Molecular Assembling of π-Conjugated Poly(pyrimido[5,4-*d*]pyrimidine-2,6-diyl)s Prepared by Organometallic Polycondensation

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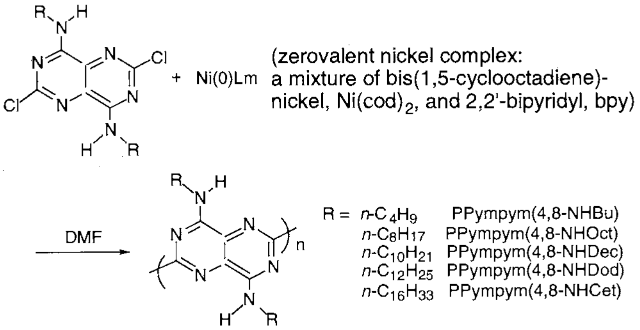
π-conjugated poly(pyrimido[5,4-*d*]pyrimidine-2,6-diyl)s prepared by an organometallic polycondensation and having long side chains are considered to take an end-to-end type packing in the solid as judged from their X-ray diffraction patterns. Their UV-visible spectra show a main absorption peak at about 450 nm, supporting the presence of an expanded π-conjugation system.

Preparation and electrical and optical properties of π-conjugated poly(arylene)s have been the subject of many papers.[1] When they bear long alkyl side chains, they often take a stacked structure assisted by side chain crystallinity (or cohesive force of the alkyl group), and this phenomenon has recently attracted attention of chemists.[2] By preparing the following new type of polymer with nitrogen at all of the *o*-positions, we have studied the assembling mode of the polymer in the solid.



The polymers[3] have been prepared by dehalogenation polycondensation of the corresponding monomer[4] by using a zerovalent nickel complex[5] in high yields, and their CPK molecular models indicate that they can take a coplanar structure due to the absence of steric repulsion caused by an *o*-CH group. The polymer is composed of the new naphthalene-like aromatic units.

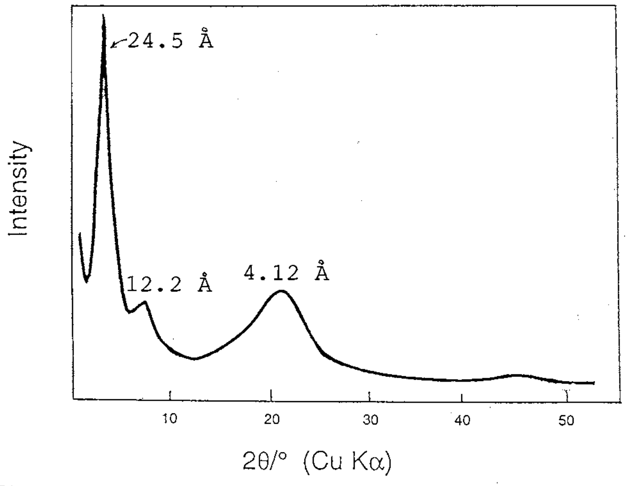


Figure 1. Powder X-ray diffraction pattern of PPympym(NHOct).

Figure 1 shows an example of the X-ray diffraction (XRD) patterns of the polymers. The XRD pattern shows a strong peak at $d = 24.5$ Å, and appearance of this peak is characteristic of aromatic polymers with long side chains and taking an assembled structure in the solid assisted by the side chain crystallinity.[6] The peak at $d = 12.2$ Å is assigned to the second peak ($d = 24.5$ Å/n; n = 2) of the diffraction at $d = 24.5$ Å. Other polymers also give rise to such a diffraction peak at the low angle region and plots of the *d* value against the number of carbon in the R chain give a roughly linear line as depicted in Figure 2.

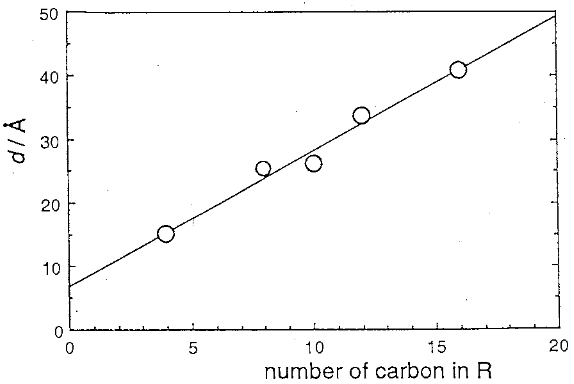


Figure 2. Plots of the *d* value against the number of carbon in the R group in the polymer.

In view of the number density of R group along the polymer chain (D = about 6.6 Å in Figure 3 as estimated from the CPK molecular model) and an effective diameter (5 Å)[2,6] of the R group, the polymer is considered to take an end-to-end packing mode rather than an interdigitation packing mode.[2,6] The *d* value estimated from the diffraction peak at the low angle is considered to correspond to the distance between the core poly(arylene) chains separated by the NHR group.

The slope of the line in Figure 2, 2.13 Å/carbon, agree with the end-to-end packing mode since one CH_2 unit has a height of 1.25 Å.[2,6] The broad peak at about $d = 4.12$ Å (Figure 1) is considered to correspond to a plane-to-plane distance between the planar polymer moleculers.

The polymers, except for PPympym(4,8-NHBu), are soluble in $CHCl_3$. In the chloroform solution, the UV-visible spectrum shows peaks at 425, 452 (main peak), and 483 nm, which are assigned to π-π* transition occurred along the polymer main chain, besides the peaks at 318 and 345 nm, which are characteristic of naphthalene-like molecules[7] and assigned to π-π* transition occurred in the monomeric unit. The π-π* transition

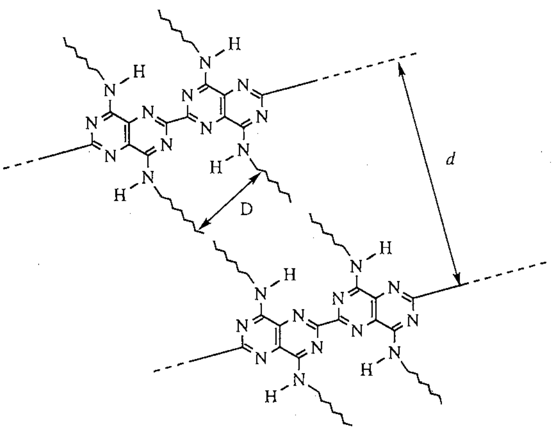


Figure 3. An end-to-end packing model of PPympym(4,8-NHR).

along the main chain occurs at a lower transition energy than that observed with poly(quinoline-2,6-diyl) (λ = 403 nm) having *o*-CH group,[8] presumably due to the highly planar structure of the present polymer. Other PPympym(4,8-NHR) gives analogous UV-visible data in $CHCl_3$.

In the film the shape of the UV-visible spectrum changes, and the peaks at the longer wavelengths (452 and 483 nm) become stronger compared with the peak at 425 nm. Similar behavior has been reported for regioregular poly(3-alkylthiophene-2,5-diyl)s and poly(4-alkylthiazole-2,5-diyl)s,[2] and the results described above suggest that peaks at the longer wavelengths (452 and 483 nm) are considered to originate from assembled molecules, similar to cases of poly(3-alkylthiophene-2,5-diyl)s and poly(4-alkylthiazole-2,5-diyl)s. The peaks at 452 and 483 nm become also stronger when the solution is passed through a needle or capillary, suggesting similar alignment of the polymer in the fluid solution.

References and Notes

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3 E.g., PPympym(NHOct): polymerization and work-up of the polymer were carried out in a manner similar to that previously reported (in DMF at 60 °C for 40 h).[5] Crude yield = 90%. Yield after reprecipitation of a chloroform solution of the polymer into acetone = 60%. Anal. Found: C, 68.0, H, 9.6; N, 20.3; Cl, 0%. Calcd. for $(C_{22}H_{36}N_6\cdot 0.2H_2O)_n$: C, 68.1, H, 9.5; N, 21.7%. ^{1}H-NMR ($CDCl_3$): δ: 0.90 (6H, CH_3), 1.2-4.4 (28H, CH_2), 9.08 (2H, NH). *M*n and *M*w (GPC; polystyrene standards in chloroform): 8000 and 15000, respectively. $[\eta]$ = 0.15 dlg^{-1} (dl = 100 cm^3) in chloroform at 30 °C. Other polymers were prepared analogously and their analytical data agreed with partly hydrated structures.

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