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Band Gap and Absorption Profile Change by Changing Molecular Weight and Conformation of Water-soluble Narrow-band-gap Polymers

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Band gaps and absorption profiles of water-soluble π-conjugated polymers, which were prepared by the addition–condensation of pyrrole with sodium o-formylbenzenesulfonate, changed with changing their molecular weights and conformations in different solvents. The band gaps were changed from less than 0.19 eV in a solid to 0.59 eV in a solution.

The band gap (E_g) is one of the most important properties for developing new electronic and photonic devices because the conductivity and photoabsorption of a substance depend on its E_g. Many studies to control the E_g have been carried out[1] and reviewed,[2] and it has been found that it can be controlled by changing molecular structure. However, it is difficult to control the E_g in the region of less than 1.0 eV, because preparation of a narrow-band-gap polymer defined as $E_g < 1.0$ eV[3] is very difficult. Common π-conjugated polymers have a medium E_g. For example, undoped polyacetylene, polypyrrole, and polythiophene have E_g values of 1.4, 2.5, and 2.0 eV, respectively.[4] As opposed to the dramatic development of doping methods for π-conjugated polymers, the study of narrow-band-gap polymers has made slow, but steady progress. For example, polymer with the lowest E_g value estimated by electrochemical and optical methods are 0.3[5,6] and 0.36 eV,[7] respectively, to the best of our knowledge. Narrow-band-gap polymers have been studied on the basis of experimental[3,5–11] and theoretical[12,13] standpoints and their synthetic principles reviewed.[2] Here, the most active study of a narrow-band-gap polymer has been carried out for those containing thiophene units from the standpoints: (i) alternating donor and acceptor units in the polymer main chain, and (ii) reducing the bond length alternation by stabilizing a quinoid structure.[3,6–8,13] These strategies led to the successful preparation of the narrowest-band-gap polymers with E_g of about 0.3 eV.[6,7] On the other hand, poly(pyrrolylenemethine) and its derivatives[9–12] have also been studied. In particular, the Bräunling group[9] and Brédas group[12] have actively investigated the polymers from synthetic and theoretical standpoints. In spite of the theoretically good prediction for the poly(pyrrolylenemethine) and its derivatives as narrow-band-gap polymers,[12] no experimental results with small E_g (<1.0 eV) have been reported except for our previous letter.[11]

These previous studies focused on the structure of repeating monomer unit, while we attempt to clarify the E_g change by changing the molecular weight and conformation of the polymers similarly prepared in the previous letter,[11] because E_g of a polymer depends on not only repeating monomer structure but also the degree of coplanar π-conjugation. Here, a higher molecular weight must lead to a narrow E_g by increasing

the π-conjugation and/or decreasing molecular motion. Slow molecular motion must maintain coplanarity. An expanded conformation must also form coplanarity. In this paper, we have clarified this hypothesis by preparing water-soluble π-conjugated polymers with different molecular weights and by measuring the absorption spectral change in different conformations. The band gap values of the polymers change from less than 0.19 eV in solid (the new lowest value) to 0.59 eV in solution, and the expanded polymer shows stronger absorption in a lower energy region.

Water-soluble π-conjugated polymers with different molecular weights were prepared by the addition–condensation of pyrrole (Py) with sodium o-formylbenzenesulfonate (BS) with the different Py/BS ratios summarized in Table 1. The synthetic route is shown in Scheme 1, and the details are described in Supporting Information (SI).[16] Figures 1 and S1[16] show the absorption spectra of the obtained polymers dissolved in a phosphate buffer (25 mM of KH_2PO_4 and 25 mM of Na_2HPO_4: pH 6.9) in order to avoid self-acid doping. The absorption profiles of the polymers are very broad and with peaks around 1.5 (800 nm) and 0.6 eV (2070 nm). It is very important that the absorption around 0.6 eV is due to the π–π^* excitation or excitation concerning the doped state. Here, we conclude that the absorption is due to the π–π^* excitation as follows: First of all,

Table 1. Band gap change of water-soluble π-conjugated polymers with different molecular weights

Abbr.[a]	Py/BS in feed	η_{sp}/C[b] /dL g^{-1}	M_w	$E_{g,solution}$ /eV[e]	$E_{g,solid}$/eV[g] [Bottom absorbance]
Py(10)	10/10	0.1250	31400[c]	0.30	<0.19 [0.30]
Py(12)	12/10	0.0655	15700[d]	0.30	<0.20 [0.28]
Py(14)	14/10	0.0488	12800[c]	0.34	<0.20 [0.22]
Py(20)	20/10	0.0405	8500[c]	(0.41)[f]	0.21 [0.18]
Py(40)	40/10	0.0355	7900[d]	0.54	0.22 [0.16]
Py(70)	70/10	0.0280	6100[d]	0.59	0.22 [0.16]

[a]The ratio of Py to BS in feed is in parenthesis. [b]Reduced viscosity (η_{sp}/C) was measured by a Ubbelohde-type viscometer using the sample solution of 0.40 g dL^{-1} at 303 K. [c]Molecular weights of the polymers were determined by an ultracentrifugal analysis. [d]Molecular weights of the polymers were roughly estimated using the following equation: $\eta_{sp}/C = kM_w{}^{\alpha}$. Here, k (1.16×10^{-5}) and α (0.894) were approximately determined from the η_{sp}/C and M_w values determined by the ultracentrifugal analysis. [e]Band gap was estimated from the absorption edge.[14] [f]This value was determined by extrapolation. [g]Band gap was estimated from the absorption edge which was defined as the photon energy of the bottom absorbance due to overlapping electronic and vibrational transitions.
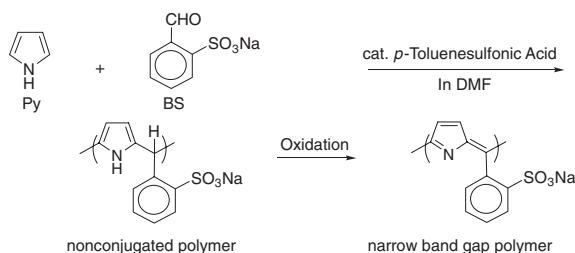
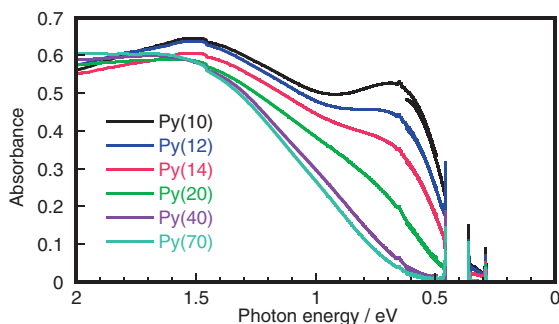**Scheme 1.** Synthetic route of water-soluble narrow-band-gap polymers.

Figure 1. Vis–NIR–IR spectra of water-soluble narrow-band-gap polymers with different molecular weights dissolved in phosphate buffer. [polymer] = 4.0 g dm^{-3}, cell length: 0.2 mm.

Figure 2. IR spectra of narrow-band-gap polymers and non-conjugated polymer [n-Py(10)] dispersed in KBr.

it should be noted that the absorption around 0.6 eV increases with the increasing molecular weight of the polymers. The preparation method for all the polymers is almost the same. Therefore, it makes no sense at all that only the higher-molecular-weight polymer is doped. Second, the absorption intensity at 0.6 eV changes by changing the molecular motion and conformation mentioned bellow. Third, the radical concentration of both higher- and lower-molecular-weight polymers are almost the same values of 1.0×10^{19} spin/g (1 spin per 230 structural units) and 1.7×10^{19} spin/g (1 spin per 140 structural units), respectively (Figure S15[16]). These values are comparable with those of neutral polyacetylene, polypyrrole, and poly-(heteroarylenemethines).[8f] On the other hand, the line shape of ESR spectrum of the higher-molecular-weight polymer is narrower than that of lower one although g-values are the same (2.0027). This suggests that both the higher- and lower-molecular-weight polymers are in the neutral state and the radical generated on the higher-molecular-weight polymer distributes on the expanded π-conjugated system. In addition, in order to rule out doping, we checked the absorption spectral change for five terms: (1) the amount of oxidant, (2) pH, (3) oxygen, (4) hydrazine reduction, and (5) electrochemistry. These experimental data, which will be mentioned in SI, show that the polymer is in the nondoped state. We confirmed that the absorption band around 0.6 eV results from the π–π^* excitation.

The E_g values of the polymers in solution determined from the absorption edges[14] are summarized in Table 1. The E_g is changed from less than 0.30 to 0.59 eV by changing the molecular weight.

Figure 2 shows the IR spectra of the polymers dispersed in KBr. The absorption of the electronic transition gradually decreases with the decreasing photon energy and overlaps with
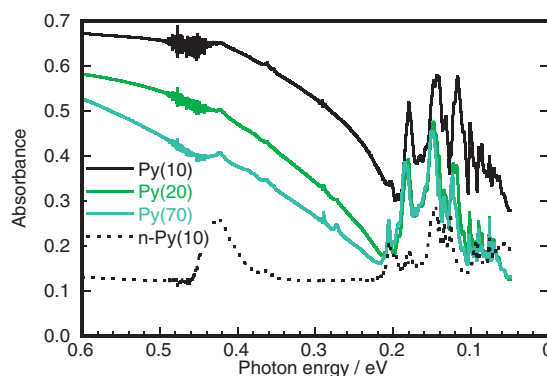
that of the vibrational transition around 0.19 eV (1530 cm^{-1}, 6540 nm). Therefore, we cannot exactly determine the E_g values of the polymers, the photon energy and absorbance at an apparent bottom caused by overlapping the electronic and vibrational transitions are summarized in Table 1. The overlapping point shifted to a lower energy and higher absorbance with the increasing molecular weight. This means that the E_g is less than the energy of the overlapping point and narrows with increasing molecular weight. The E_g value of less than 0.19 eV is about half that of the previous world record (0.36 eV[7]) determined by an optical method.

The low absorbance at 0.6 eV in the solution of Py(40) and Py(70) in Figure 1 becomes higher in the solid (Figure 2). In order to clarify this behavior, absorption spectra of polymer solutions dissolved in pure water and of spin-coated polymer films on FTO (fluorine-doped tin oxide) glass prepared from the same solution were measured (Figure S16[16]). The absorption band around 0.6 eV (2070 nm) of Py(40) generated in the process removing the solvent. That is the absorption band is caused by not doping but the restriction of molecular motion leading to increasing the coplanar π-conjugation. On the other hand, the absorption band of Py(10) decreased in that process. This behavior will be discussed later.

We expect that the π-conjugated system of this polymer expands in the expanded polymer conformation caused by increasing coplanarity. It is well known that a polyanion expands in pure water caused by electrostatic repulsion between the anions on the polymer side chain. On the other hand, the polyanion shrinks in an ionic solution and in an organic solvent. The absorption spectra of the polymer dissolved in pure water, phosphate buffers, or water–methanol mixed solvents were measured (Figure 3). Here, MeOH 80% means a mixed solvent containing 20% water with 80% methanol (v/v) and 50 mM means a phosphate buffer including 25 mM KH_2PO_4 and 25 mM Na_2HPO_4, which is the same solution in Figures 1 and S1.[16] The absorbance around 0.6 eV (2070 nm) increases with the increasing reduced viscosity (η_{sp}/C) of the polymer solution, which changes from 0.157 for the 50 mM phosphate buffer to 0.600 for pure water shown in parentheses of the explanatory note in Figure 3. Based on similar spectral profiles in 1.5 mM phosphate buffer and in MeOH 33%, the absorption band around 0.6 eV is strongly dependent on the reduced viscosity and weakly dependent on both the dielectric constant and ionic strength of
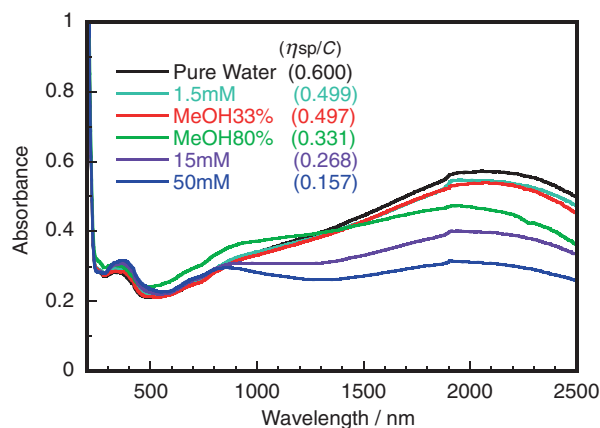
Figure 3. UV–vis–NIR absorption spectra of the polymer solutions (4.0 g dm^{-3}). Py(10) (M_w = 42000, repreparaed) dissolved in pure water, phosphate buffers, or water–methanol mixed solvents; cell length: 0.1 mm. Parenthesis means reduced viscosity of the polymer solution.

the solvent. Although we cannot exactly estimate the E_g values of the polymer in pure water due to strong absorption of the solvent, the band gap becomes narrower than that in the phosphate buffer because the absorbance of the polymer in pure water at 0.30 eV is higher than that in the phosphate buffer (not shown in Figure 3). These results mean that the expanded polymer conformation leads to increasing the coplanar π-conjugation. In other words, the band gap of this polymer is partially controllable by changing the polymer conformation in the solution state. The band gap change by changing the molecular weight and the conformation is similar to a study of porphyrin tapes.[15]

Finally, we discuss the absorption decreasing around 0.6 eV from the solution to the film of Py(10) in Figure S16.[16] We have clarified that the slow molecular motion and the expanded polymer conformation lead to increasing the coplanar π-conjugation. During spin-coating, the molecular motion becomes slow, however, the polymer conformation must shrink due to the strong ionic strength of concentrated polyanion solution. Thus, spin-coating induces an antithetical effect for the absorptional change. Since a spectral narrowing is observed in the NMR of lower molecular weight polymer (Figure S2[16]), we conclude that the effect of the motional change overcomes that of the conformational change for Py(40) and contrary for Py(10). On the other hand, the spectrum of Py(10) shown in Figure 2 is almost flat from 0.6 (2070 nm) to 0.4 eV (3100 nm) and gradually decreasing. This is caused by the slow/rigid molecular motion and the expanded conformation of Py(10), which was prepared by freeze-drying using pure water as a solvent.

In conclusion, we prepared water-soluble π-conjugated polymers with different molecular weights. The band gap values of the polymers are changed from less than 0.19 eV in a solid to 0.59 eV in a solution. Higher molecular weight and expanded conformation lead to narrowing the band gap due to increasing the degree of coplanar π-conjugation.

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