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Synthesis of Poly(pyrimido[5,4-*d*]pyrimidine-2,6-diyl) with Nitrogen Atoms at All of the *o*-Positions

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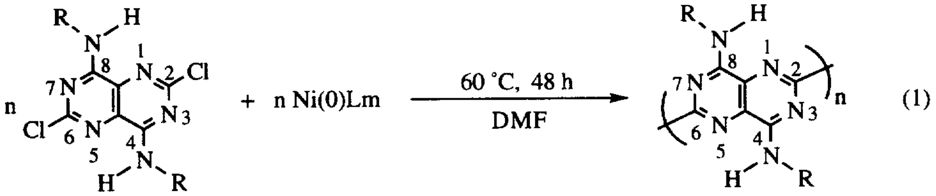
Abstract: Poly(pyrimido[5,4-*d*]pyrimidine-2,6-diyl)s, π-conjugated poly(arylene) with nitrogen atoms at the four *o*-positions, have been prepared. The polymers give UV-vis and photoluminescence peaks at about 450 and 470 nm, respectively, and receive electrochemical reduction at -2.20 V vs Ag/Ag^+. © 1998 Elsevier Science Ltd. All rights reserved.

π-Conjugated poly(arylene)s such as poly(*p*-phenylene), polypyrroles and polythiophenes have been the subject of many papers [1]. In view of their basic interesting chemical and physical properties, some of them have found practical usage [2].

In order to reach better understanding of the π-conjugation along the polymer main chain, it is desired to obtain polymer molecules with a coplanar structure. However, six-membered ring poly(arylene)s such as poly(*p*-phenylene) and poly(naphthalene-2,6-diyl) apparently receive *o*-hydrogen repulsion and are thus caused to twist out of the π-conjugated main chain. Reduction of the *o*-hydrogen repulsion by replacement of two *o*-CH groups of poly(naphthalene-2,6-diyl) with N was carried out, and preparation of poly(1,5-naphthyridine-2,6-diyl) has been reported [3]. However, this π-conjugated polymer has very low solubility, and it may still be subject to some steric repulsion between the *o*-CH group and N. We now report preparation of a soluble π-conjugated poly(naphthalene-2,6-diyl) type polymer with four N atoms at all of the four *o*-positions together with optical properties of the polymer.

The following dehalogenation polymerization using a zerovalent nickel complex [4] gives the polymer, poly(4,8-di(*N*-alkylamino)pyrimido[5,4-*d*]pyrimidine-2,6-diyl) PPympym(4,8-NHR), in high yield(> 80%).



(1)

Ni(0)Lm = zerovalent nickel complex
(a mixture of bis(1,5-cyclooctadiene) nickel ($Ni(cod)_2$) and 2,2'-bipyridyl (bpy))

R = n-C_8H_{17} PPympym(4,8-NHOct)
= n-$C_{12}H_{25}$ PPympym(4,8-NHDod)

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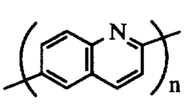
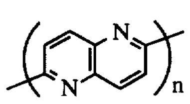
The starting monomers were prepared[1] by modifying a literature method for the preparation of their analogues [5]. PPympym(4,8-NHOct)[2] had *M*n (number average molecular weight) and *M*w (weight average molecular weight) of 8000 and 15000, respectively, as estimated by gel permeation chromatography (*vs* polystyrene standards). It gave an intrinsic viscosity [η] of 0.15 dlg^{-1} in $CHCl_3$ at 30 °C. The IR spectrum of the polymer resembles that of the starting monomer; however, the ν(C-Cl) peak of the monomer at 980 cm^{-1} completely disappeared in the IR spectrum of the polymer.

Figure 1 exhibits a UV-visible spectrum of PPympym(4,8-NHOct) in $CHCl_3$. Films of the polymer cast on a SiO_2 glass plate give an analogous UV-visible spectrum. PPympym(4,8-NHOct) in $CHCl_3$ shows an absorption peak at 452 nm, besides the π-π^* absorption band at 318 nm originated from the monomeric unit and characteristic of aromatic compounds having a naphthalene-like frame [6]. The film of the polymer also gives rise to a main peak at 452 nm, although the shoulder peak at 482 nm becomes stronger in the film. The lowest energy transition peak at 452 nm appears at a longer wavelength compared with those of poly(quinoline-2,6-diyl) (P(2,6-Q)) [3] (λ_{max} = 403 nm in formic acid and 391 nm in the solvent-free film) and poly(1,5-naphthyridine-2,6- diyl) (P(2,6-Nap)) [3] (two λ_{max}'s at 380 and 402 nm in the solvent-free film). Although of a possible bathochromic effect of the NHR substituent must be taken into account, these optical data[3] suggest that



P(2,6-Q)
391 nm
(film)
shift (ΔE) from monomeric unit (quinoline [6]) = 6300 cm^{-1}



P(2,6-Nap)
380 and 402 nm
(film)
ΔE (for 402 nm peak) = 6600 cm^{-1}

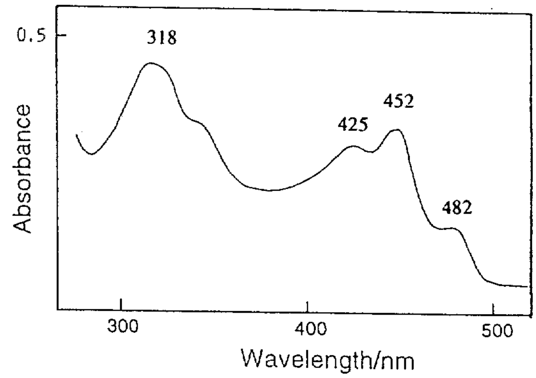


Figure 1. UV-visible spectrum of PPympym(4,8-NHOct) in chloroform.

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[1] Procedure for the dioctyl monomer: 2,4,6,8-tetrachloropyrimido[5,4-*d*]-pyrimidine [5] (1,2 mmol), *N*-octylamine (6.0 mmol), 10 °C, 50 min, in chloroform; isolated by silica chlomatography; 86%. ^{1}H-NMR δ ($CDCl_3$) 0.88 (t, 6H, CH_3), 1.28-1.42 (m, 20H, CH_2), 1.68 (dt, 4H, β-CH_2), 3.57 (qui, 4H, α-CH_2), 6.86 (t, 2H, NH). Didodecyl monomer: 86%. ^{1}H-NMR δ ($CDCl_3$) 0.88 (t, 6H, CH_3), 1.26-1.39 (m, 36H, CH_2), 1.68 (dt, 4H, β-CH_2), 3.57 (qui, 4H, α-CH_2), 6.86 (t, 2H, NH).

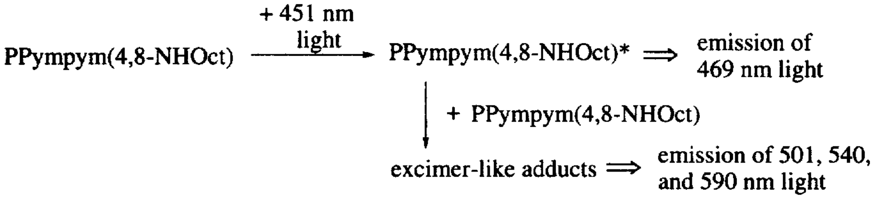
[2] ^{1}H-NMR δ ($CDCl_3$) 0.90 (6H, CH_3), 1.2-4.4 (28H, CH_2), 9.08 (2H, NH). Elemental analysis agreed with a hydrated structure with 0.2 H_2O per monomer unit.

[3] Shifts of the absorption peak from the monomeric compound [6] to polymer: P(2,6-Q): 313 nm (quinoline) to 391 nm or a 6300 cm^{-1} shift; P(2,6-Nap): 308 nm (1,5-naphthyridine) to 402 nm or a 6600 cm^{-1} shift. The absorption peak of the monomeric unit of the present polymer is not known. If the peak at 318 nm originates from the monomeric unit, the shift from 318 nm to 452 nm corresponds to a 9300 cm^{-1} shift. UV-visible spectrum of the dichloro monomer shows a main peak at 304 nm in $CHCl_3$.

PPympym(4,8-NHOct) can have a longer effective π-conjugation due to its coplanar structure. The CPK molecular model of the polymer shows that the coplanar structure of PPympym(4,8-NHOct) receives no steric repulsion. The shoulder absorption peak at 482 nm (Fig. 1) may be associated with molecular stacking of the polymer molecules, which is a subject of recent interest [7-9]. As described above, the peak at 482 nm becomes stronger in the solid, and the detailed analysis of this absorption peak will be reported elsewhere.

PPympym(4,8-NHOct) exhibits four photoluminescence peaks at 469 (main), 501, 540, and 590 nm when irradiated with 451 nm light in chloroform. The position of the main peak agrees with the edge of the main absorption peak at 452 nm as usually observed with aromatic compounds and aromatic polymers. However, the appearance of the three additional photoluminescence peaks at the longer wavelength implies formation of excimer-like adducts [9, 10] between photoexcited PPympym(4,8-NHOct) and the polymer in the ground state; from the excimer-like adducts, emission of the longer wavelength light is considered to take place. The excitation spectrum monitored at any of the photoluminescence peaks shows peaks at 451 and 428 nm, agreeing with the absorption spectrum.

For the cast film of PPympym(4,8-NHOct), the photoluminescence peak at 540 nm becomes the main peak, suggesting that formation of the excimer-like adduct becomes easier in the film due to the presence of polymer molecules near the photoexcited polymer molecule. The excitation spectrum of the PPympym(4,8-NHOct) film, on the other hand, is similar to that observed with a chloroform solution of PPympym(4,8-NHOct), revealing that both the light emission from the chloroform solution and the film is initiated by the same activation of the PPympym(4,8-NHOct) molecule by light.



The cyclic voltammogram (CV) of the film of PPympym(4,8-NHOct) on a Pt plate in a CH_3CN solution of $[NEt_4]BF_4$ (0.10 M) shows a reduction (n-doping) peak at -2.20 V and oxidation (n-undoping) peak at -2.02 V *vs* Ag/Ag^+. Repeated scanning gives essentially the same CV, and these CV data indicate that the polymer is susceptible to the reduction as it contains electron-withdrawing imine nitrogens, in spite of its having the electron-donating NHR substituents. According to the electrochemical reduction (n-doping) at -2.20 V *vs* Ag/Ag^+, the yellow color of the polymer film turns into dark brown, and the polymer film returns to yellow by the n-undoping at -2.02 V *vs* Ag/Ag^+. PPympym(4,8-NHOct) is an insulating material with electrical conductivity (σ) of below 10^{-11} Scm^{-1}. Treatment of powdery PPympym(4,8-NHOct) with sodium naphthalenide in THF gave a Na-doped material which shows a somewhat higher conductivity of 1.3×10^{-8} Scm^{-1}. PPym(4,8-NHDod) (cf. eqn. 1) gave UV-vis, photoluminescence, and CV data similar to those of PPympym(4,8-NHOct).

As described a above, new π-conjugated poly(naphthalene) type polymer, which has nitrogen at all of the four *o*-positions and is considered to be subject to only negligible steric repulsion, has been prepared.

Typical polymerization procedure

A mixture of the monomer (1.0 mmol), $Ni(cod)_2$ (1.5 mmol), bpy (1.6 mmol), and 1,5-cyclooctadiene (0.3 cm^3) in DMF (20 cm^3) was stirred at 60 °C for 40 h. After quenching with NH_4OH(aq) the obtained polymer was washed with NH_4OH(aq) and EDTA(aq). Yield = 90%. The polymer was further dissolved in chloroform and reprecipitated in acetone to yield samples for the instrumental analysis.

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