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Continuous Band Gap Control from 0.3 to 1.1 eV of π-Conjugated Polymers in Aqueous Solution

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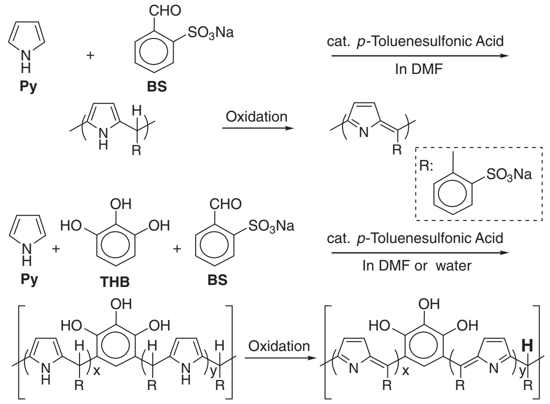
Band gap controllable, water-soluble, and π-conjugated polymers were prepared by the addition–condensation of pyrrole (Py), 1,2,3-trihydroxybenzene (THB), and sodium *o*-formylbenzenesulfonate (BS) with different Py/THB/BS ratios. Band gap values are continuously controlled from 0.3 to 1.1 eV in aqueous solutions by changing molecular weights and monomer unit sequences.

The band gap (E_g) is one of the most important properties for developing new electronic and optical devices including solar cells because the conductivity and photoabsorption of a substance depends 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. Narrow-band-gap polymers have been studied on the basis of experimental[3–5] and theoretical[6,7] observations. Most studies have used thiophene[3,4,6] or pyrrole[5,7] units in their polymer chains. The discussion points of the studies have been mainly polymer structures as (i) alternating donor and acceptor units in the polymer main chain, and (ii) reducing the bond length alternation by stabilizing a quinoid structure. On the other hand, we recently showed the preparation of water-soluble narrow-band-gap polymers with band gap values from less than 0.19 eV as a solid to 0.59 eV in solution by changing molecular weight.[8] We also showed that the absorption spectral profiles of the polymers strongly depends on their conformations. That is band gap control is possible by changing the molecular weight and the conformation of the polymers.

In order to prepare a high-efficiency solar cell, the control of the E_g value around 1.0 eV is very important. However, it was difficult to control the value by only changing the molecular weight and the conformation in our previous study. In this paper, we attempt to prepare a polymer including some benzene units instead of pyrrole shown in Scheme 1. The benzene rings will break the π-conjugation and the E_g value will increase. Therefore, we will show continuous band gap control from 0.3 to 1.1 eV of the polymer in aqueous solution in concert with the previous study.[8]

Water-soluble polymers with different molecular weights and the different monomer-unit sequences were prepared by the addition–condensation of pyrrole (Py) and 1,2,3-trihydroxybenzene (THB) with sodium *o*-formylbenzenesulfonate (BS) with different Py/THB/BS ratios. Here THB was used for two reasons, high reactivity for the addition–condensation and good solubility in water. The synthetic routes of the polymers are shown in Scheme 1 and polymerization results are summarized in Table 1. The details of the polymerization are described in Supporting Information (SI).[11] The introduction of THB units generates the nonconjugated portion of the polymer chain shown in Scheme 1, therefore, the high content of THB will lead to less π-conjugated polymers.



Scheme 1. Synthetic routes of band gap controllable polymers. Upper: previous study.[8] Lower: this study.

Figures 1 and S1 in SI[11] 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 prepared without THB[8] shown as solid lines in Figures 1 and S1[11] are very broad and have peaks at around 1.50 (800 nm) and 0.65 eV (1900 nm). We showed that the longer-wavelength absorptions were due to π–π^* excitation of the expanded π-conjugation.[8] The E_g values estimated from the absorption edges[9] shown in Figures 1 and S2[11] increase from 0.3_0 to 0.5_9 eV with decreasing molecular weight summarized in Table 1. Here, a wider-band-gap polymer may be prepared from a higher Py/BS ratio, however, the molecular weight must be lower than 6100. In order to prepare a wider-band gap polymer, THB was introduced instead of pyrrole. The absorption spectra of the polymers prepared with different ratios of Py/THB/BS were measured (dotted lines in Figures 1 and S1[11]). The absorption intensity around 1.50 eV decreases with increasing THB content. Here the absorption around 1.50 eV is also due to π–π^* excitation and this phenomenon is similar to porphyrin tapes.[10] These polymers have almost the same molecular weight, however, the numbers of π-conjugated sequences formed by Py–BS units shown as x

Table 1. Properties of band gap controllable polymers

Abbr.	Py/THB/BS in feed	η_{sp}/C[b] /dL g^{-1}	M_w	E_g/eV[e]
Py(10)[a]	10/0/10	0.125	31000[c]	0.30 ± 0.05
Py(12)[a]	12/0/10	0.066	16000[d]	0.30 ± 0.05
Py(14)[a]	14/0/10	0.049	13000[c]	(0.34 ± 0.05)[f]
Py(20)[a]	20/0/10	0.041	8500[c]	(0.41 ± 0.05)[g]
Py(40)[a]	40/0/10	0.036	7900[d]	0.54 ± 0.05
Py(70)[a]	70/0/10	0.028	6100[d]	0.59 ± 0.05
Py(8)THB(2)	8/2/10	0.038	8600[d]	0.68 ± 0.05
Py(7)THB(3)	7/3/10	0.038	8600[d]	0.82 ± 0.05
Py(6)THB(4)	6/4/10	0.033	7300[d]	0.96 ± 0.05
Py(5)THB(5)	5/5/10	0.027	6000[d]	1.06 ± 0.05
Py(3)THB(7)	3/7/10	0.032	7100[d]	1.11 ± 0.05

[a]Ref. 8. [b]Reduced viscosity (η_{sp}/C) was measured with an Ubbelohde viscometer using a sample solution of 0.40 g dL^{-1} at 303 K. [c]Molecular weights of the polymers were determined by 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.[9] [f]Band gap was estimated from the absorption edge which was defined as the photon energy of the absorbance at 0.02 (about 3% of the absorbance around 1.5 eV for the polymers without THB). [g]This value was determined by extrapolation.

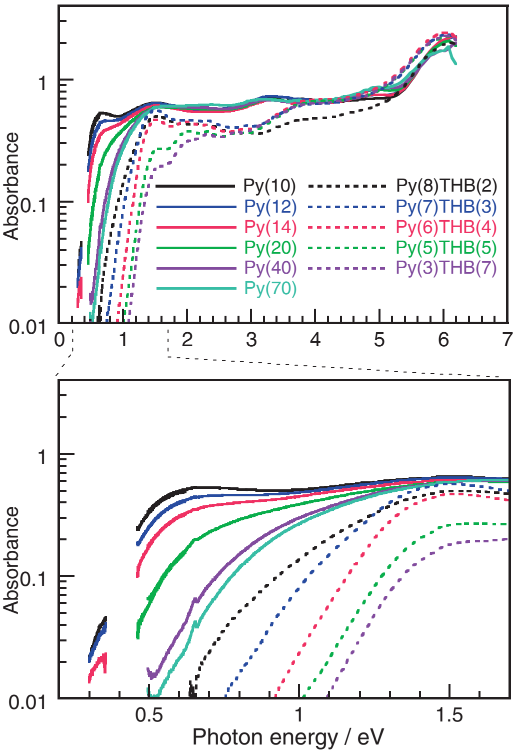


Figure 1. Absorption spectra of π-conjugated polymers dissolved in the phosphate buffer (4.0 g dm^{-3}): cell length 0.2 mm. Solid lines show the polymers without THB and dotted lines with THB.

and y in Scheme 1 decrease with increasing THB content. The E_g values estimated from the absorption edges[9] shown in Figures 1 and S3[11] increase from 0.6_8 to 1.1_1 eV with increasing THB content as summarized in Table 1.

We have shown new strategies for continuous band gap control from 0.3_0 to 1.1_1 eV by changing molecular weight and monomer unit sequences. In the near future, it will be possible to prepare a polymer having the desired band gap which will contribute to chemistry and material science, especially in solar cells.

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11 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.