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LETTERS TO THE EDITOR

A New Approach to Polymerization of Heterocycles

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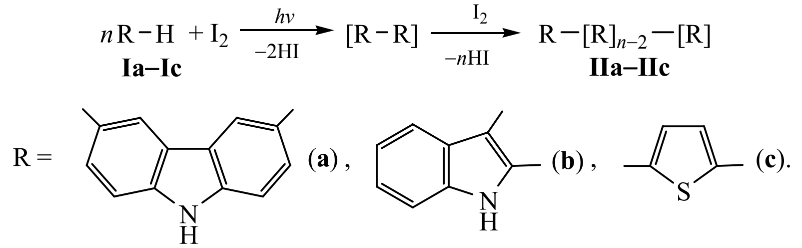
Polyheteroarylenes are of interest due to a wide range of their properties (electrical conductivity, luminescence, electroluminescence, etc.). These compounds can be recommended for use as organic conductors and semiconductors, sensors, photodetectors, light emitting diodes, transistors, photovoltaic cells [1–11].

The main methods of synthesis of polyheteroarylenes are based on oxidative, electrochemical, or metal-catalyzed polycondensation of heterocycles and their derivatives [12–19], Yamamoto coupling [20, 21], Suzuki [22], Stille [23] and Heck reactions [24].

We found that irradiation of the melts of carbazole **Ia**, indole **Ib** and thiophene **Ic** in the presence of iodine in argon atmosphere leads to the oxidative polycondensation of heterocyclic compounds to form polyheteroarylenes **IIa**–**IIc**.



$$n\mathrm{R{-}H} + \mathrm{I_2} \xrightarrow[-2\mathrm{HI}]{h\nu} [\mathrm{R{-}R}] \xrightarrow[-n\mathrm{HI}]{\mathrm{I_2}} \mathrm{R{-}[R]}_{n-2}\mathrm{{-}[R]}$$

Ia–**Ic** **IIa**–**IIc**

According to the IR and ^{13}C NMR spectroscopy data, the centers of polymerization of carbazole **Ia** are 3,6-position of carbazole ring due to presumed dehydrogenation by the formed iodine radicals. This is evidenced by the presence in the IR spectrum of polycarbazole **IIa** of the characteristic bending vibrations of C–H bonds of 1,2,4-substituted benzenes at 806 cm^{-1} [25] and the absence of absorption bands of C^{3,6} carbon atoms of unsubstituted carbazole ring in the range of 723 and 748 cm^{-1} [26]. The broad absorption band at 3389 cm^{-1} is due to stretching vibrations of N–H bond in the carbazole fragment [27, 28].

The polymerization centers in indole **Ib** are 2,3-positions: In the IR spectrum of polyindole **IIa** there is no signals of the bending vibrations characteristic of 2,3-unsubstituted C–H bonds of indole in the range of 720–730 cm^{-1} [29, 30]. Benzene ring of indole is not involved in the oligomerization as the IR spectrum of polyindole **IIa** contains intensive absorption band of out-of-plane vibrations of unsubstituted benzene ring at 745 cm^{-1} [31]. A broad intensive band at 3411 cm^{-1} corresponds to stretching vibrations of N–H bonds in indole fragment [31].

The absence in the IR spectrum of polymer **IIc** of absorption band at 3100 cm^{-1} corresponding to the stretching vibrations of C–H bond in the positions 2 and 5 relative to the sulfur atom [32, 33] indicates the substitution of hydrogen atoms in the polymer.

During the polycondensation of heterocyclic compounds **Ia**–**Ic** the resulting polymers **IIa**–**IIc** are doped with iodine. This is evidenced by absorption bands at 293 and 358 nm in their UV spectra, which are characteristic of the triiodide ion (I_3^-) [34]. The synthesized polyarylenes **IIa**–**IIc** are black high-melting powders (decomp. > 350°C). Their solutions in organic solvents form coatings with high adhesion on different substrates (quartz, glass, aluminum). Conductivity of polyarylenes **IIa**–**IIc** is 1.6×10^{-10}, 7.6×10^{-10}, and 7.6×10^{-7} S cm^{-1}, respectively. The absence of the covalently bonded iodine atom in **IIa**–**IIc** is confirmed by the ease of removal of triiodide ion at a two-fold reprecipitation by water.

Thus, the obtained data provide new synthetic routes to useful polyheteroarylenes excluding the use of a catalyst and a solvent to form new hetaryl C–C bond.

General procedure for the polymerization of heterocycles. Melt of heterocyclic compound **Ia**–**Ic** with iodine in an argon atmosphere was irradiated with UV light (λ 254 nm) under stirring for 2 h. Resulting oligomer **IIa**–**IIc** was extracted with acetone (30 ml) and precipitated by hexane (90 ml). After removing excess of elemental iodine (extraction with diethyl ether in a Soxhlet apparatus for 5 h, monitoring by UV spectroscopy), the powder was twice reprecipitated (acetone–hexane, 1:3), and dried in a vacuum.

Poly(2,6-carbazole) (IIa) was obtained from 2 g (12 mmol) of carbazole **Ia** and 2.5 g (12 mmol) of iodine. Yield 1.8 g (50% relative to $C_{168}H_{128}I_{15}N_{14}$), black powder, decomp. > 350°C. IR spectrum (film), ν, cm^{-1}: 3389 (N–H). ^1H NMR spectrum, δ_H, ppm: 7.26–7.43 m (Ar), 9.03 s (NH). ^{13}C NMR spectrum, δ_C, ppm: 111.91–143.38 m (Ar). M_w 4200, M_n 1500, M_w/M_n (polydispersity degree) 2.8. Found, %: C 46.86; H 2.99; I 45.31; N 4.44. $C_{168}H_{128}I_{15}N_{14}$. Calculated, %: C 47.51; H 3.04; I 44.89; N 4.62.

Poly(2,2',3,3'-indole) (IIb) was obtained from 1.0 g (8 mmol) of indole **Ib** and 2 g (8 mmol) of iodine. Yield 0.95 g (73% relative to $C_{80}H_{52}N_{10}I_3$), black powder, decomp. > 350°C. IR spectrum (film), ν, cm^{-1}: 3367 (N–H). ^1H NMR spectrum, δ_H, ppm: 6.88–8.84 m (Ar), 10.97 s (NH). ^{13}C NMR spectrum, δ_C, ppm: 111.46–143.76 m (Ar). M_w 1600, M_n 600, M_w/M_n 2.6. Found, %: C 61.69; H 2.88; I 25.47; N, 8.27. $C_{80}H_{52}I_3N_{10}$. Calculated, %: C, 62.62; H, 3.42; I, 24.81; N, 9.13.

Poly(2,5-thiophene) (IIc) was obtained from 2.0 g (24 mmol) of thiophene **Ic** and 2.5 g (24 mmol) of iodine. Yield 0.15 g (5% relative to $C_{128}H_{66}S_{32}I_{12}$), black powder, decomp. 330°C. M_w 4100, M_n 1800, M_w/M_n 2.27. ^1H NMR spectrum, δ_H, ppm: 7.12–7.93 m (thienyl). ^{13}C NMR spectrum, δ_C, ppm: 128.93–142.02 m (thienyl). Found, %: C 37.85; H 1.79; I 35.80; S 24.62. $C_{128}H_{66}I_{12}S_{32}$. Calculated, %: C 37.02; H 1.60; I 36.67; S 24.11.

The fraction insoluble in acetone was repeatedly washed with chloroform, THF, and diethyl ether. Yield 2.0 g, black powder, decomp. > 460°C. Found, %: C 37.10, H 1.50; S 25.15; I 36.17.

The IR spectra were recorded on a FT-IR Vertex 70 Ram II spectrometer (KBr, film). The UV spectra were registered on a Lambda 35 Perkin Elmer spectrophotometer. The ^1H and ^{13}C NMR spectra were obtained on a Bruker DPX-400 spectrometer (^1H, 400, ^{13}C 100 MHz) from solutions in acetone-d_6 relative to the residual proton signals of acetone. Molecular weight of polyarylenes **IIa**–**IIc** was determined on a Waters gel-chromatograph equipped with refractometric detector at 25°C eluting with THF. Electrical conductivity was measured on a BK2-16 electrometric amplifier. Photolysis of heterocyclic compounds **Ia**–**Ic** was carried out in a quartz flask irradiated by mercury-quartz lamp DRT-230 (λ 254 nm). The reaction progress and purity of the compounds were monitored by TLC on Silufol UV-254 plates, eluting with chloroform and detecting with iodine vapor.

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