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I_2-doped and pyrrole ring-iodinated semi-conducting oligomers of N-vinyl-3-alkyl-2-phenylpyrroles

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ABSTRACT

I_2-doped and pyrrole ring-iodinated semi-conducting oligomers of N-vinyl-3-alkyl-2-phenylpyrroles have been synthesized by free-radical polymerization of the above monomers (AIBN, 2–5 wt%, 60–80 °C) and further exposure of the oligomers obtained to I_2 vapor. The parent oligomers exhibit paramagnetic and fluorescent properties and stable up to 300–370 °C.

1. Introduction

Polymers of N-vinylpyrroles provoke increasing interest since they represent precursors of organic semiconductors [1–6], polymer azo-dyes [7,8], absorbents of noble metals [9], biologically active compounds and protecting agents for plants [10].

Ladder polymers of N-vinylpyrrole and N-vinyl-3-decylpyrrole, prepared through the radical polymerization across the vinyl group followed by the oxidation of the pyrrole moieties possess electroconductivity of 10^{-2}–10^{-3} S/cm [2–5]. Polymers of N-vinylpyrroles bearing aryl substituents such as 1,4-bis[2-(N-vinyl)pyrrolyl]benzene, N-vinyl-2,5-diphenylpyrrole, N-vinyl-2,3,5-triphenylpyrrole, 9-methyl-3-(N-vinylpyrrole-2-yl)carbazole, N-vinyl-2-(1-anthracenyl)- and N-vinyl-2-(2-anthracenyl)pyrroles have been claimed as novel highly efficient luminescent materials which are promising for the design of conducting electrochromic layers in optoelectronic devises (thin-film displays, fluorescent sensors) [11].

Herein we present the results on the polymerization of N-vinyl-3-alkyl-2-phenylpyrroles and further modification of the oligomers obtained by their reaction with iodine (doping and ring-iodination). The combination of phenyl substituent in the position 2 of the pyrrole ring with alkyl group in the position 3 allows the angle between planes of the pyrrole and benzene rings to be controlled, thus changing the conjugation degree in the monomer and hence altering the nano-, micro- and macro-characteristics of the polymer materials.

Nowadays, a virtually unlimited series of N-vinyl-3-alkyl-2-arylpyrroles became easily accessible due to the development of expedient synthesis of N-vinylpyrroles from acylated aromatic compounds, hydroxylamine and acetylene [12–17] (Scheme 1).

Despite availability of the above monomers, the polymerization of N-vinyl-3-alkyl-2-phenylpyrroles remained unexplored. Previously [18–21], it was reported on radical polymerization of N-vinyl-2-phenylpyrrole (AIBN or UV irradiation or both), delivering paramagnetic (6.0×10^{17} spin/g, after doping with iodine vapor) oligomers (molecular weight 2100–3000) in up to 40% yields. The oligomers were shown to be electroconducting (1.3×10^{-6} S/cm) and fluorescent (355–358 nm, acetonitrile).

The present work is aimed at the synthesis and modification by the reaction with I_2 of new semi-conducting and paramagnetic oligomers. The effect of various alkyl substituents in the position 3 of the pyrrole ring of N-vinyl-3-alkyl-2-phenylpyrroles on yields and properties of the oligomers is also addressed.

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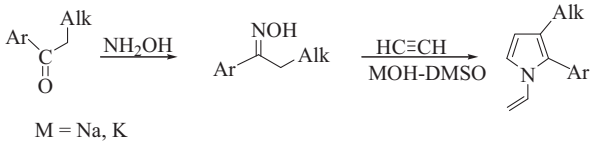

Scheme 1. Trofimov reaction (synthesis of N-vinylpyrroles).

2. Experimental

2.1. Materials

The solvents (benzene, *n*-hexane) were purified according to the protocols [22], DMSO (Aldrich) was used without additional purification.

AIBN (azobisisobutyronitrile) was recrystallized twice from methanol.

N-Vinyl-3-alkyl-2-phenylpyrroles **4–6** were synthesized by the procedures [23–25] from the corresponding oximes of alkylphenylketones and acetylene in the KOH-DMSO system. Below their full spectral characteristics, lacking in the works indicated, are given.

2.2. Measurements

IR spectra of the compounds synthesized were registered in the region 400–4000 cm^{-1} with a Bruker "Vertex" instrument as films or KBr pellets. NMR spectra were recorded on a Bruker DPX 400 spectrometer [400.13 MHz (^{1}H), 100.6 MHz (^{13}C)] using $CDCl_3$ as solvent and HMDS as the internal standard.

Absorption and fluorescence spectra were recorded on Perkin-Elmer Lambda 35 spectrophotometer and Perkin-Elmer LS-55 luminescent spectrometer, respectively. Fluorescence quantum yields of oligomers were determined in relation to 2-phenylpyrrole (F_{rel} = 1.0). Optical densities of solutions were <0.1 upon thickness 1 cm and excitation wavelength λ_{ex} = 290 nm. Oxygen was removed from solutions by argon bubbling for 20 min.

The ESR spectra were measured with an ELEXSYS E580 Bruker radiospectrometer in CW or pulse mode at room temperature. The concentration of paramagnetic centers was calculated by the method of double integration using the calibrated diphenylpycrylhydrazyl standard. The following pulse sequences were used to determine relaxation characteristics: $\pi - T - \pi/2 - \tau - \pi$ for T_1, $\pi/2 - \tau - \pi$ for T_2, where $\pi/2$ = 20 ns, τ = 250 ns and T = 750 ns.

The electrical conductivity of the polymers was measured with an E6-13A teraohmmeter. Studied samples were prepared as pellets by molding under a pressure of 700 kg/cm^2. The oligomers were doped with iodine using diffusion technique from gas phase for 19–168 h.

The thermogravimetric analysis (TGA) of the polymers was performed on a Q-1500D derivatograph (MOM, Hungary), maximal temperature 700 °C, at heating rate 10 °C/min in static air atmosphere; the sensitivity for DTA was 1/10.

Molecular weights of the oligomers were measured by the isopiestic method in benzene at 60 °C, using azobenzene as standard [26].

2.3. Synthesis

N-Vinyl-3-n-amyl-2-phenylpyrrole (**4**), b.p. 145–146 °C (1 mm Hg). IR (microlayer, cm^{-1}): 3108, 3082, 3060 (ν, =C–H), 2956, 2928, 2756 (ν, CH_2, CH_3), 1951, 1885, 1812, 1760 (C–H of the phenyl cycle), 1641 (ν, C=C), 1603, 1564, 1500, 1477 (ν, C=C of the pyrrole and phenyl rings), 1430, 1381, 1318 (ν, C–N), 1269, 1228, 1179, 1072, 1033 (δ, C–C of the skeleton), 990 (τ, C=C), 964, 916, 856 (ω, C=C), 772, 726, 701, 678 (τ, =C–H), 601 (ω, C–C).

^{1}H NMR ($CDCl_3$, δ, ppm, *J*/Hz): 7.37 (2H, m, *m*-Ph), 7.31 (1H, m, *p*-Ph), 7.25 (2H, m, *o*-Ph), 7.03 (1H, d, H-5, $^3J_{H5\text{-}H4}$ 3.2 Hz), 6.65 (1H, q, H_x, $^3J_{Hx\text{-}Hb}$ 7.9 Hz, $^3J_{Hx\text{-}Ha}$ 15.8 Hz), 6.19 (1H, d, H-4, $^3J_{H4\text{-}H5}$ 3.2 Hz), 5.00 (1H, d, H_a, $^3J_{Ha\text{-}Hx}$ 15.8 Hz), 4.48 (1H, d, H_b, $^3J_{Hb\text{-}Hx}$ 7.9 Hz), 2.35 (2H, t, CH_2-1, ^{3}J 7.9 Hz), 1.49 (2H, m, CH_2-2), 1.22 (4H, m, CH_2-3,4), 0.81 (3H, t, CH_3, ^{3}J 6.6 Hz).

^{13}C NMR ($CDCl_3$, δ, ppm): 132.0 (C-*i*, C-α), 131.1 (C-*m*), 130.3 (C-2), 128.2 (C-*o*), 127.4 (C-*p*), 124.0 (C-3), 116.2 (C-5), 110.6 (C-4), 96.8 (C-β), 31.7, 31.0, 26.0, 22.6 (CH_2-1,2,3,4), 14.1 (CH_3).

N-Vinyl-3-n-heptyl-2-phenylpyrrole (**5**), b.p. 160–161 °C (1–2 mm Hg). IR (microlayer, cm^{-1}): 3108, 3083, 3060 (ν, =C–H), 2955, 2926, 2870 (ν, CH_2, CH_3), 1950, 1883, 1810, 1759 (C–H of the phenyl cycle), 1641 (ν, C=C), 1604, 1565, 1500, 1477 (ν, C=C of the pyrrole and phenyl rings), 1441, 1431, 1415, 1381, 1318 (ν, C–N), 1227, 1178, 1072, 1030 (δ, C–C of the skeleton), 990 (τ, C=C), 963, 916, 855 (ω, C=C), 772, 724, 701, 678 (τ, =C–H), 636, 619, 601 (ω, C–C).

^{1}H NMR (δ, ppm, *J*/Hz): 7.39 (2H, m, *m*-Ph), 7.31 (1H, m, *p*-Ph), 7.25 (2H, m, *o*-Ph), 7.03 (1H, d, H-5, $^3J_{H5\text{-}H4}$ 2.7 Hz), 6.66 (1H, q, H_x, $^3J_{Hx\text{-}Hb}$ 8.9 Hz, $^3J_{Hx\text{-}Ha}$ 15.8 Hz), 6.18 (1H, d, H-4, $^3J_{H4\text{-}H5}$ 2.7 Hz), 5.02 (1H, d, H_a, $^3J_{Ha\text{-}Hx}$ 15.8 Hz), 4.50 (1H, d, H_b, $^3J_{Hb\text{-}Hx}$ 8.9 Hz), 2.36 (2H, m, CH_2-1), 1.49 (2H, m, CH_2-2), 1.20 (8H, m, CH_2-3,4,5,6), 0.83 (3H, t, CH_3, ^{3}J 7.1 Hz).

^{13}C NMR (δ, ppm): 131.9 (C-*i*, C-α), 131.0 (C-*m*), 130.3 (C-2), 128.2 (C-*o*), 127.3 (C-*p*), 123.9 (C-3), 116.2 (C-5), 110.5 (C-4), 96.7 (C-β), 31.9, 31.3, 29.5, 29.3, 26.0, 22.7 (CH_2-1,2,3,4,5,6), 14.2 (CH_3).

N-Vinyl-3-n-nonyl-2-phenylpyrrole (**6**), b.p. 170–171 °C (1 mm Hg). IR (microlayer, cm^{-1}): 3109, 3083, 3048 (ν, =C–H), 2955, 2925, 2870 (ν, CH_2, CH_3), 1950, 1884, 1811 (C–H of the phenyl cycle), 1641 (ν, C=C), 1604, 1564, 1500, 1477 (ν, C=C of the pyrrole and phenyl rings), 1441, 1415, 1381, 1318 (ν, C–N), 1265, 1227, 1180, 1070, 1031 (δ, C–C of the skeleton), 990 (τ, C=C), 963, 916, 856 (ω, C=C), 772, 739, 701, 678 (τ, =C–H), 636, 619 (ω, C–C).

^{1}H NMR ($CDCl_3$, δ, ppm, *J*/Hz): 7.39 (2H, m, *m*-Ph), 7.32 (1H, m, *p*-Ph), 7.25 (2H, m, *o*-Ph), 7.03 (1H, d, H-5, $^3J_{H5\text{-}H4}$ 2.8 Hz), 6.66 (1H, q, H_x, $^3J_{Hx\text{-}Hb}$ 8.8 Hz, $^3J_{Hx\text{-}Ha}$ 15.6 Hz), 6.19 (1H, d, H-4, $^3J_{H4\text{-}H5}$ 2.8 Hz), 5.01 (1H, d, H_a, $^3J_{Ha\text{-}Hx}$ 15.6 Hz), 4.50 (1H, d, H_b, $^3J_{Hb\text{-}Hx}$ 8.8 Hz), 2.36 (2H, m, CH_2-1), 1.49 (2H, m, CH_2-2), 1.24 (4H, m, CH_2-3,4), 1.20 (8H, m, CH_2-5,6,7,8), 0.85 (3H, t, CH_3, ^{3}J 7.0 Hz).

^{13}C NMR ($CDCl_3$, δ, ppm): 132.0 (C-*i*, C-α), 131.1 (C-*m*), 130.3 (C-2), 128.2 (C-*o*), 127.4 (C-*p*), 124.0 (C-3), 116.3 (C-5), 110.5 (C-4), 96.8 (C-β), 31.9, 31.3, 29.8, 29.6, 29.4, 26.1, 22.8 (CH_2-1,2,3,4,5,6,7,8), 14.2 (CH_3).

Purity of the monomers was 99% (GLC, IR and ^{1}H NMR).

Radical polymerization of N-vinyl-3-n-amyl-2-phenylpyrrole (typical example). Pyrrole **4** (1.00 g, 4.178 mmol) and AIBN (0.02 g, 2 wt%) were heated in an ampoule under argon (80 °C, 30 h). The oligomer **7** formed was isolated by the precipitation from benzene solution to ethanol, filtered off, washed with ethanol and dried in vacuum until the constant weight to give 0.76 g (76%) of white powder, soluble in benzene, chloroform, dioxane and acetonitrile, m.p. 141–148 °C. Elem. Anal. $C_{17}H_{21}N$– calcd.: C, 85.31%; H, 8.84%; N, 5.85%; Found: C, 85.11%; H, 8.89%; N 6.00%.

Pyrroles **5** and **6** were polymerized analogously, the polymerization conditions are given in Table 1.

Doping and iodination of oligo-N-vinyl-2-phenylpyrrole (**10**) *with iodine.* Oligo-N-vinyl-2-phenylpyrrole **10** (0.151 g, 0.892 mmol calculated per one unit) was doped with iodine for 168 h using diffusion technique from gas phase to give brown-black powder **10**-3 (0.529 g, growth in weight 0.378 g, 250.3%). Found, %: C, 23.74; H, 1.59; I, 70.63; N, 2.71.

Oligomer **10**-3 was washed with ether, ethanol (until the solution became transparent), dissolved in acetone and precipitated in hexane. The residue obtained was filtered off, washed with hex-