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Synthesis and modification of 1-vinylpyrrole-2-carbaldehyde polymers

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1-Vinylpyrrole-2-carbaldehydes, *viz.*, 5-phenyl-1-vinylpyrrole-2-carbaldehyde, 5-(2-thienyl)-1-vinylpyrrole-2-carbaldehyde, 1-vinyl-4,5,6,7-tetrahydroindole-2-carbaldehyde, and 1-vinyl-4,5-dihydrobenz[*g*]indole-2-carbaldehyde, are polymerized in the presence of 2,2-azobisisobutyronitrile to form soluble paramagnetic oligomers. A possibility of oligomer modification through the aldehyde moiety with amines and thiols was shown.

Key words: 1-vinylpyrrole-2-carbaldehydes, radical polymerization, modification, thioacetales, Schiff bases, ESR spectroscopy.

Intensive investigation of pyrrole derivatives is caused by their wide abundance in natural objects, for instance, as structural fragments of antibiotics, pheromones, and toxins and due to the unique properties of related polymers.[1—3] Pyrrole moieties are components of porphyrin and phthalocyanine systems, namely, hemin, chlorophyll, bile pigments, hemoglobin, cytochromes, and vitamin B_{12}.[3] Formylpyrroles are important intermediates and building blocks in the synthesis of various oligopyrrolic systems,[4] porphyrins,[5,6] and ligands for metal complexes[7—9] and conjugated polymers.[10,11]

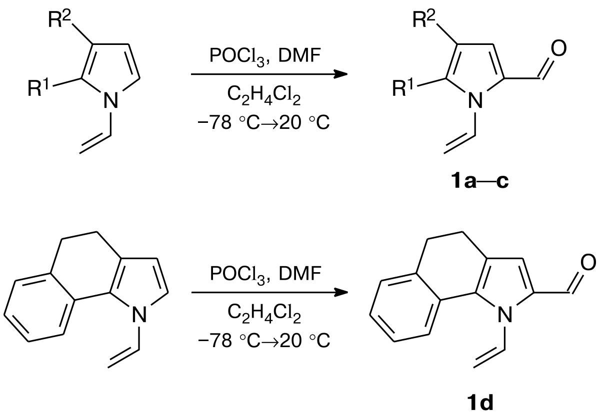
Recently synthesized 1-vinylpyrrole-2-carbaldehydes[12] are especially interesting as monomers. The study of their polymerization will provide route for the preparation of new oligomers with pyrrole cycles and aldehyde moiety in each elementary unit, which is promising for the further modification of polymers.

The purpose of the present work is to study radical polymerization of a series of 1-vinylpyrrole-2-carbaldehydes, synthesize new polymers, and examine their reactivity.

Results and Discussion

The starting 1-vinylpyrrole-2-carbaldehydes, *viz.*, 5-phenyl-1-vinylpyrrole-2-carbaldehyde (**1a**), 5-(2-thienyl)-1-vinylpyrrole-2-carbaldehyde (**1b**), 1-vinyl-4,5,6,7-tetrahydroindole-2-carbaldehyde (**1c**), and 1-vinyl-4,5-dihydrobenz[*g*]indole-2-carbaldehyde (**1d**), were synthesized[12] by the modified Vilsmeier—Haak reaction (yields up to 91%) (Scheme 1).

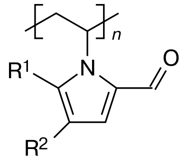
Scheme 1



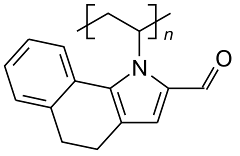
1: R^1 = Ph, R^2 = H (**a**); R^1 = 2-thienyl, R^2 = H (**b**); R^1R^2 = $(CH_2)_4$ (**c**)

Homopolymers of 1-vinylpyrrole-2-carbaldehydes were synthesized by radical polymerization in the presence of 2,2-azobisisobutyronitrile (AIBN). The conditions for synthesis of the polymers and their characteristics are given in Table 1.

According to the IR and ^{1}H NMR spectral data, the polymers have structures **2a—d**.



2a—c



2d

2: R^1 = Ph, R^2 = H (**a**); R^1 = 2-thienyl, R^2 = H (**b**); R^1R^2 = $(CH_2)_4$ (**c**)

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Table 1. Conditions of radical polymerization of 1-vinylpyrrole-2-carbaldehydes (AIBN, 2 wt.%) and the yields, melting points, and molecular weights (M) of the polymers obtained

T/°C	t^a/h	Yield (%)	M.p. of polymer/°C	M
5-Phenyl-1-vinylpyrrole-2-carbaldehyde[b]				
60	24	18.7	86—90	3200
80	24	27.4	90—94	2900
5-(2-Thienyl)-1-vinylpyrrole-2-carbaldehyde[b]				
60	50	12.9	100—104	2400
80	50	23.0	102—106	2000
1-Vinyl-4,5,6,7-tetrahydroindole-2-carbaldehyde[b]				
60	45	3.3	246—250	2100
80	45	12.3	248—252	1800
1-Vinyl-4,5-dihydrobenz[*g*]indole-2-carbaldehyde[c]				
60	50	11.2	175—177	1800
80	50	19.8	174—178	2000

[a] Polymerization duration.
[b] Bulk polymerization.
[c] Polymerization in solution (monomer : benzene = 1 : 1).

The IR spectra of poly(1-vinylpyrrole-2-carbaldehydes) contain no absorption bands of vinyl groups (3121, 1640, 982, 868, and 599 cm^{-1}). The bands of other groups and bonds are broadened, which is characteristic of polymers. The absorption bands of the pyrrole ring at 1540, 1372, 1300, and 716 cm^{-1} and of the carbonyl group at 1660 cm^{-1} are retained in the spectra.[3,12]

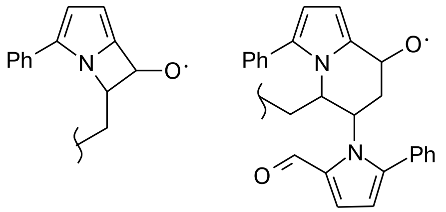
The signals from the vinyl group at δ 5.27 and 5.37 (C=CH$_2$) and 6.84 (CH=C) disappear from the ^{1}H NMR spectra of the polymers, and broad signals at δ 3.48 (N—CH) and 2.70 (—CH$_2$ of the polymer chain) appear. The signals of the pyrrole ring (δ 6.72, 6.80) and formyl group HC=O (δ 9.36) remain unchanged.

Oligomer formation characteristic of 1-vinylpyrrole-2-carbaldehydes should probably be ascribed, as in the case of 1-vinylpyrroles, to the processes of chain transfer to the monomer.[3]

As shown in Experimental, 1-vinylpyrrole-2-carbaldehydes are characterized by low activity in radical polymerization. The yield increases by 8—10% with an increase in the reaction temperature by 20 °C, but does not exceed 27.4% (see Table 1). It is most likely that steric factors play a significant role in the step of chain propagation; in addition, the active radical center itself is sterically hindered.[3]

Intra- and intermolecular interactions of the growing radical with the adjacent carbonyl substituents exert, most likely, an inhibitory effect on the polymerization (exemplified by compound **1a**).

Thus, the low activity of 1-vinylpyrrole-2-carbaldehydes in radical polymerization is caused by enhanced affinity to the formation of stable radicals. This is especially pronounced when comparing the reactivities of substituted and unsubstituted 1-vinyl-4,5,6,7-tetrahydroindoles: under similar conditions, the latter forms polymers in quantitative yield.[3]



The study of the ESR spectra of the polymers of 1-vinylpyrrole-2-carbaldehydes revealed that all the samples in the powder state are paramagnetic (Table 2).

The ESR spectra exhibit slightly asymmetric, rather narrow singlets corresponding to concentrations of lone electrons of 10^{17}—10^{18} spin g^{-1}. The *g*-factors are close to the values for free radicals.

The nature of paramagnetism can be explained by the formation of a radical center on the carbon atom of the aldehyde moiety due to the attack of the initiating radical I$^•$. This radical should be stabilized by coupling with the adjacent pyrrole system, which is accompanied by spin transfer to the neighboring units of the polymer to form, possibly, several resonance structures.

It is known[13,14] that paramagnetism of polymers having no developed system of conjugated bonds can be induced by polarons (radical ions) appeared due to the intra- and (or) intermolecular electron transfer from the donor moiety of the molecule (in the given case, pyrrole fragment) to the acceptor moiety (aldehyde group).

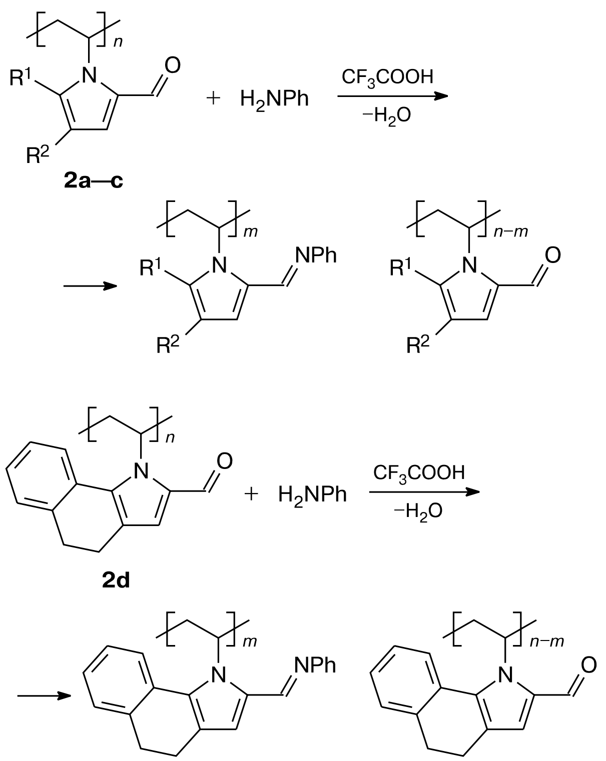
For the preliminary evaluation of the reactivity of oligomers synthesized, we studied their reactions with aniline and ethanethiol.

The ability of poly(1-vinylpyrrole-2-carbaldehydes) to reaction with amines with the formation of Schiff bases was illustrated by the reaction of polymeric aldehydes **2a—d** with aniline (Scheme 2). The products with 10% and 78% conversion (determined by the ^{1}H NMR spectra and in parallel by the weight of the modification product) were synthesized at room temperature or on heating (80 °C, 1% CF$_3$COOH, 5 h, 1.5 moles of aniline per 1 mole of the polymer (based on one unit)), respectively.

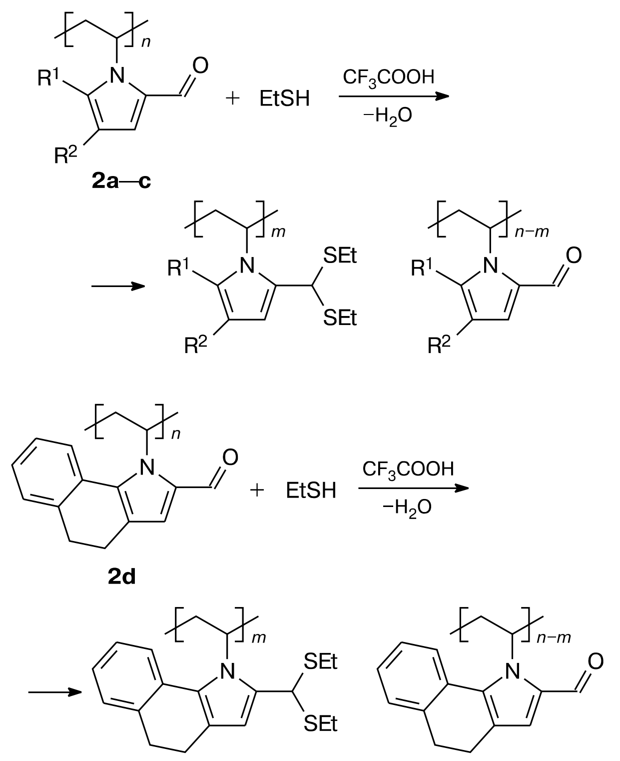
Table 2. Characteristics of signals in the ESR spectra of poly(1-vinylpyrrole-2-carbaldehydes) **2a—d**

Polymer	N /spin g^{-1}	ΔH /mT	g-Factor	Asymmetry parameter A/B
2a	$3.5 \cdot 10^{17}$	0.58	2.0027	0.82
2b	$1.2 \cdot 10^{18}$	0.60	2.0031	0.76
2c	$1.3 \cdot 10^{18}$	0.78	2.0031	0.96
2d	$2.7 \cdot 10^{17}$	0.66	2.0024	0.85

Scheme 2



Scheme 3



An analysis of the IR and ^{1}H NMR spectra of the products obtained and their comparison with the spectra of the starting polymer indicate, as assumed, that the carbonyl group is involved in the reaction. In the IR spectra of the modified polymers, the intensity of the absorption bands of the C=O group (1660 cm^{-1}) decreases, absorption bands characteristic of the —C—N (1185, 1120 cm^{-1}) and —C=N fragments (1680 cm^{-1}) appear, and the absorption bands of the benzene ring in polymers **2b**,**c** lie at 1615, 1580, 1485, 980, 850, 820, 715, and 505 cm^{-1}.

In the ^{1}H NMR spectra, the intensity of the signal from the HC=O group (δ 9.36) decreases, signals at δ 8.00 ppm (H—C=N) appear, and the signals of the benzene ring in polymers **2b,c** lie at δ 7.70, 7.40, and 7.08.

The condensation of 1-vinylpyrrole-2-carbaldehydes with ethanethiol in the presence of 0.25% CF_3COOH is known[15] to occur with the formation of 1-vinylpyrrole-2-carbaldehyde thioacetals in yields up to 99%. Thioacetals are of considerable interest because of the use in the synthesis of functionalized compounds of different types, including natural porphyrins, pigments, and alkynes.[16,17]

The addition of ethanethiol to poly(1-vinylpyrrole-2-carbaldehydes) was carried out in benzene in the presence of 1% CF_3COOH at ambient temperature or on heating (Scheme 3, Table 3).

The structures of the synthesized products were proved by IR spectroscopy and ^{1}H NMR spectroscopy and using elemental analysis data (see Table 3).

In the IR spectra of the modified polymers, the intensity of the absorption bands of the formyl C=O group

Table 3. Conditions of the reactions of poly(1-vinylpyrrole-2-carbaldehydes) **2a**,**d** with ethanethiol (1% CF_3COOH) and the yields, conversion values, and elemental analysis data for the modified polymers

Polymer	*t*/h	*T* /°C	Yield (%)	Conversion[a] (%)	Found/Calculated[b] (%) C	H	N	S
2a	8	20	70	21	75.64	6.01	6.37	4.67
					67.30	6.98	4.62	21.10
2a	8	60	77	33	76.09	6.05	5.88	6.92
					67.30	6.98	4.62	21.10
2b	8	20	73	18[c]	68.58	4.17	5.40	16.79
					58.25	6.15	4.53	31.07
2c	8	20	75	22	71.82	7.68	7.06	5.01
					64.05	8.19	4.98	22.78
2d	3	20	69	10	79.02	6.03	5.98	1.94
					69.47	7.23	4.26	19.52

[a] Calculated by the S content.

[b] For the 100% conversion.

[c] Calculated by the ^{1}H NMR spectral data.

(1670 cm^{-1}) decreases accompanied by the appearance of absorption bands characteristic of the $-CH_2-S-$ (688 cm^{-1}), $-CH-S$ (600 cm^{-1}), and $-CH_3$ (2975 cm^{-1}) groups.

In the ^{1}H NMR spectra, the intensity of the signal at δ 9.36 (HC=O) decreases with the appearance of a broad signal at δ 4.64 (HCS) and signals at δ 2.53 (SCH_2) and 1.25 (CH_3).

The conversion increases with an increase in the reaction temperature and achieves 33% (see Table 3).

Thus, the principal possibility of radical polymerization of 1-vinylpyrrole-2-carbaldehydes (oligomer yield up to 27.4%) has been shown for the first time. The paramagnetic oligomers containing pyrrole, tetrahydroindole, and dihydrobenz[*g*]indole moieties and aldehyde groups in the side chain were synthesized. They are able to undergo various polymer-analogous transformations due to the presence of the aldehyde moieties and pyrrole rings and seem to be potent to a great extent for the directed synthesis of optoelectronic materials, organic semiconductors, supramolecular complexes, and novel analytical reagents.

Experimental

Monomers purified by column chromatography (basic alumina, hexane—ether (3 : 1) mixture as eluent) were used for polymerization. Their purity was monitored by IR and NMR spectroscopy. The constants of the monomers corresponded to published data.[12]

Solvents (benzene, hexane) were purified according to commonly accepted procedures.[18] The initiator was AIBN doubly recrystallized from ethanol.

Polymerization was carried out under argon, in block or in benzene. Polymers were isolated by precipitation from a benzene solution into hexane. Poly(1-vinylpyrrole-2-carbaldehydes) are red—brown powders, they are highly soluble in chloroform, benzene, acetone, and dioxane and are insoluble in hexane and ethanol.

Molecular weights of polymers were determined by the isopiestic method[19] (several parallel measurements for each oligomer, error ±110).

IR spectra of polymers of 1-vinylpyrrole-2-carbaldehydes were recorded on a Bruker ISF-25 spectrometer in KBr pellets.

^{1}H NMR spectra were measured on a Bruker instrument (DPX 400 model, 400 MHz) in $CDCl_3$, using hexamethyldisiloxane as an internal standard.

ESR spectra of powders were recorded at ~20 °C on an SE/X-2547 radiospectrometer (Radiopan) with a sensitivity of $5 \cdot 10^{10}$ spin g^{-1} equipped with a magnetometer and a high-frequency meter. The concentration of paramagnetic centers was calculated according to a known procedure described previously[20] using calibrated diphenylpicrylhydrazyl standards and the nomograms of double integration of the absorption line derivative.[21]

Reaction of aniline with poly(5-phenyl-1-vinylpyrrole-2-carbaldehyde). A mixture of polymer **2a** (0.056 g, 0.28 mmol based on one unit), aniline (0.039 g, 0.42 mmol), benzene (0.60 mL), and CF_3COOH (0.001 g, 1%) was heated in a sealed ampule for 5 h at 80 °C. The product was precipitated with hexane, filtered off, washed, and dried to a constant weight. The polymer was obtained in a yield of 0.073 g (95%), m.p. 208—212 °C. Found (%): C, 81.22; H, 5.48; N, 9.04. Calculated (%): C, 82.67; H, 5.58; N, 9.55.

The reactions of aniline with polymers **2b—d** were carried out analogously.

Reaction of ethanethiol with poly(5-phenyl-1-vinylpyrrole-2-carbaldehyde). A mixture of polymer **2a** (0.070 g, 0.35 mmol based on one unit), ethanethiol (0.087 g, 1.40 mmol), benzene (0.70 mL), and CF_3COOH (0.002 g, 1%) was heated in a sealed ampule for 8 h at 60 °C. The product was precipitated with hexane, filtered off, washed, and dried to a constant weight. The polymer was obtained in a yield of 0.083 (77%), m.p. 236—240 °C. Found (%): C, 76.09; H, 6.05; N, 5.88; S, 6.92. Calculated (%): C, 75.06; H, 6.06; N, 6.25; S, 7.15 (for the 21% conversion).

The reactions of ethanethiol with polymers **2b—d** were carried out analogously.

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References

1. L. I. Boguslavskii and A. V. Vannikov, *Organicheskie poluprovodniki i biopolimery* [*Organic Semiconductors and Biopolymers*], Nauka, Moscow, 1968, 180 pp. (in Russian).
2. T. Skotheim, I. Lundstrom, and J. J. Prejra, *Electrochem. Soc.*, 1981, **128**, 1625.
3. B. A. Trofimov and A. I. Mikhaleva, *N-Vinilpirroly* [*N-Vinylpyrroles*], Nauka, Novosibirsk, 1984, 260 pp. (in Russian).
4. V. N. Krustalev and J. A. Ustynyuk, *Org. Lett.*, 2005, **7**, 5277.
5. H. Furuta, H. Maeda, T. Furuta, and A. Osuka, *Org. Lett.*, 2000, **2**, 187.
6. A. Wiehe, C. Ruppa, and M. O. Senge, *Org. Lett.*, 2002, **4**, 3807.
7. L. Y. Yang, Q. Q. Chen, G. Q. Yang, and J. S. Ma, *Tetrahedron*, 2003, **59**, 10037.
8. L. Yang, Y. Zhang, Q. Chen, and J. S. Ma, *Monatsch. Chem.*, 2004, **135**, 223.
9. G. Zhang, G. Yang, Q. Chen, and J. S. Ma, *Cryst. Growth Des.*, 2005, **5**, 661.
10. C. I. Simionescu, M. Grovu-Ivanoiu, I. Cianga, M. Grigoras, A. Duca, and I. Cocarla, *Angew. Makromol. Chem.*, 1996, **239**, 1.
11. G. Zotti, S. Zecchin, G. Schiavon, A. Berlin, G. Pagani, A. Canavesi, and G. Casalbore-Miceli, *Synth. Met.*, 1996, **78**, 51.
12. A. I. Mikhaleva, A. B. Zaitsev, A. V. Ivanov, E. Yu. Schmidt, A. M. Vasil´tsov, and B. A. Trofimov, *Tetrahedron Lett.*, 2006, **47**, 3693.

13. M. Thakur and B. S. Elman, *J. Chem. Phys.*, 1989, **90**, 2042.
14. M. Thakur, *J. Macromol. Sci. Chem.: Pure Appl. Chem.*, 2001, **38**, 1337.
15. A. M. Vasil´tsov, A. V. Ivanov, I. A. Ushakov, A. I. Mikhaleva, and B. A. Trofimov, *Synthesis*, 2007, **3**, 452.
16. A. D. Abell, B. K. Nabbs, and A. R. Battersby, *J. Org. Chem.*, 1998, **63**, 8163.
17. M. C. Willis, H. E. Randell-Sly, R. L. Woodward, and G. S. Currie, *Org. Lett.*, 2005, **7**, 2249.
18. A. Weissberger, E. Proskauer, J. Riddick, and E. Toops, *Organic Solvents. Physical Properties and Methods of Purification*, Interscience, New York, 1955.
19. J. Rabek, *Experimental Methods in Polymer Chemistry*, Wiley and Sons, Chichester—New York—Brisbane—Toronto, 1980.
20. Ch. Poole, *Electron Spin Resonance. Comprehensive Treatise on Experimental Techniques*, Interscience Publ., New York—London—Sydney, 1967.
21. Yu. N. Molin, V. M. Chibrikin, V. A. Shabalkin, and V. F. Shuvalov, *Zav. Labor.* [*Factory Laboratory*], 1966, **88**, 933 [*Ind. Lab.*, 1966, **88** (Engl. Transl.)].

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