of the alkyl chain) and is consistent with the end-to-end model. Similar plots with reported data[2] of HT-P3RThs also give a straight line with a slope of 1.8 Å per carbon. In the case of Copoly-1, the number density of the R group is half of HH-P4RTzs, and the interdigitation type packing is expected. In this case, the effective length of the R group is to be taken as about half, compared with the case of the end-to-end type packing. The d value of Copoly-1 actually corresponds to the data point for R = Et of HH-P4RTz. As described above, the light scattering analysis, filtration experiments, and X-ray crystallography give important informations on the π-stacking of the π-conjugated polymers including recently prepared HH-P4RTzs.





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