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## LETTERS TO THE EDITOR

# New Approach to Poly(2,7-carbazoles)

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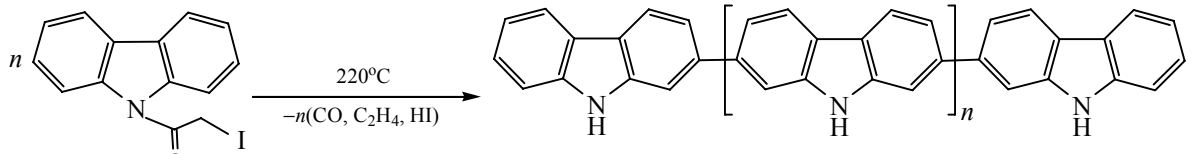
Polycarbazoles and heteropolymers containing carbazole fragments possess unique electric and photoelectric properties. They are used as sensors, light-emitting diodes, transistors, and photogalvanic elements [1–9]. Special interest to poly(2,7-, 3,6-, and 1,8-carbazoles) and their copolymers is due to their ability to fluorescence in the blue region of the spectrum [10].

General methods for the synthesis of polycarbazoles are based on the reactions of chemical and electrochemical oxidation of carbazole [10] and its dihalogenated derivatives [11–15], on Yamamoto [16, 17], Suzuki [18], Stille [19], Heck coupling reactions [20].

We have developed a new method for the synthesis of poly(2,7-carbazoles) based on thermal polymerization (220–270°C) of the first prepared α-iodoacetylcarbazoles (**I, II**) in an argon atmosphere in the absence of catalyst and solvent.

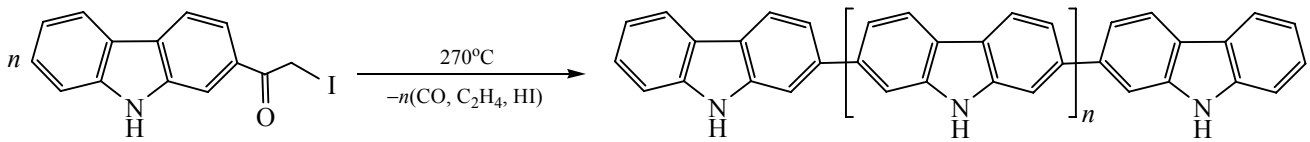
When heating 1-(9*H*-carbazol-9-yl)-2-iodo-1-ethanone (**I**) to 220°C carbon monoxide, ethylene, hydrogen iodide are evolved, and polycarbazole **III** with $M_w$ 1400, $M_n$ 1000, $M_w/M_n$ (degree of polydispersity) 1.4 is formed in 65% yield. Compound **III** is soluble in organic solvents.




**I** **III**

IR spectroscopic study has shown that the centers of polymerization, most probably, are the 2,7-positions of the carbazole ring due to the presumed elimination of hydrogen atoms by the formed iodine radical. This is confirmed by the presence of absorption bands of the out-of-plane bending vibrations $\delta_{CH}$ (723, 748 $cm^{-1}$) typical for 3,6-unsubstituted carbon atoms of the carbazole fragment [21, 22]. The appearance of the $\nu_{NH}$ absorption band at 3389 $cm^{-1}$ in the IR spectrum of oligomer **III** [21], and the NH proton signal in the $^1H$ NMR at 8.46 ppm prove the above structure [23].

We have also studied the possibility of the formation of poly(2,7-carbazoles) by thermal polymerization of 1-(9*H*-carbazol-2-yl)-2-iodo-1-ethanone (**II**). The reaction proceeds at 270°C and leads to the formation of two modifications of polycarbazole: soluble in acetone **IV** ($M_w$ 1600, $M_n$ 1100, $M_w/M_n$ 1.4, yield 21.4%) and soluble in THF, DMSO, DMF (**V**) ($M_w$ 1700, $M_n$ 940, $M_w/M_n$ 1.7, yield 53.57%).




**II** **IV, V**

NMR, IR, and UV spectra of polymers synthesized by thermal polymerization of iodoketones **I** and **II** are fully identical.

In the process of thermal polymerization of iodoketones **I, II**, polycarbazoles **III–V** are doped with iodine. This is confirmed by the presence of the absorption bands in the UV spectra at 293 and 358 nm, characteristic for the $I_3^-$ ion [24, 25]. The absence of the covalently bound iodine in the polymer is proved by easy removal of the $I_3^-$ ion upon reprecipitation of polycarbazole **III** dissolved in DMSO into water.

Polycarbazoles **III–V** are black powders decomposed at >450°C. When coated from solution onto quartz, glass, or metal they form dark lilac films of high adhesion. The electroconductivity of polycarbazole (**III**) is $3.1\times10^{-10}$ S cm$^{-1}$.

**1-(9*H*-Carbazol-9-yl)-2-iodo-1-ethanone (I).** To the solution in 150 ml of acetone of 3 g (1.2 mmol) of 1-(9*H*-carbazol-9-yl)-2-chloro-1-ethanone prepared as described in [26] the solution of 2.16 g (1.4 mmol) of sodium iodide was added and stirred for 5 h. Yield 3.9 g (95%), mp 116–117°C (chloroform). IR spectrum, ν, cm$^{-1}$: 1677 (C=O), 484 ($CH_2I$). $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 4.38 s (2H, $CH_2I$), 7.18–8.05 m (Ar). $^{13}$C NMR spectrum ($CDCl_3$), $\delta_C$, ppm: 1.69 (C–I), 110.72–138.37 (Ar), 167.29 (C=O). Mass spectrum, *m*/*z* ($I_{rel}$, %): 335(40) [$M^+$]. $M_{calc}$ 335. Found, %: C 49.85; H 2.90; N 4.29; I 38.05. $C_{14}H_{10}NOI$. Calculated, %: C 50.15; H 2.98; N 4.18; I 37.91.

**1-(9*H*-Carbazol-2-yl)-2-iodo-1-ethanone (II).** Prepared similar to **I** from 3 g (1.2 mmol) of 1-(9*H*-carbazol-2-yl)-2-chloro-1-ethanone (synthesized as described in [27]) and 2.16 g (1.4 mmol) of sodium iodide. Yield 3.8 g (92%), mp 189–190°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 4.69 s (2H, $CH_2I$), 7.21–9.15 m (Ar), 11.56 (1H, NH). $^{13}$C NMR spectrum (DMSO-$d_6$), $\delta_C$, ppm: 111.41–141.42 (Ar), 193.57 (C=O). IR spectrum, ν, cm$^{-1}$: 3328 (NH), 1655 (C=O), 472 ($CH_2I$). Mass spectrum, *m*/*z* ($I_{rel}$, %): 335(54) [$M^+$]. $M_{calc}$ 335. Found, %: C 49.93; H 2.82; N 4.08; I 38.09. $C_{14}H_{10}NOI$. Calculated, %: C 50.15; H 2.98; N 4.18; I 37.91.

**Polymerization of 1-(9*H*-carbazol-9-yl)-2-iodo-1-ethanone (I).** 1-(9*H*-Carbazol-9-yl)-2-iodo-1-ethanone (**I**), 2.5 g (7.5 mmol), was heated in an argon atmosphere to 220°C during 2–3 min. The formed polymer was extracted with acetone (15 ml), and precipitated with hexane (30 ml). The precipitate formed was thoroughly washed with ether, dried in a vacuum. Yield of compound (**III**) 1.1 g (65% to $C_{72}H_{44}N_6I_3$), dark lilac powder, decomp. above 450°C. $^1$H NMR spectrum (acetone-$d_6$), δ, ppm: 7.14–8.10 (Ar), 8.46 (NH). $^{13}$C NMR spectrum (acetone-$d_6$), $\delta_C$, ppm: 142.20–107.80 (Ar). IR spectrum (film), ν, cm$^{-1}$: 3389 (NH). Found, %: C 63.18; H 3.47; N 5.36; I 27.92. $C_{72}H_{44}N_6I_3$. Calculated, %: C 62.88; H 3.20; N 6.11; I 27.72.

**Polymerization of 1-(9*H*-carbazol-2-yl)-2-iodo-1-ethanone (II).** 1-(9*H*-Carbazol-9-yl)-2-iodo-1-ethanone (**II**), 0.5 g (1.5 mmol), was heated in an argon atmosphere at 270°C during 3 min, extracted with acetone (15 ml), and precipitated with hexane (30 ml) to obtain 0.06 g (21%) of compound **IV** as a dark lilac powder decomp. above 450°C. $^1$H NMR spectrum (acetone-$d_6$), δ, ppm: 7.35–8.16 (Ar), 8.19 (NH). $^{13}$C NMR spectrum (acetone-$d_6$), $\delta_C$, ppm: 141.88–105.28 (Ar). IR spectrum (film), ν, cm$^{-1}$: 3423 (NH). Found, %: C 65.21; H 3.41; N 5.79; I 25.92. $C_{84}H_{51}N_7I_3$. Calculated, %: C 65.62; H 3.19; N 6.38; I 24.80.

Polycarbazole **V** soluble in THF, DMSO, DMF, 0.15 g (53.57%), black glittering powder decomp. above 450°C. Found, %: C 66.55; H 3.17; N 5.98; I 22.56. $C_{96}H_{58}N_8I_3$. Calculated, %: C 67.42; H 3.30; N 6.58; I 22.39.

FT–IR spectra were recorded on a Vertex 70 Ram II spectrometer (KBr, film). $^1$H and $^{13}$C NMR spectra were registered on a Bruker DPX-400 spectrometer (400 and 100 MHz, respectively). The molecular mass of polycarbazoles **III–V** was determined on a gel-chromatograph Waters, with refractometric detector, at 25°C, eluent THF. Specific electroconductivity was measured by electrometric amplifier VK-16. Purity of the products was monitored by TLC on Silufol UV-254 plates, eluent acetone.

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