Preparation of Poly(diphenylamine-4,4'-diyl) and a Related Polymer by Organometallic Polycondensation and Their Properties

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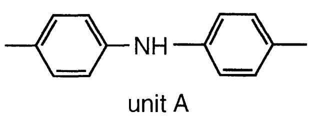
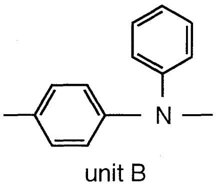
Nickel-promoted dehalogenation polymerization of bis(4-bromophenyl)amine gives poly(diphenylamine-4,4'-diyl) with a [η] value of 0.66 dLg^{-1} in high yield. The polymer has been characterized by IR, ^{1}H-NMR and UV-visible spectroscopy and shows semiconductivity when treated with acids. Poly(azobenzene-4,4'-diyl) has been prepared in an analogous way.

Electrically conducting poly(arylamine)s have been the subject of recent many papers.[1] They have usually been prepared by chemical and electrochemical oxidation of arylamines, $ArNH_2$ or ArAr'NH, and are considered to have essentially a linear structure formulated as $(ArNH)_n$ or $(ArAr'N)_n$.[1] However, there seems to exist some ambiguity concerning microstructures of the polymers. For example, even poly(aniline) may contain *o*- and *m*-phenylene units in addition to the main *p*-phenylene units. When the monomer arylamine has a larger aryl group, there will be more ways for the arylene unit to be bonded to another monomer unit in the produced polymer. Actually, two kinds of poly(diphenylamine) (or poly(4-aminobiphenyl)) prepared by oxidation polymerization of $C_6H_5NHC_6H_5$[2] and $C_6H_5C_6H_4NH_2$,[2a,b] respectively, present essentially the same IR spectra[2b] and are considered to consist of the following two units.

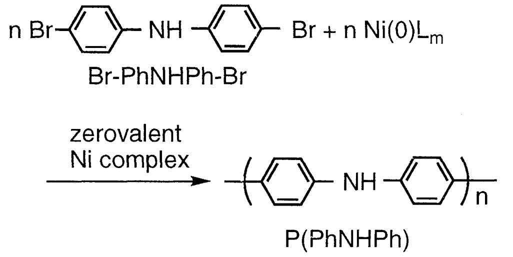


unit A



unit B

In order to give basis for structural analysis of poly(arylamine), we have carried out Ni-promoted dehalogenation polycondensation[3] of bis(4-bromophenyl)amine Br-PhNHPh-Br to yield the corresponding polymer P(PhNHPh); the polycondensation is considered to proceed selectively at the C-Br bond and the polymer is considered to have a well defined structure.



(1)

Stirring a DMF (20 cm^3) solution containing Br-PhNHPh-Br[4] (400 mg, 1.22 mmol), bis(1,5-cyclooctadiene)nickel(0) $Ni(cod)_2$ (403 mg, 1.46 mmol), and 2,2'-bipyridyl bpy (229 mg, 1.46 mmol) at 60 °C for 16 h gave light green P(PhNHPh)[5] in 97% yield. P(PhNHPh) is soluble in N-methyl-2-pyrrolidone (NMP) and trifluoroacetic acid, and partly soluble in DMF, THF, and DMSO. The polymer gives a [η] value of 0.66 dL g^{-1} (dL = 100 cm^3) in NMP at 30 °C and shows Mn and Mw values of 6400 and 20000, respectively, as determined by GPC (eluent = DMF; polystyrene standard). The relatively large [η] value for the Mn value is attributed to a stiff structure of the polymer. At shorter polymerization time, e.g., 4 h, the polymer shows a smaller [η] value of 0.32 dL g^{-1} and a lower Mw value of 4000. The previously reported poly(diphenylamine) seems not to have good solubility in solvents according to the literature.

Figure 1 depicts IR spectra of P(PhNHPh) and its reaction product[6] with concentrated HCl(aq). The IR spectra resemble those of poly(diphenylamine) prepared by the oxidation polymerization and its HCl salt, respectively.[2] However, IR spectra of the present samples exhibit simpler absorption patterns and show some difference from those of the previously reported samples. For example, the ν(N-H) band of P(PhNHPh) is considerably sharper than that of previously reported poly(diphenylamine). P(PhNHPh) and its HCl adduct give rise to one sharp out of plane vibration δ(CH) band at 803 cm^{-1}

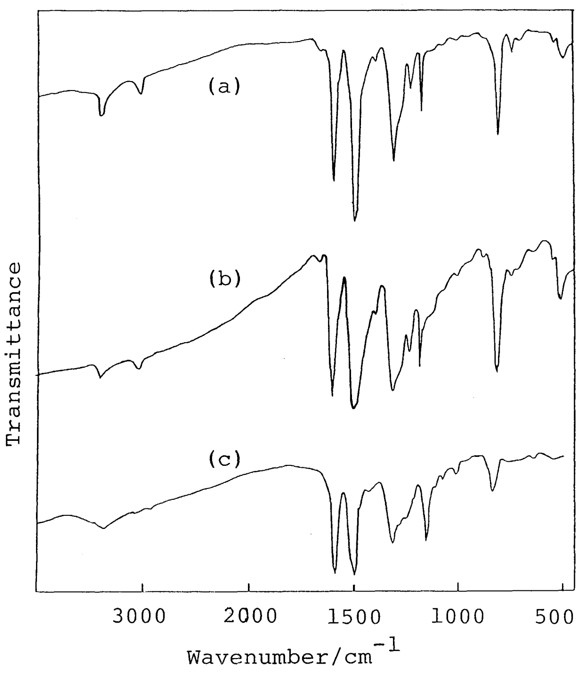


Figure 1. IR spectra of (a) P(PhNHPh), (b) its reaction product with HCl(aq), and (c) P(PhN=NPh).

(with a weak satellite peak at 750 cm^{-1}) characteristic of *p*-phenylene unit.[3] On the other hand, the previously reported samples give multiple (2 or 3) strong absorption bands in this region,[2] presumably due to the presence of unit B (*vide ante*). A sharp absorption band of Br-PhNHPh-Br at 1069 cm^{-1}, which is assigned to ν(C-Br), was not observed in the IR spectrum of P(PhNHPh). ^1H-NMR spectrum of P(PhNHPh) in trifluoroacetic acid exhibits an AB quartet pattern (δ 7.62 ppm and 7.73 ppm with J = 9.5 Hz) characteristic of the *p*-phenylene unit. $^{13}C\{^1H\}$-NMR spectrum shows sharp four peaks at δ 115.0, 124.3, 129.8, and 140.3 ppm in NMP (Figure 2).

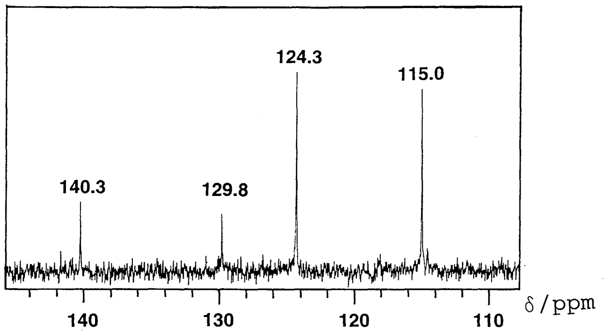


Figure 2. $^{13}C\{^1H\}$-NMR spctrum of P(PhNHPh) in NMP.

UV-visible spectrum of P(PhNHPh) in DMF shows a π-π* absorption peak at 365 nm, which is somewhat shifted to a longer wavelength from that of leucoemeraldine base type poly(aniline) PLM $(C_6H_4NH)_n$ at 325 nm.[1] The monomer Br-PhNHPh-Br shows a π-π* absorption peak at 295 nm. Oxidized polyaniline, poly(emeraldine base) PEM $(C_6H_4NHC_6H_4NH)_m$-$(C_6H_4N{=}C_6H_4{=}N)_n$, gives a characteristic absorption band at 630 nm,[1] however, P(PhNHPh) shows no absorption band in the region even in the DMF solution under air, in contrast to facile oxidation of PLM to PEM under air.[1b] All the above described data indicate P(PhNHPh) shown in eqn. 1 is obtained and the polymer is air-stable. However, cyclic voltammogram of a cast film of P(PhNHPh) in a CH_3CN solution of 0.1M $[Et_4N]BF_4$ shows clear two-step redox cycles at E_{pa} values of 0.27 and 0.65V *vs* Ag/Ag^+ and E_{pc} values of 0.12 and 0.54 V *vs* Ag/Ag^+, respectively. During the first oxidation step, the colorless film becomes red, whereas, during the second step, a color change to purple is observed. On the reduction, the film becomes colorless, and the electrochemical redox reactions can be repeated without changes in the cyclic voltammogram. Poly(aniline) also shows similar two-step electrochemical processes,[7] and the redox potentials of P(PhNHPh) are somewhat higher (by about 0.2 V) than those of poly(aniline).

Obtaining well-characterized poly(arylamine) is expected to contribute to comprehension of chemical properties of poly(arylamine)s. P(PhNHPh) shows strong photoluminescence with a quantum yield of about 20% in NMP when irradiated with 379 nm light. P(PhNHPh) treated with 0.1 M HCl(aq)[8] has electrical conductivity of 1.1 x 10^{-5} S cm^{-1} as measured with a compressed powder. A film of P(PhNHPh) prepared by casting from NMP is insulating with electrical conductivity (σ) less than 10^{-9} S cm^{-1}, however, it shows electrical conductivity of 1.6 x 10^{-2} S cm^{-1} at room temperature when treated with 10% H_2SO_4 (aq). Partial oxidation of P(PhNHPh) to give quinoid units may take place in 10% H_2SO_4 (aq).

In relation to the polycondensation of Br-PhNHPh-Br (eqn. 1), we have also carried out similar dehalogenation polycondensation of 4,4'-dibromoazobenzene Br-PhN=NPh-Br to yield poly(azobenzene-4,4'-diyl) P(PhN=NPh). Stirring a DMF (20 cm^3) solution containing Br-PhN=NPh-Br (0.44 mmol), $Ni(cod)_2$ (0.53 mmol) and bpy (0.53 mmol) for 16 h at 60 °C and work-up gave dark purple P(PhN=NPh) with Mn and Mw of 2700 and 6000, respectively, as determined by GPC (*vs* polystyrene). IR spectrum of the polymer is shown in Figure 1 and ^1H-NMR spectrum of the polymer shows somewhat broad peaks at δ 7.2 ppm and 7.8 ppm. It is known that oxidation of aniline gives various by-products such as benzidine, azobenzene, and hydrazobenzene depending on reaction conditions.[9] Such by-products may lead to incorporation of an azobenzene-like unit in polyaniline produced by the oxidation polymerization, and obtaining the polymer constituted of the -PhN=NPh- unit will also contribute to comprehension of structure and properties of poly(arylamine)s.

We are grateful to Mrs. A. Nishino and Miss F. Yamaguchi for measurement of the electrical conductivity of film of P(PhNHPh).

References and Notes

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5 The polymer was worked-up in a manner similar to that previously reported.[3] Anal. Found: C, 84.5; H, 5.4; N, 8.3; Br, 0%. Calcd for $(C_{12}H_9N)_n$: C, 86.2; H, 5.4; N, 8.4%. The difference between the found and calcd. values may be attributed high thermal stability of the polymer (cf. text) and partial incorporation of water.

6 Prepared by stirring powdery P(PhNHPh) in concentrated HCl (aq.). Reference 2b reports IR spectrum of Cl-doped (or HCl-doped) poly(diphenylamine).

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8 Powdery P(PhNHPh) was stirred in an aqueous solution of HCl (0.1 M) for 1 day at room temperature. The powder was collected by filtration and dried under vacuum.

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