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Random π-Conjugated Copolymers Constituted of Electron-donating Thiophene Units and Electron-accepting Pyridine Units

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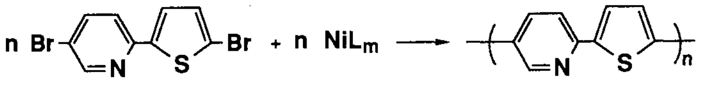
Dehalogenation copolymerization of 2,5-dibromothiophene and 2,5-dibromopyridine with zero-valent nickel complex gives random copolymers with molecular weight of $5\mathrm{x}10^4$-$5\mathrm{x}10^6$. They show unique doping-undoping cycles which are accounted for by shift of lone pair electron of pyridine ring to p-doped thiophene ring.

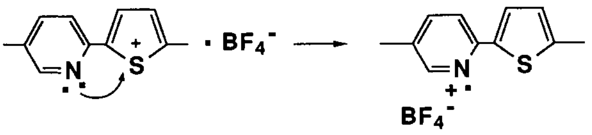
It was previously reported that electrically conducting π-conjugated copolymer PTpy (Eq. 1, Mw = 5400), which was constituted of electron-donating thiophene units and electron-accepting pyridine units and prepared by dehalogenation polycondensation of the following monomer with zero-valent nickel complex, showed unique



(1)

Br-Th-Py-Br **PTpy**

optical and electrochemical (doping and undoping) properties, the latter being accounted for by assuming an EC mechanism involving shift of lone pair electron of a pyridine ring to a p-doped thiophene ring.$^{1)}$



(2)

In order to obtain further information on the chemical and physical properties of such unique polymers constituted of electron-donating and electron-accepting aromatic units and to prepare similar copolymers with higher molecular weight and various compositions from simpler monomers, we have carried out random copolymerization of 2,5-dibromopyridine (Br-Py-Br) and 2,5-dibromothiophene (Br-Th-Br).As for the zero-valent Ni complex, we used a mixture of bis(1,5-cyclooctadiene)nickel and 2,2'-bipyridine, and work up of the copolymers was carried out in a similar manner as reported previously.$^{2)}$

$$\mathrm{a\,Br\text{-}Py\text{-}Br + b\,Br\text{-}Th\text{-}Br + NiL_m \longrightarrow \!\!-\!\!(Py)_x\!\!-\!\!(Th)_y} \quad (3)$$

Table 1 summarizes results of the copolymerization. As seen in Table 1, reddish brown copolymers were obtained in high yields. IR spectrum of NS11 showed a different pattern from that of a mixture of poly(pyridine-2,5-diyl) PPy and poly(thiophene-2,5-diyl) PTh, revealing that the product was neither a mixture of PPy and PTh nor a block copolymer. The higher molecular weight of the copolymer than PTpy seems to be attributable to its lower crystallinity. The degree of depolarization (ρv) of NS31 and NS11 in formic acid was almost 0, indicating that they essentially took a random coil structure.[3] However, refractive index increment($\Delta n/\Delta c$) was very large (0.53-0.69 cm^3 g^{-1}) presumably due to the presence of mobile electrons along the polymer chain. Spreading the formic acid solution of the copolymer on substrates and removal of formic acid afforded mechanically strong smooth films. Iodine-doped copolymers showed medium electrical conductivity ($3x10^{-5}$-10^{-2} S cm^{-1}).

Table 1. Random Copolymerization[a)]

Copolymer	Monomer ratio (Br-Py-Br : Br-Th-Br)	Yield[b)] %	Mw[c)]	λmax/nm[d)]
NS31	3 : 1	92	$5.1x10^4$	431
NS11	1 : 1	99	$3.3x10^5$	471
NS13	1 : 3	99	$5.1x10^6$	483

a) In DMF for 20 h at 70 ℃. b) Based on carbon recovered. c) By light scattering method.[3)] d) In formic acid.

Figure 1 shows a cyclic voltammogram (CV) of NS13 laid on ITO glass plate. The CV curve is similar to that of PTpy (Eq. 1),[1)] showing a couple of an anodic peak at 0.86 V related to p-doping of the thiophene ring and its undoping peak at -1.96 V as well as a couple of cathodic peak at -2.22 V related to n-doping of the pyridine ring and its undoping peak at -1.98 V. Color changes accompanied with the doping and undoping processes were similar to those observed for PTpy.

As described above interesting poly(arylene) copolymers constituted of electron-donating and electron-accepting arylene units and with high Mw can be prepared from the simple monomers. Such type copolymers are expected to show interesting optical[4)] and electrical properties.

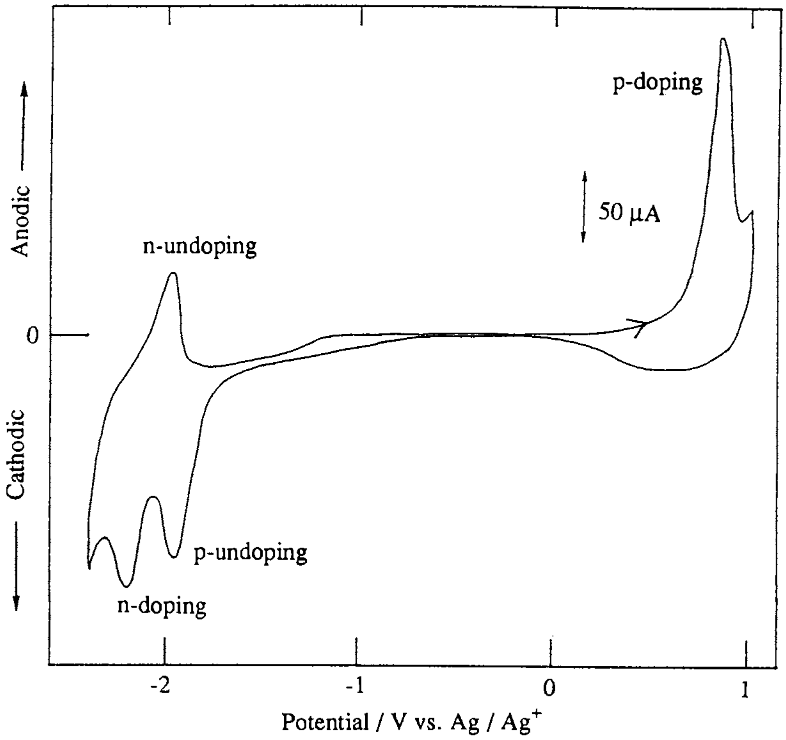


Fig. 1. CV curve of NS13 laid on ITO electrode. In an CH_3CN solution of $[N(n-C_4H_9)_4][ClO_4]$ (0.10 M). At 10 mV s^{-1} at room temperature.

References

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