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Piezochromic behaviour of regioregular poly(3-hexylthiophene-2,5-diyl) and poly(5,8-dihexadecyloxyanthraquinone-1,4-diyl)

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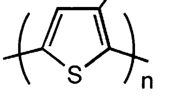
Abstract

Head-to-tail regioregular poly(3-hexylthiophene), HT-P3HexTh, and poly(5,8-dihexadecyloxyanthraquinone-1,4-diyl), P(5,8-$OC_{16}H_{33}$-1,4-AQ), showed piezochromism at high pressures (5–11 GPa). The yellow colour ($\lambda_{max} = 520$ nm) of P(5,8-$OC_{16}H_{33}$-1,4-AQ) at ambient pressure turned to dark red ($\lambda_{max} = 625$ nm) at 11 GPa. © 2001 Elsevier Science Ltd. All rights reserved.

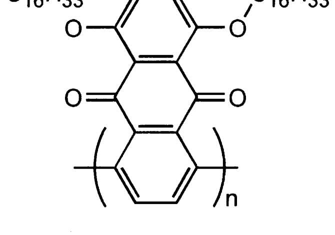
Keywords: π -Conjugated polymer; Piezochromism; High pressure

π-Conjugated polymers exhibit interesting optical and electrical properties [1–3]. It has been reported that some π-conjugated polymers change their optical properties upon altering the solvent (solvatochromism) [4–6], temperature (thermochromism) [2,7,8], and pressure (piezochromism) [9–12]. However, in comparison with solvatochromism and thermochromism, examples of piezochromism have been limited.

We have examined changes in optical properties of highly regioregular head-to-tail poly(3-hexylthiophene-2,5-diyl), HT-P3HexTh [13,14] with an HT content higher than 98.5% and poly(5,8-dihexadecyloxyanthraquinone-1,4-diyl), P(5,8-$OC_{16}H_{33}$-1,4-AQ) [15] up to 5–11 GPa, by using a diamond-anvil pressure cell. Studies on the piezochromism of π-conjugated polymers have been concentrated on poly(3-alkylthiophene-2,5-diyl)s; P(5,8-$OC_{16}H_{33}$-1,4-AQ) presents another example of piezochromism.



HT-P(3HexTh)



P(5,8-$OC_{16}H_{33}$-1,4-AQ)

Both polymers take ordered structures in the solid state [6,13–15] assisted by side-chain crystallisation [16]. Although piezochromism of P3RTh with reduced regioregularity (HT content of about 70%) was reported by Iwasaki et al. [11] and that of HT-P3HexTh up to 0.5 GPa by Kaniowski et al. [12], piezochromism of HT-P3RTh at higher pressures has not been reported.

Solid samples (powders) of the polymers shown above were placed in a diamond-anvil pressure cell and pressed. A small piece of ruby was added to the solid sample and the applied pressure was determined based on the pressure shift in the sharp R-line photoluminescence (PL) of ruby [17]. On applying high pressure, the powdery sample became films. PL and UV–vis. spectra were measured with an optical system consisted of a standard microscope and a monochromator with an associated photodetection system [18].

HT-P3HexTh has so intense a π–π^* absorption peak (ϵ on the order of $10^4\ M^{-1}\ cm^{-1}$) [13,14] that monitoring of its piezochromism through the change in the UV–vis. absorption peak in the diamond-anvil pressure cell was not possible using our optical system. We obtained

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the piezochromic data for HT-P3HexTh by monitoring its PL peak, which is considered to correspond to the band gap of the polymer [1–3,14]. On the contrary, P(5,8-$OC_{16}H_{33}$-1,4-AQ) has a moderate UV–vis. absorption peak ($\epsilon = 1400\,M^{-1}\,cm^{-1}$) in the visible range and its piezochromism can be monitored by UV–vis. spectroscopy.

Fig. 1 shows the pressure dependence of the PL peak of HT-P3HexTh. As shown in Fig. 1b, the energy of the PL peak decreased linearly with an increase in pressure. Up to 3 GPa, the PL peak of HT-P3HexTh appears at a much lower energy (by about 0.4 eV), than that of P3HexTh with 70% HT content [11]. In the case of P3HexTh with 70% HT content, the energy in the PL peak became minimum at 3 GPa, and further increase of pressure to 4.2 GPa caused an increase in the energy of the PL peak. However, in the case of HT-P3HexTh, the energy decreased linearly in the measured pressure range up to 5 GPa, as shown in Fig. 1b. The slope ($0.028\,eV\,GPa^{-1}$) of the line in Fig. 1 is smaller than that ($0.085\,eV\,GPa^{-1}$) obtained based on shifts in the UV–vis. peak of HT-P3OctTh (R = octyl) up to 0.4 GPa [12]. Recently, Samuelsen et al. presented interesting results on the solid structure of P3OctTh with 75% HT content under high pressures up to about 8 GPa [19]. They found that both the distance between polythiophene main chains separated by the alkyl side chains and the face-to-face distance between polythiophene planes were shortened at high pressure, e.g., about 8% shortening of the face-to-face distance at about 8 GPa. The shortening of the face-to-face distance will increase the intermolecular electronic interaction between P3RTh molecules, and this may be the reason for the lowering of the band-gap energy of HT-P3HexTh determined based on the PL peak at a high pressure.

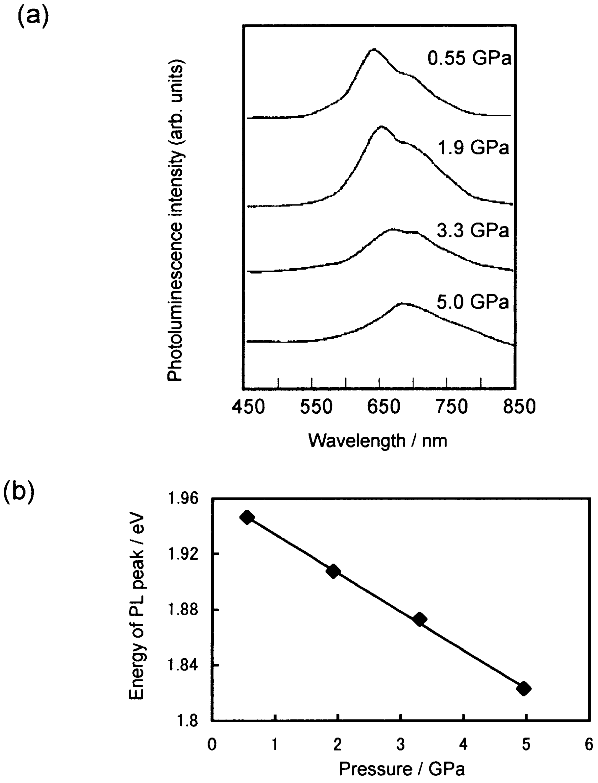

Fig. 1. Shift of PL peak at high pressure.

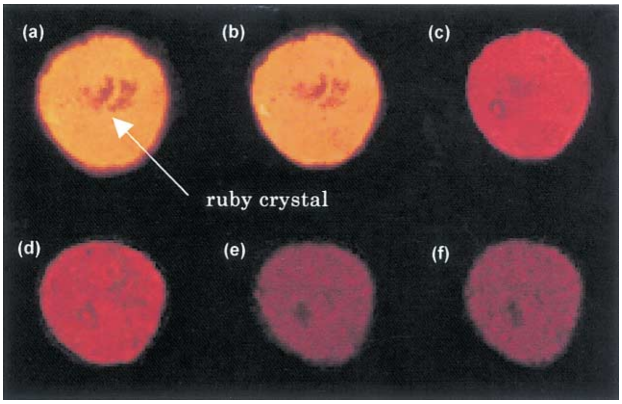

Fig. 2. Images of P(5,8-$OC_{16}H_{33}$-1,4-AQ) at: (a) 0.55 GPa, (b) 1.1 GPa, (c) 3.3 GPa, (d) 6.1 GPa, (e) 6.9 GPa and (f) 11 GPa. Shadows in the images are due to nonuniformity of the film due to the presence of ruby for monitoring pressure.

Colour changes of P(5,8-$OC_{16}H_{33}$-1,4-AQ) are shown in Fig. 2. By applying a high pressure, the colour of the pressed film of P(5,8-$OC_{16}H_{33}$-1,4-AQ) changes from yellow to dark red. As described above, P(5,8-$OC_{16}H_{33}$-1,4-AQ) has a strong tendency to form an ordered structure in the solid state [15]. Its spin-coated film shows a bathochromic shift of the UV–vis. absorption peak of 17 nm from λ_{max} of 413 nm in a $CHCl_3$ solution (Fig. 3). Under a high pressure, the absorption peak shifts to a longer wavelength, as depicted in Fig. 4. The band gap of P(5,8-$OC_{16}H_{33}$-1,4-AQ) evaluated from the onset position also decreases from 2.3 eV at 0.1 MPa to about 1.7 eV at 12 GPa (or $0.05\,eV\,GPa^{-1}$). P(5,8-$OC_{16}H_{33}$-1,4-AQ) showed too weak a PL band to determine the band gap from its PL peak. The red shift of the UV–vis. absorption

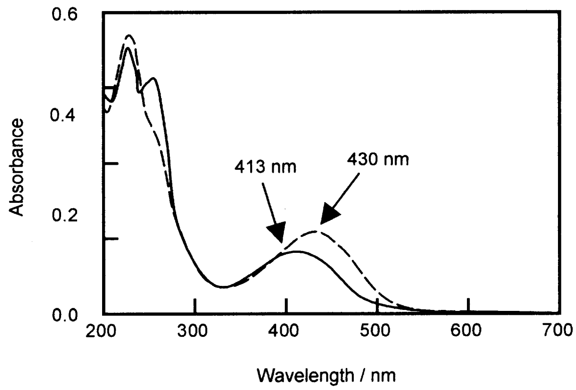

Fig. 3. UV–vis. spectra of P(5,8-$OC_{16}H_{33}$-1,4-AQ) in $CHCl_3$ (solid line) and spin-coated film (dashed line). Measured at 0.1 MPa.

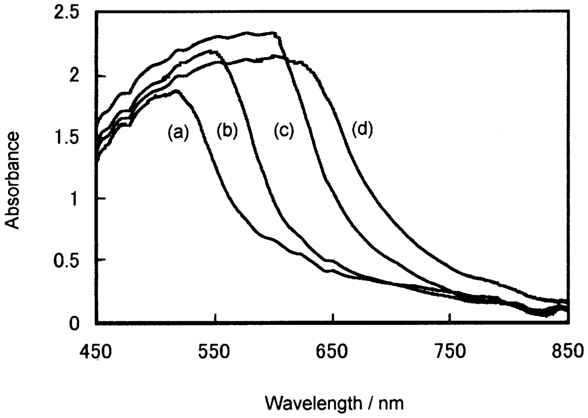

Fig. 4. UV–vis. spectra of P(5,8-$OC_{16}H_{33}$-1,4-AQ) at: (a) 0.55 GPa, (b) 3.3 GPa, (c) 6.9 GPa and (d) 11 GPa.

band of P(5,8-$OC_{16}H_{33}$-1,4-AQ) at a high pressure also most probably originates from the increase in the intermolecular interaction between the polymer molecules cause by the shortening of the distance between the polymer molecular planes. It has been reported that the application of high pressure to solids of planar metal complexes also leads to a red shift in their absorption bands (e.g., from about 550 nm at 0.2 GPa to 700 nm at 4.1 GPa for bis(dimethylglyoximato)nickel(II)) through the increase of the intermolecular interaction at a high pressure [17,20].

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