Russian Chemical Bulletin, Vol. 46, No. 11, November, 1997 1855

Polymerization of 1-allenylpyrroles

L. V. Morozova,* O. A. Tarasova, A. I. Mikhaleva, M. V. Markova, G. F. Myachina, and B. A. Trofimov

Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences,
1 ul. Favorskogo, 664033 Irkutsk, Russian Federation.
Fax: 007 (395 2) 46 0331

1-Allenylpyrroles are polymerized under the conditions of thermal (60 °C) and radical initiation at both 1,2- and 2,3-positions of the allenyl group to form soluble reactive polymers with various ethylenic, including polyvinylic, fragments. The possibility to prepare 1-allenylpyrrole copolymers has been demonstrated using 1-vinylpyrrolidone and ethylene glycol vinylglycidyl ether as an example. Doped layers based on poly-1-allenyl-4,5,6,7-tetrahydroindole are photosensitive.

Key words: 1-allenylpyrroles, polymers, IR spectra, ^{1}H NMR spectra.

The interest in pyrrole structures is due to their abundance in natural objects (chlorophyll, hemoglobin, antibiotics, porphyrins, corrins, and phthalocyanines) and the unique properties of pyrrole polymers, which serve as electroconducting materials and organic metals for solar energy conversion.[1—6]

The discovery of the reactions of ketoximes with acetylene[1] has supplemented substantially the series of accessible 1*H*- and 1-vinylpyrroles appropriate for polymerization, stimulated their study, and made it possible to develop traditional and reveal new ways of polymerization.[1,7,8]

1-Allenylpyrroles are a new class of pyrrole monomers, the synthesis of which we have recently developed.[9] The study of the polymerization of 1-allenylpyrroles can increase our knowledge of the effect of the structure of monomers on their reactivity and the physicochemical properties of the polymers formed; in particular, new reactive polymers with pyrrole cycles and ethylenic fragments in the side chain can be obtained, which gives additional possibilities for the direct modification of their electrophysical properties.

Experimental

1-Allenylpyrroles, 1-allenyl-4,5,6,7-tetrahydroindole (**1**) and 1-allenyl-2-phenylpyrrole (**2**), were obtained by a known procedure.[9]

Polymerization was carried out in tubes in an argon atmosphere. Freshly distilled monomers were used, allenylpyrroles **1** and **2** were purified by chromatography on a column (alumina, diethyl ether : hexane (1 : 3) as the eluent), and the constants of the monomers corresponded to published data[9,10,11] (Table 1). 1-Allenyl-4,5,6,7-tetrahydroindole (**3**) and 1-allenyl-2-phenylpyrrole (**4**) homopolymers and copolymers with ethylene glycol vinylglycidyl ether (**5**) and *N*-vinylpyrrolidone (**6**) were obtained by initiation with azobisisobutyronitrile (ABIBN) in block or benzene. Thermally initiated polymerization of monomer **1** was carried out at 60 °C (Table 2).

Procedure of polymerization. Weighed samples of the initiator (0.005 g, 0.5 wt.%) and monomer **1** (1.00 g) were placed in a tube, and anhydrous benzene (0.5 mL) was added. Argon was bubbled through the reaction mixture, and the tube was sealed and thermostatted at 60 °C. After 14 h, the polymer obtained (a glass-like block) was dissolved in benzene (5 mL) and reprecipitated with hexane. The polymer was obtained in 91% yield (0.91 g). Found (%): C, 82.80; H, 8.30; N, 8.90. $C_{11}H_{13}N$. Calculated (%): C, 83.00; H, 8.17; N, 8.80.

All polymers synthesized are cream-colored powders, which are well soluble in benzene, chloroform, and DMSO, but insoluble in aliphatic hydrocarbons. The composition of copolymers with ethylene glycol vinylglycidyl ether was estimated from elemental (nitrogen) analysis data. The composition of copolymers with *N*-vinylpyrrolidone was estimated by the previously developed method[12] from the intensity of the characteristic absorption band of the carbonyl group at 1690 cm^{-1} in the IR spectrum. The molecular weight was determined by the isopiestic method.[13]

IR spectra of polymers were recorded on an IR-75 spectrometer in benzene films. ^{1}H NMR spectra were recorded on a Tesla BS-567 instrument (100 MHz) in $CDCl_3$ using TMS as the internal standard.

Electrophotographic layers 2—7 μm thick from a solution of polymer **3** and its solutions with an acceptor-sensitizer (chloranil, 2,7-dinitrofluorenone, 2,4,7-trinitro-9-fluorenone, 2,4,5,7-tetranitro-9-fluorenone, or 2,4,6-trinitrophenylpyrilium perchlorate) in DMF were prepared and studied by a procedure described previously.[14]

Table 1. Constants of monomers

Monomer	B.p./°C (p/Torr)	n_D^{20}	d_4^{20}	Refs.
1*	—	1.5790	—	9
2*	—	1.6370	—	9
5	76(6)	1.4480	1.0333	10
6	71(3)	1.5117	1.0458	11

* The monomer is polymerized during fractionation; it was chromatographically purified on a column (alumina, diethyl ether—hexane (1 : 3) as the eluent).

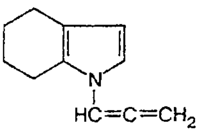
Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 11, pp. 1958—1961, November, 1997.

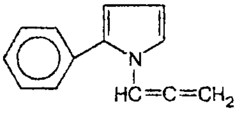
1066-5285/97/4611-1855 $18.00 © 1997 Plenum Publishing Corporation

Results and Discussion

The few examples of polymerization of allenyl monomers testify that they possess a sufficiently high reactivity in radical polymerization.[15–17] For example, under these conditions (3% ABIBN, 60—100 °C, block or solution), methoxyallene and allenylglycidyl ether form linear polymers in 64—99% yield, which are cross-linked during isolation.[15,16]

We have shown that *N*-allenylpyrroles **1** and **2** are also readily polymerized in the presence of ABIBN (Table 2), but form no cross-linked structures, and the properties of their polymers do not change during reprecipitation and drying.


1


2

Probably, this difference is either related to a sharply decreased (compared to alkoxyallenes) content of reactive ethylenic fragments, or the result of steric factors: bulkyness and rigidity of lateral pyrrole structures can impede the formation of intermolecular bonds and thus prevent gel formation.

Table 2. Polymerization and copolymerization of 1-allenyl-4,5,6,7-tetrahydroindole (**1**) and 1-allenyl-2-phenylpyrrole (**2**)

CM		ABIBN	τ	*T*	Yield	CP		*M*
M_1	M_2	(wt.%)	/h	/°C	(wt.%)	M_1	M_2	
mol. fractions						mol. fractions		
1-Allenyl-4,5,6,7-tetrahydroindole (**1**)								
1.00	—	0.2	14	60	85	1.00	—	4900
1.00	—	0.5	14	60	91	1.00	—	—
1.00	—	1.0	14	60	93	1.00	—	4700
1.00	—	0.5	14	70	95	1.00	—	4600
1.00	—	0.5	14	80	97	1.00	—	4400
1.00	—	0.5	7	60	60	1.00	—	4800
1.00	—	—	20	80	81	1.00	—	4700
0.80	0.20[a,b]	1.0	20	70	58	0.95	0.05	3100
0.50	0.50[a,b]	1.0	20	70	42	0.88	0.12	2800
0.25	0.75[a,b]	1.0	20	70	23	0.67	0.33	2300
0.50	0.50[c]	0.5	7	60	73	0.70	0.30	6800
1-Allenyl-2-phenylpyrrole (**2**)								
1.0	—	0.5	12	60	43	1.0	—	1700
1.0[b]	—	0.5	12	60	60	1.0	—	—
1.0	—	—	12	60	30	1.0	—	1500
1.0	—	1.0	4	60	71	1.0	—	1800

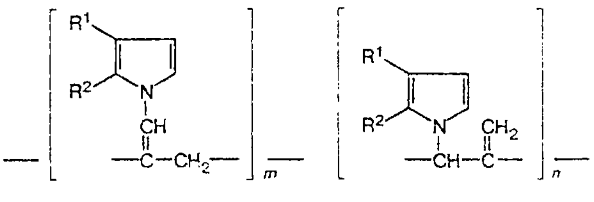
Note. ABIBN is the initiator, and benzene is the solvent (50 wt.%). CM is the composition of the monomeric mixture; CP is the composition of the copolymer; τ is the reaction time; *M* is the molecular weight (isopiestic method). M_1 is the fraction of **1** or **2**. [a] M_2 is the fraction of ethylene glycol vinylglycidyl ether (**5**). [b] Block polymerization. [c] M_2 is the fraction of *N*-vinylpyrrolidone (**6**).

The structures of the polymers synthesized were proved by ^{1}H NMR and IR spectra and analysis of published data on the structures of allenyl polymers.[15–17] The ^{1}H NMR spectrum of polymer **3** exhibits broadened signals, which are typical of polymers, and the position of protons of the pyrrole ring undergoes almost no changes. The spectrum contains signals of two types, which are characteristic of protons of the vinyl group: a doublet at 4.3 ppm, a singlet at 4.50 ppm ($CH_2=C$), and a singlet at 6.6 ppm ($CH=C$). The ^{1}H NMR spectrum contains no signals of protons of the allene group (5.5 ppm, doublet). The ^{1}H NMR spectra of polymers obtained by thermal polymerization without an initiator in the presence of ABIBN (Table 1) differ only in intensity of the CH=C band (6.6 ppm).

The IR spectra of the polymers indicate that they contain at least two types of double bonds: N—CH= (1640 cm^{-1})[1] and CH_2=C, the exomethylene group of the lateral chain (1655 cm^{-1}).[18] The fact that both these groups are present is confirmed by the spectral pattern in the region of 3000—3100 cm^{-1}, where the $=CH_2$ group is represented by the band at 3080 cm^{-1}, and the band at 3020 cm^{-1} corresponds to the absorption of the =CH— group.[16] In addition, the IR spectra exhibit an absorption at 890—900 cm^{-1}, which is assigned[16,18] to bending vibrations of the "exomethylene" double bond of allenyl polymers. The intensity of the band of the —CH= group is always greater than that of the exomethylene group and is maximum for the thermoinitiated polymer. According to the IR spectra, an approximate ratio between the —CH= and CH_2= groups is (1.2—1.8) : 1 (when the molecular absorption coefficients are equal).

A series of bands of the pyrrole ring (708, 1370, and 1490 cm^{-1}) and C—N bond (1300 cm^{-1})[1] remains unchanged in the IR spectra of all samples. The intense band at 1960 cm^{-1}, which is typical of the allenyl double bond of the monomer,[9] is not observed in the IR spectra of the polymers.

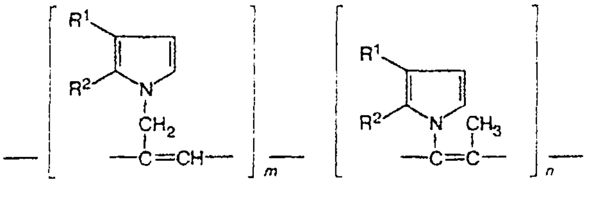
The experimental data do not confirm that two types of polymer products are formed, because no fractional separation similar to that described in Ref. 16 occurs during reprecipitation. This fact along with the data of spectral analysis of poly-1-allenylpyrroles suggests the formation of peculiar copolymers containing the following blocks:



where m/n = 1.2—1.9

$R^1 = R^2 = (CH_2)_4$ (**3**), R^1 = H, R^2 = Ph (**4**)

Polyconjugated fragments appear in the macromolecules due to prototropic isomerization:



These structures predominate in polymer **4**, whose ^1H NMR spectrum contains an intense signal of Me groups (a singlet at 0.9 ppm). The presence of these structures in polymers **3** is favored by the fact that their ^1H NMR spectra exhibit a singlet of the methyl group in the region of 1.9—2.0 ppm (a shoulder on the intense broad signal at 1.7 ppm of methylene protons of the cyclohexane fragment) and a singlet of the methine NCH_2C group at 2.8 ppm (a shoulder on the intense broad signal at 2.5 ppm of methylene protons of the cyclohexane fragment), and broad blurred signals at 6.35 and 5.88 ppm (=CH in polyconjugated blocks).

The IR spectra contain a broad absorption band in the region of 1580—1720 cm^{-1} with maxima at 1580, 1620, 1640, and 1680 cm^{-1} and a background with weak maxima in the region of 950—990 cm^{-1} (bending vibrations of C—H in polyenes[18]), which testifies that the polymers contain a series of different double bonds, including those in polyconjugated blocks. The ESR spectra of polymers **1** and **2** are typical of polyconjugated systems, the signal is a symmetric singlet, the concentration of unpaired electrons is $3.1 \cdot 10^{16}$ and $8.8 \cdot 10^{16}$ spin g^{-1}, and ΔH is 0.98 and 0.97, respectively.

N-Allenylpyrroles are somewhat more active in radical polymerization than *N*-vinylpyrroles[1] and form higher-molecular products. For example, under similar conditions, 1-vinyl-4,5,6,7-tetrahydroindole forms a polymer with molecular weight 2800 in 51% yield,[1] while 1-allenyl-4,5,6,7-tetrahydroindole forms a polymer with M = 4400 in 97% yield (Table 2). The yield of the 1-allenyl-2-phenylpyrrole polymer reaches 71%, while the yield of the polymer of 1-vinyl-2-phenylpyrrole does not exceed 18%.

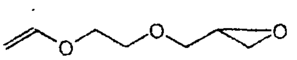
Table 3. Photoelectric parameters of poly-1-allenyl-4,5,6,7-tetrahydroindole in the absence and presence of sensitizers

Sensitizer	U/V	λ_{max}/nm	Φ /m^2 J^{-1} (S = 0.5)
—	80	380	0.024
Chloranil	160	400	0.070
2,7-Dinitrofluorenone	200	440	0.088
2,4,7-Trinitro-9-fluorenone	250	440	0.108
2,4,5,7-Tetranitro-9-fluorenone	280	440	0.260
2,4,6-Trinitrophenylpyriliumperchlorate	250	440	0.260

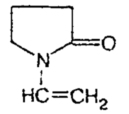
Note. U is the potential, λ_{max} is the spectral maximum, and Φ is the photosensitivity.

Polymerization of **1** shows normal behavior: as the reaction temperature and concentration of the initiator increase, the yield of polymers increases and the molecular weight somewhat decreases (Table 2).

The copolymerization of **1** with ethylene glycol vinylglycidyl ether (**5**) results in the formation of polymers with free epoxide groups, which are appropriate for various polymer-analogous transformations. The process occurs with a considerably lower rate, and the maximum yield of copolymers is 73% (reaction time 20 h, Table 2). When the reaction mixture is enriched in low-reactivity[12] vinyl ether **5**, the yield of the copolymers and their molecular weights decrease sharply (Table 2).



5



6

In the electrophotographic regime, polymeric layers based on **3** are charged to a potential of 80 V in the positive corona discharge and possess an electrophotographic sensitivity of 0.024 m^2 J^{-1} (S 0.5) with a spectral maximum at 380 nm (Table 3).

Sensitization of the polymers by various electron acceptors results in an increase in the charge on the layer up to 280 V, a substantial increase in the electrophotographic sensitivity, and the bathochromic shift of the absorption maximum to 440 nm.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 95-03-09303a).

References

1. B. A. Trofimov and A. I. Mikhaleva, *N-Vinilpirroly* [*N-Vinylpyrroles*], Nauka, Novosibirsk, 1984, 260 pp. (in Russian).
2. B. A. Trofimov, *Pyrroles*, Part 2: *The Synthesis, Reactivity and Physical Properties of Substituted Pyrroles*, Ed. A. Jones, Wiley, Inc., New York, 1992, p. 131.
3. T. J. Simpson, *Ann. Repts. Progr. Chem.*, 1986, **83**, 347.
4. A. R. Baffersby, M. G. Baker, H. A. Broadbent, C. J. R. Fookes, and F. J. Leeper, *J. Chem. Soc., Perkin Trans.*, 1987, **9**, 2027.
5. E. Bibault, *Actual. Chim.*, 1983, 7, 23.
6. D. C. Curran and S. D. Perera, *Chem. Soc. Rev.*, 1991, **20**, 391.
7. B. A. Trofimov, L. V. Morozova, M. V. Sigalov, A. I. Mikhaleva, and M. V. Markova, *Makromol. Chem.*, 1987, **188**, 2251.
8. B. A. Trofimov, L. V. Morozova, E. I. Brodskaya, A. I. Mikhaleva, D. S. Toryashinova, and M. V. Markova, *Vysokomol. Soedin.: Krat. Soobshch.*, 1989, **31**, 897 [*Polym. Sci. USSR, Ser. B*, 1989, **31** (Engl. Transl.)].

9. O. A. Tarasova, L. Brandsma, and B. A. Trofimov, *Synthesis*, 1993, **6**, 571.
10. B. A. Trofimov, *Geteroatomnye proizvodnye atsetilena* [*Heteroatomic Acetylene Derivatives*], Nauka, Moscow, 1981, 319 pp. (in Russian).
11. F. P. Sidel'kovskaya, *Khimiya N-vinilpirrolidona i ego polimerov* [*Chemistry of N-Vinylpyrrolidone and Its Polymers*], Nauka, Moscow, 1970, 150 pp. (in Russian).
12. T. T. Minakova, L. V. Morozova, and B. A. Trofimov, *Zh. Prikl. Khim.*, 1984, **6**, 1667 [*J. Appl. Chem. USSR*, 1984, **6** (Engl. Transl.)].
13. J. Rabek, *Experimental Methods in Polymer Chemistry*, Wiley, Chichester (U.K.), 1982, **1**.
14. L. V. Morozova, A. I. Mikhaleva, and G. F. Myachina, *Zh. Prikl. Khim.*, 1987, **60**, 1193 [*J. Appl. Chem. USSR*, 1987, **60** (Engl. Transl.)].
15. I. Yokozava, M. Tanaka, and T. Endo, *Chem. Soc. Jpn., Chem. Lett.*, 1987, **9**, 1831.
16. J. Mizuya, I. Yokozava, and T. Endo, *J. Pol. Sci., Pol. Chem.*, 1988, **26**, 3119.
17. J. Leland, J. Boucher, and K. Anderson, *J. Pol. Sci., Pol. Chem. Ed.*, 1977, **15**, 2784.
18. K. Nakanishi, *Infrared Absorption Spectroscopy*, Nankodo Company, Ltd., Tokyo, 1962.

Received December 30, 1996;
in revised form May 30, 1997