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To the 80th Anniversary of B.I. Ionin

Preparation and Properties of Co-Oligomers of 1-Vinyl-1,2,4-triazole with *N*-Vinyl-2-phenylpyrrole

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Abstract—Novel water-soluble co-oligomers of 1-vinyl-1,2,4-triazole and *N*-vinyl-2-phenylpyrrole have been prepared by radical copolymerization. Copolymerization constants of the monomers and the parameters of co-oligomers microstructure have been determined. 1-Vinyl-1,2,4-triazole is more reactive in the monomers pair. The prepared co-oligomers are thermally stable and reveal properties typical of paramagnetic organic semiconductors.

Keywords: 1-vinyl-1,2,4-triazole, *N*-vinyl-2-phenylpyrrole, radical copolymerization, oligomer

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Development of functional polymer materials with a set of desired properties is a topical issue of modern materials science. Nitrogen-containing polymers, especially heterocyclic ones, are of considerable interest in view of wide spread of heterocyclic compounds in nature; they constitute most of biologically active compounds, drugs, and dyes. Polymerization of five-membered nitrogen heterocycles containing vinyl group yields important class of polymers bearing triazole and pyrrole fragments in the macromolecules; such materials are highly attractive for both fundamental and applied studies [1–5].

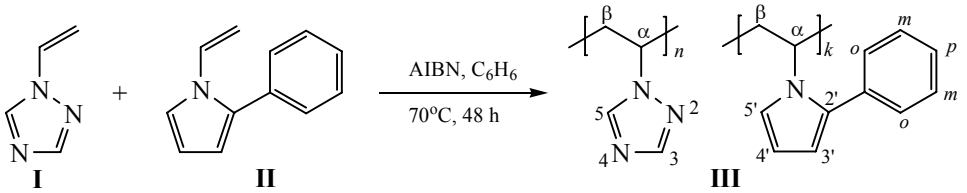
Among the vinylazole-based polymers, water-soluble poly-1-vinyl-1,2,4-triazole holds a special place due to the low toxicity (LD_{50} > 5 g/kg), hydrophilicity, chemical as well as thermal stability, and ability towards quaternization and complexes formation [6, 7]. (Co)polymers of 1-vinyl-1,2,4-triazole and their functional nanocomposites containing metal (Ag, Cu, or Fe) nanoparticles are promising for medical, food, and technical applications [8–14].

Modern polymer materials for advanced technologies are to a large extent based on functionalized pyrroles and *N*-vinylpyrroles [15–17]. In particular, pyrrole-based compounds have been used for production of fluorescent azaindene-type BODIPY dyes; electroconductive, light-sensitive, and nonlinear optical materials; drug precursors and biologically active components [3, 18–25]. Despite the high practical importance and wide range of synthetic possibilities of *N*-vinylpyrroles, their studies are strongly limited by their poor availability. However, development of highly efficient single-stage method of *N*-vinylpyrroles preparation from ketoximes and acetylene in superbasic media (the Trofimov reaction), this limitations was majorly eliminated [18, 19].

To our knowledge, preparation and properties of copolymers of vinyltriazole and vinylphenylpyrrole have been lacking in the literature so far. The combination of these units in the copolymer molecule is attractive in view of potential applications as components of semiconductor and light-sensitive materials for electrophotography and holography, polymeric azo-dyes, noble metals sorbents, and biologically active materials including plant protectants.

In this work we elaborated a procedure to prepare co-oligomers (**III**) of 1-vinyl-1,2,4-triazole (**I**) with *N*-vinyl-2-phenylpyrrole (**II**) and studied the monomers

Scheme 1.



reactivity as well as selected properties of the obtained products.

Copolymerization of compounds **I** and **II** was performed under conditions of initiation with azobisisobutyronitrile AIBN at 70°C during 48 h. The reaction resulted in the linear co-oligomer products according to the Scheme 1.

The reaction conditions and the syntheses results are collected in the Table. The prepared co-oligomers **IIIa**–**e** were cream-colored powders readily soluble in DMF, DMSO, 1,4-dioxane, ethanol, acetonitrile, and acetone.

The co-oligomers composition was calculated taking into account the elemental analysis data (carbon content) and ^{1}H NMR data (averaged integral intensities of H^3 and H^5 protons of the triazole ring as well as of $H^{3'}$ and $H^{4'}$ protons of the pyrrole ring; see table). Independently of the initial monomers mixture composition, the resulted products were enriched by monomer **I**. Increasing the monomer **II** ratio resulted in decreasing of the intrinsic viscosity of the co-oligomer solution and lower yield of the product, coinciding with poor reactivity of vinylphenylpyrrole in radical polymerization [22, 26]. That was likely due to steric hindrance arising from the presence of bulky phenyl substituent limiting accessibility of the macroradical to the monomer [27].

The relative reactivity of the monomers in radical polymerization was described with the copolymerization rate constants calculated taking advantage of the Kelen–Tudos method [28]: $r_{\mathbf{I}} = 1.19\pm0.01$ and $r_{\mathbf{II}} = 0.16\pm0.05$. The higher reactivity of monomer **I** favored the addition of that monomer to the both macroradicals and led to the product enrichment with monomer **I**.

IR spectra of co-oligomers **III** contained no stretching bands of vinyl C=C bonds (582, 946, 1582, and 1654 cm^{-1}), whereas the bands assigned to the vibrations of triazole [1502–1505, 1434, 662–665 (C–N, C=N), 1275–1277 (N–N) and 3102–3112, 1140, 1003 (C–H) cm^{-1}] and pyrrole [3102–3110 (C–H), 1641, 1602–1603, 1575, 1494, 1466–1467 (C=C), 1403, 1073–1074 (C–C), 917–918, 881, 760–764 (C–H) cm^{-1}] rings were retained. The bands intensity coincided with the quantitative composition of the co-oligomers.

^{1}H NMR spectra of co-oligomers contained no signals of *N*-vinyl protons; the broadened unresolved signals the backbone protons were observed: methylene (β) ones at 1.5–2.4 ppm and methine (α) ones at 2.9–4.7 ppm. The broadened signals of triazole ring protons were found at 7.5–8.7 ppm (H^3, H^5). The spectra contained the signals of phenyl fragment (6.4–7.6 ppm) and pyrrole ring (5.8–6.5 ppm, $H^{3'}$, $H^{4'}$) as well.

Copolymerization of 1-vinyl-1,2,4-triazole with *N*-vinyl-2-phenylpyrrole (C_6H_6, AIBN 2 wt %, 70°C, 48 h)

Co-oligomer	Monomer **I** content in the starting mixture, mol %	Yield, %	Carbon content in co-oligomer **III**, wt %	Monomer **I** content in the co-oligomer, mol %		[η], dL/g
				elemental analysis	^{1}H NMR	
IIIa	10	2	79.37	26	–	0.08
IIIb	30	5	72.18	51	47	0.10
IIIc	50	15	67.29	65	63	0.17
IIId	70	22	61.56	79	79	0.21
IIIe	90	35	55.14	92	93	0.32

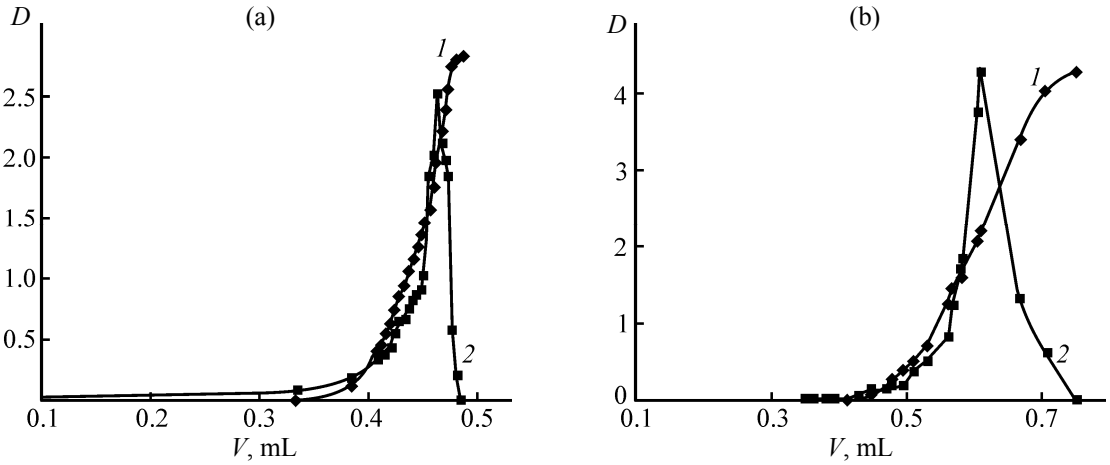


Fig. 1. Turbidity titration curves of co-oligomers (a) **IIIb** and (b) **IIIc**. (*1*) Integral curves and (*2*) differential curves.

^{13}C NMR spectra of co-oligomers contained no signals of *N*-vinyl carbons; the broadened unresolved signals the backbone carbons were observed: methylene (β) ones at 23.8–31.0 ppm and methine (α) ones at 51.2–56.0 ppm. The signals of carbon atoms of triazole ring were found at 149.9–153.4 (C^5) and 141.6–145.9 (C^3) ppm, phenylpyrrole carbon atoms resonated at 107.5–135.5 ppm.

Formation of the co-oligomers was evidenced by the turbidimetry titration data: the smooth sigmoid shape of the integral curves with a single inflection point pointed at the unimodal molecular mass distribution, typical of statistical copolymers (Fig. 1). The differential turbidimetry curves contained a single sharp peak, further confirming the specimen uniformity.

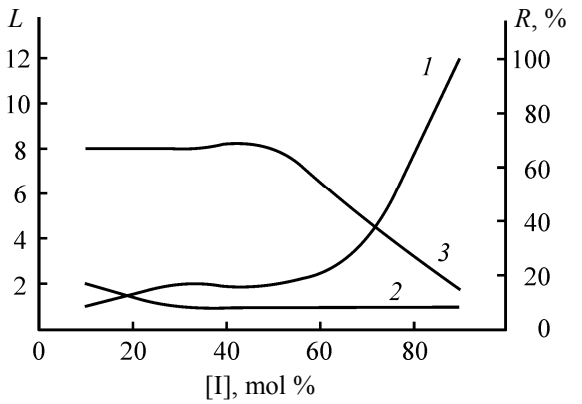


Fig. 2. Number of units (*L*) of (*1*) 1-vinyl-1,2,4-triazole and (*2*) *N*-vinyl-2-phenylpyrrole in co-oligomer **III** along with (*3*) the mosaicity parameter *R* as function of the monomer **I** content in the starting mixture.

In order to estimate the compositional heterogeneity of the co-oligomers, we described the monomer units distribution along the macromolecule chain taking into account the previously determined copolymerization rate constants [29]. The polymer chained contained of blocks of the more reactive monomer **I** (*L* units at the average) separated by single units of the less reactive monomer **II**. The length of blocks of units **I** reached 12 with 90 mol % of the monomer **I** in the starting mixture; with the monomer **I** content down to 10–50 mol % the tendency towards the units alternation was observed (Fig. 2).

Thermogravimetry analysis revealed that the co-oligomers were thermally stable up to 310°C. Prominent mass loss was observed at 320–390°C (35–40%), the decomposition being complete at 700°C.

The co-oligomers revealed properties of high-ohmic organic semiconductors, their electric conductance reaching (2.4–3.3) × 10^{-14} S/cm. Doping of the polymers with iodine led to the conductivity increase by seven orders of magnitude, to (2.1–4.8) × 10^{-7} S/cm.

ESR spectra of the co-oligomers showed an asymmetric singlet with the signal width of 11.8 G, g-factor of 2.0049, and the paramagnetic centers concentration of 7.6 × 10^{15} sp/g.

To conclude, we prepared novel reactive soluble co-oligomers of varied composition containing triazole and phenylpyrrole fragments. 1-Vinyl-1,2,4-triazole was much more reactive in radical copolymerization as compared with *N*-phenyl-2-vinylpyrrole. The prepared

products were thermally stable up to 310°C, and revealed electric conductivity of 10^{-14} S/cm and paramagnetic properties, making them promising materials for development of conductive materials.

EXPERIMENTAL

1-Vinyl-1,2,4-triazole **I** was prepared and purified as described elsewhere [30]; bp 43°C (3 mmHg), n_D^{20} 1.5100. *N*-Vinyl-2-phenylpyrrole **II** was prepared from acetophenone and acetylene via the Trofomov reaction in KOH–DMSO medium [18, 31]: bp 94°C (1 mmHg). The solvents (benzene and diethyl ether) were distilled before use [32]. Azobisisobutyronitrile AIBN was twice re-crystallized from ethanol.

Elemental analysis was performed using a Thermo Finnigan Flash EA 1112 analyzer. IR spectra (KBr pellet or thin film) were recorded using a Bruker Vertex 70 spectrometer at 400–4000 cm^{-1}. ^1H (400.13 MHz) and ^{13}C (100.61 MHz) NMR spectra (solution in DMSO-d_6) were recorded using a Bruker DPX-400 instrument at room temperature, relative to TMS. Intrinsic viscosity was measured using an Ubbelohde viscometer at 20°C (DMF). Copolymerization rate constants were calculated using the Kelen–Tudos method [29]. Turbidimetry titration was performed at 20°C registering the absorbance with a KFK-2 photometer (λ 670 nm; 0.1 wt % solution in dioxane; water as precipitating agent). ESR spectra were recorded using an ELEXSYS E-580 Bruker impulse radio spectrometer at room temperature. Thermal analysis was run using a MOM Q-1500 Paulik–Paulik–Erdey (Hungary) during heating at 10 deg/min up to 700°C at DTA sensitivity of 1/10. Electric conductivity was determined using an E6-13A standard teraohmmeter (the specimens were pelletized at 700 kg/cm^2). Doping with iodine was performed via gas diffusion during 24 h.

Copolymerization affording product IIIc. A mixture of 0.54 g (5.7 mmol) of monomer **I**, 0.96 g (5.7 mmol) of monomer **II**, 0.03 g (0.18 mmol, 2 wt %) of AIBN, and benzene (0.75 g) was put in an ampoule and bubbled with argon; the ampoule was sealed. The reaction was run at 70°C during 48 h. The product was isolated via precipitation in a 3 : 1 diethyl ether – petroleum ether mixture, washed with diethyl ether, and dried in vacuum (1 mmHg) at room temperature to constant mass. Yield 0.23 g (15%); light-yellow powder, soluble in ethanol, acetone, acetonitrile, DMSO, DMF, and 1,4-dioxane. IR spectrum, ν, cm^{-1}: 664, 704, 763, 881, 918, 1003, 1074, 1140, 1276, 1306, 1434, 1467, 1503, 1543, 1602, 3112. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 0.7–2.4 (CH_2), 2.9–4.6 (CH), 7.5–8.7 (H^3, H^5), 6.4–7.4 (Ph, $H^{5'}$), 5.8–6.5 ($H^{3'}$, $H^{4'}$). Found, %: C 67.00; H 5.71; N 27.29. $C_{20}H_{21}N_7$. Other copolymers (**IIIa**, **IIIb**, **IIId**, and **IIIe**) were prepared similarly.

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