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Copolymerization of *N*-allenylimidazole with di(ethylene glycol) divinyl ether and complexation of the copolymers with $CuCl_2$

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Polyfunctionalized linear copolymers of *N*-allenylimidazole and di(ethylene glycol) divinyl ether with polyconjugated (polyvinylene) blocks in the main chain and exomethylene bonds and vinyloxyethoxyethyl groups in the side chain were prepared. Using the reaction of the copolymers with $CuCl_2$, a possibility of synthesis of polymeric metal complexes for catalysis of organic reactions was shown. The IR and ESR spectra of the complexes were studied.

Key words: *N*-allenylimidazole, di(ethylene glycol) divinyl ether, copolymerization, metal complexes, IR spectra, ESR spectra.

The chemistry of allenyl monomers is being actively developed due to prospects of synthesis of unique reactive polymers on their basis: macromonomers and precursors for design of block and grafted copolymers or materials with a specified combination of physicochemical properties.[1—5]

A series of available allenyl monomers includes alkoxyallenes,[2—5] vinyloxyallenes,[6,7] allenyl glycidyl ether,[1] poly(ethylene glycol) allenylmethyl ether,[8,9] and 2-allenyloxymethylnaphthalene.[10]

Recently[11—13] synthesized allenylazoles are of special interest. They provide new opportunities for preparation of biologically active polymers, because nitrogen-containing heterocycles, beginning from pyrroles, are known[14] to constitute a structure of many natural compounds and participate in key processes of living activities.

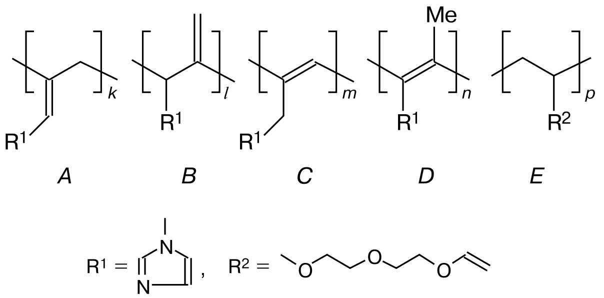
In the present work, we studied the copolymerization of *N*-allenylimidazole (AI) with di(ethylene glycol) divinyl ether (DEGDVE) to prepare new polymers with *N*-vinyl and vinyloxy groups in the side chain as potential biologically active substances and compounds promising for use in catalysis of organic reactions. The presence of free vinyloxy groups of DEGDVE in the macromolecules extend synthetic possibilities of the resulting macromonomers and can favor the formation of cross-linked polymeric matrices in synthesis of metal-polymeric complexes with metal salts.

Results and Discussion

Radical polymerization of AI with DEGDVE in the presence of azobis(isobutyronitrile) (AIBN) was carried out in a wide range of ratios of the initial monomers (Table 1). It was found that AI easily undergoes copolymerization with DEGDVE to form functionalized linear soluble copolymers with exomethylene and free vinyloxy groups in the side chain.

The data of turbidimetric titration, namely, the smooth run of the plot of the absorbance *vs.* fraction of the precipitating agent (ethanol—diethyl ether system) and no platforms, confirm the formation of copolymers and the absence of admixtures of the corresponding homopolymers (Fig. 1).

The spectral data along with previously[15—17] obtained information on the structure of polyheteroallenes indicate the following structure of macromolecules of copolymers AI—DEGDVE.



Macromolecules of the copolymers are formed at positions 1,2 and 2,3 of the allenyl group. Conjugated polyacetylene blocks appear due to prototropic isomerization of olefin fragments in the main chain.[15—17]

The structure of copolymers AI—DEGDVE was proved by an analysis of the IR and ^{1}H NMR spectra. The IR spectra of the copolymers contain no characteristic

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Table 1. Copolymerization of *N*-allenylimidazole (AI) with di(ethylene glycol) divinyl ether (DEGDVE) (AIBN (1%), reaction duration 19 h)

Content of AI[a]		*T* /°C	Yield of copolymer (wt.%)	M[b]	M.p. /°C
Initial mixture	Copolymer[c]				
0.10	0.74	70	5	1200	143—149
0.20	0.87	60	8	1350	162—167
0.20	0.86	70	12	1450	160—165
0.20	0.84	80	14	1550	158—161
0.30	0.90	60	19	1700	179—185
0.30[d]	0.90	60	17	1770	178—184
0.40	0.91	60	40	2000	194—198
0.50	0.92	60	43	2300	198—202
0.70	0.94	60	74	2500	200—204
1.00	1.00	60	92	3900	204—207

[a] In mole fractions.
[b] Molecular weight.
[c] Calculation based on the N content.
[d] Reaction duration 10 h.

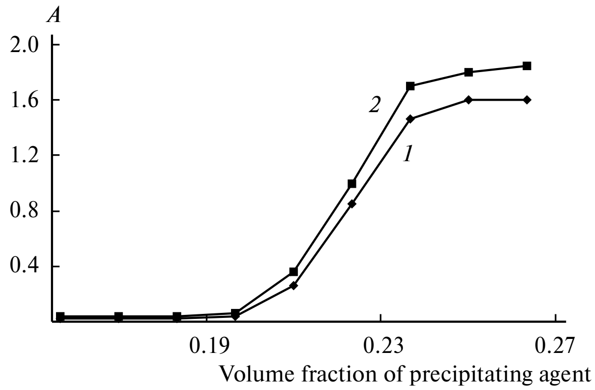


Fig. 1. Turbidimetric titration of the copolymers of *N*-allenylimidazole with di(ethylene glycol) divinyl ether: AI : DEGDVE = 0.86 : 0.14 (*1*) and 0.92 : 0.08 (*2*).

band of stretching vibrations of the C=C=C allene fragment of the initial AI at 1960 cm^{-1}. The bands of stretching vibrations of imidazole rings (1492, 1397, 1289, and 1227 cm^{-1}) remain unchanged.[12]

The IR spectra show that the copolymers contain several types of double bonds, which are presented by a series of medium-intensity bands with absorption maxima at 1685, 1650, 1625, and 1597 cm^{-1}: N—CH= (1650 cm^{-1}) and exomethylene C=CH_2 group in the side chain (1670 and 3100 cm^{-1}).[1,18] The background and weak maxima at 900—904 cm^{-1} (bending vibrations of C—H in polyenes) are caused by the presence of polyconjugated double bonds.[1,18]

The bands of stretching vibrations of the C=C bonds in the free vinyloxy groups of DEGDVE (1620 and 1640 cm^{-1})[3] are overlapped with the bands of the N—CH= groups and exomethylene groups in the side chain of AI. Stretching vibrations of the ether bond of DEGDVE appear in the IR spectra of the copolymers as a band at 1200 cm^{-1}; the bands of ether bonds at 1000—1100 cm^{-1} are overlapped with bending vibrations of C—H of the ring of AI.[18]

The ^{1}H NMR spectra have typical of polymers broadened signals that detect all the above indicated structural units. They contain signals of the polymeric chain —CH—, —CH_2— (δ 1.30 and 1.67), Me groups in structure *D* (s, δ 2.65), CH group of structure *B* (δ 2.99), terminal CH_2= groups of DEGDVE (two d, δ 3.96 and 4.16) and CH= (m, δ 6.50), CH_2= group of structure *B* (s, δ 4.92), and CH= group in structure *A* (δ 6.66) and imidazole ring (δ 6.91—7.76).

The experimental data show that AI exhibits typical of heteroallenes high activity in combined polymerization: the forming copolymers are enriched in AI units (see Table 1). The yield of copolymers mainly depends on the composition of the initial mixture of the monomers, and its increase with an increase in the reaction temperature (60, 70, and 80 °C) and duration (10 and 19 h) does not exceed 2—6% (see Table 1).

As shown previously,[17] poly(*N*-allenylazoles) have low molecular weights (1500—4000) because of processes of chain transfer to the monomer during their polymerization and a possibility to form macrocyclic structures. An additional contribution to the decrease in the molecular weights upon copolymerization is made by the use of poorly reactive DEGDVE (see Table 1). The molecular weight of the DEGDVE copolymers decreases compared to homopolymers of allenylimidazole also because of the known high affinity of vinyl ethers to reactions of chain transfer to the monomer.[19]

A series of the copolymers was obtained at low conversions (down to 8.7%, Table 2) to estimate the reactivity and calculate the copolymerization constants.

The copolymerization constants were calculated by a known method[20] modified according to published data[21] with preliminary planning of experiment (calculation of

Table 2. Data on copolymerization of AI with DEGDVE for calculation of the relative activity constants of the monomers (AIBN (1%), 60 °C)

Initial mixture*		*t*** /h	Yield (%)	Copolymer*	
AI	DEGDVE			AI	DEGDVE
0.10	0.90	1.0	4.0	0.73	0.27
0.20	0.80	2.0	8.2	0.77	0.23
0.30	0.70	1.5	6.0	0.82	0.28
0.50	0.50	1.1	8.3	0.90	0.10
0.70	0.30	1.0	8.7	0.92	0.08

* Composition in mole fractions.
** Reaction duration.

the region of the copolymer composition taking into account the minimum experimental error). It was found that AI is a more active comonomer toward both growing macroradicals in copolymerization with DEGDVE (r_1 = 4.30±0.20, r_2 = 0.01±0.003, $1/r_1$ = 23, $1/r_2$ = 100).

As a whole, high activity in radical copolymerization is inherent in allenyl monomers.[8,16] For instance, in the copolymerization of poly(ethylene glycol) allenylmethyl ether with styrene, the relative activity of the ether is by 2.5 times higher than that of styrene.[8]

Di(ethylene glycol) divinyl ether exhibits low activity in radical polymerization and copolymerization,[19] which is typical of vinyl ethers. In addition, inactivity of DEGDVE in the copolymerization can be explained in part by the presence in copolymer macromolecules of polyvinylene blocks with a high concentration of unpaired electrons,[17] being a unique trap for radicals that can inhibit the polymerization of DEGDVE.

The ability of the synthesized copolymers to bind heavy metal salts was illustrated by the formation of complexes with $CuCl_2$. As known,[22,23] polymeric metal complexes are promising for use in catalysis. Efficient medicines, biologically active substances of wide spectrum, and materials for technics were found among the metal complexes of 1-vinylazoles.[24,25]

Synthesis of earlier unknown metal complexes based on the copolymers AI—DEGDVE provides new possibilities in the indicated directions. Metal-containing polymeric complexes are easily and efficiently formed on mixing of alcoholic solutions of the copolymers and $CuCl_2$, and the composition of the complexes corresponds to that of the initial components and can vary to the equimolar composition (Table 3).

Depending on the ratio of the initial reactants (copolymer : $CuCl_2$), one can obtain complexes with higher or lower salt content and, hence, the copper content in different complexes ranges from 12.5 to 32% according to analysis data.

Table 3. Characteristics of the complexes of the copolymers AI—DEGDVE with copper dichloride

Content of AI in copolymer[a]	Copolymer : : $CuCl_2$[b]	Yield (%)	Found (%)			
			C	H	Cl	N
0.91	1 : 1	91	37.25	3.75	22.84	13.32
0.86	1 : 1	87	35.30	3.58	18.07	12.34
0.91	2 : 1	94	51.63	5.23	11.57	19.09
0.74	1 : 1	62	40.47	4.42	18.07	14.19
0.74	1 : 2	60	35.70	3.75	21.22	12.62
1.00[c]	1 : 1	68	30.73	3.24	23.31	10.88
1.00[c]	2 : 1	94	39.25	3.76	18.40	14.87
1.00[c]	4 : 1	87	44.90	4.72	13.70	18.50

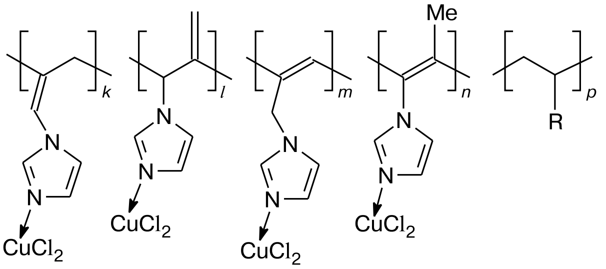
[a] In mole fractions.

[b] Mole ratio.

[c] Homopolymer AI.

Since solubility of the copolymers and their complexes differs drastically, an admixture of the free copolymer in the latter can virtually be excluded. Copolymers highly soluble in ethanol become insoluble upon complex formation and precipitate. Unlike the initial copolymers that melt at 160—200 °C, the complexes do not melt on heating to 350 °C.

The structures of the complexes were determined from a comparative analysis of the free and coordinatively bound copolymers AI—DEGDVE and homopolymer AI by IR and ESR spectroscopy using elemental analysis data. For example, the structure of the following metal-polymeric equimolar complex was determined.



As in the complexes of monomeric AI,[24] the coordination center is the N(3) atom of imidazole.

The involvement of the nitrogen atom of the imidazole ring in the formation of complexes with $CuCl_2$ and a change in its electronic structure are indicated by the shift of bands of stretching and bending vibrations to higher frequencies by 5—20 cm^{-1} (Table 4). The intense band of stretching vibrations of the ring with the absorption maximum at 1492 cm^{-1} and the shoulder at 1506 cm^{-1} appears in the spectrum of the complex as a single intense band at 1511 cm^{-1}. The resolved medium-intensity bands at 1441, 1397, and 1352 cm^{-1}, which are also assigned to stretching vibrations of the ring, are presented in the spectrum of the copolymer complex by a broad band with an absorption maximum at 1370 and 1431 cm^{-1}.

Bending vibrations of the ring also change substantially: in addition to the high-frequency shift, the intensity of the doublet at 1289 and 1302 cm^{-1} is halved. The most significant shift (~45 cm^{-1}) was observed for the band at 905 cm^{-1}.

Changes are also observed in the region of stretching vibrations of the ether group in DEGDVE: the bands at 1250 and 1199 cm^{-1} decrease in intensity and appear as shoulders on the bands at 1245 and 1200 cm^{-1}.

A series of medium-intensity bands of stretching vibrations of double bonds of different earlier indicated types (1685, 1653, 1625, and 1597 cm^{-1}) in the IR spectra of the complexed copolymers are transformed into intense bands with absorption maxima at 1636 and 1624 cm^{-1}. The bands of bending vibrations δ(=CH) at

Table 4. IR spectra of the AI polymers and their complexes with $CuCl_2$

Polymer	IR, ν(δ)/cm^{-1}					
	N=CH	N—C=C (vinyl.)	ν(C=C) (ring)	δ(C—H) (ring)	δ(=CH) (vinyl.)	δ(=CH) (ring)
Homopolymer AI	3104	1699, 1685, 1653, 1625	1506 sh, 1492, 1437, 1397, 1351	1300 sh, 1287, 1226, 1107, 1075, 1029, 905	817	736
Complex of homopolymer AI	3123	1632, 1625	1511, 1431 sh, 1407, 1370 sh	1307 sh, 1294, 1234, 1108, 1091, 1034, 948	834	750
Copolymer AI—DEGDVE (0.86 : 0.14)	3107	1685, 1650, 1620, 1597	1506 sh, 1492, 1441, 1397, 1352	1302 sh, 1289, 1227, 1107, 1077, 1032, 905	980, 818	741
Complex of copolymer AI—DEGDVE	3123	1636, 1624	1508, 1431 sh, 1410, 1370 sh	1310 sh, 1294, 1245 sh, 1232, 1105, 1092, 1034, 950	835	748

Table 5. Characteristics of the ESR spectra of the complexes of poly(*N*-allenylimidazole) (PAI) and copolymers of AI with DEGDVE

Initial polymer	Polymer : : $CuCl_2$*	Content of Cl (%)	Spin concentration /spin g^{-1}	*g*-Factor	Δ*H* /Oe
PAI	1 : 1	23.31	$4.0 \cdot 10^{19}$	2.127	287
PAI	2 : 1	18.40	$1.7 \cdot 10^{20}$	2.112	200
PAI	4 : 1	13.70	$1.8 \cdot 10^{20}$	2.112	120
Copolymer AI—DEGDVE (0.86 : 0.14)	1 : 1	18.07	$1.0 \cdot 10^{21}$	2.104	280
Copolymer AI—DEGDVE (0.91 : 0.09)	1 : 1	22.84	$7.0 \cdot 10^{20}$	2.111	320

* Mole ratio.

3107 and 818 cm^{-1} are shifted to a high-frequency region by ~15 cm^{-1}.

Similar changes are also observed in the IR spectra of the complexes of the homopolymer AI (see Table 4).

The study of the ESR spectra of the complexes of homo- and copolymers AI—DEGDVE found that all powdered samples are paramagnetic and correspond to the bivalent copper complexes (Table 5). The character of the ESR signals for the samples with the equimolar polymer to $CuCl_2$ ratio is independent of the structure of the initial polymer (homopolymer or copolymer). The signals are asymmetric singlets. No hyperfine structure of the copper ion is observed.

The two- and fourfold increase in the number of the polymeric ligand over $CuCl_2$ results in considerable narrowing of the absorption line and some decrease in the *g*-factor value. The singlet becomes nearly symmetric. The data obtained indicate the axial type of symmetry of the complexes under study.

Thus, the polyfunctional copolymers of *N*-allenylimidazole with di(ethylene glycol) divinyl ether were obtained under free-radical conditions, and a possibility of synthesis from them of polymeric metal complexes with $CuCl_2$ was shown. These complexes are promising for use in catalysis of organic reactions and preparation of potential biologically active substances.

Experimental

N-Allenylimidazole was synthesized and purified using a known method.[12]

N-Allenylimidazole freshly distilled under argon was used for polymerization. Purity was monitored by IR and ^{1}H NMR spectroscopy. The constants of the monomer corresponded to published data[12]: b.p. 92 °C (10 Torr), n_D^{20} 1.5628.

Di(ethylene glycol) divinyl ether (pilot product, Irkutsk Institute of Chemistry, Siberian Branch of the RAS) was washed with water, dried with potash, and doubly fractionated. The constants of the monomer corresponded to published data[3]: b.p. 85 °C (14 Torr), n_D^{20} 1.4430. Purity of the monomer was monitored by GLC and IR and ^{1}H NMR spectroscopy.

Azobis(isobutyronitrile) was twice recrystallized from methanol.

Copolymerization was carried in ampules under an argon atmosphere in the comonomer bulk at 60, 70, and 80 °C under the action of AIBN. The synthesis conditions and characteristics of the copolymers are given in Table 1.

Copolymers were purified by precipitation from ethanol into diethyl ether and dried *in vacuo* to constant weight. The synthesized copolymers are cream-colored powders soluble in DMSO, DMF, alcohols, and *N*-methylpyrrolidone and insoluble in water, diethyl ether, and aliphatic hydrocarbons. The composition of the AI copolymers with DEGDVE was calculated from the elemental analysis data based on nitrogen.

IR spectra were recorded on a Bruker IFS 25 instrument in ethanol films, microlayer, or KBr pellets. ^{1}H NMR spectra were obtained on a Bruker DPX 400 instrument (400 MHz) in DMSO-d$_6$ using HMDS as standard.

ESR spectra of solid powders were measured at room temperature on an SE/X-2547 spectrometer (Radiopan, Poland) with a sensitivity of $5 \cdot 10^{10}$ spin Oe^{-1} and the resolution ability not lower than 10^{-5} *in vacuo* (10^{-4} Torr) and in air.

Molecular weights of the polymers were determined by the isopiestic method[26] using several parallel measurements for each copolymer, the error being ±130, *i.e.*, ~1 monomeric unit.

Turbidimetric titration was carried out on a KFK-2 spectrophotometer (λ = 590 nm). For titration, copolymer (0.03 g) was dissolved in ethanol (5 mL), and the precipitating agent (diethyl ether) was added by portions (0.1 mL) with stirring.

Below we present the typical procedure for the synthesis of the copolymer metal complex.

Synthesis of metal complex. A solution of the copolymer AI—DEGDVE (0.132 g, 0.9 mole fraction of AI, 0.5 mmol per unit) in ethanol (2 mL) at ~20 °C was mixed with a solution of $CuCl_2 \cdot 2H_2O$ (0.085 g, 0.5 mmol) in ethanol (1 mL). The resulting precipitate was filtered off, washed with ethanol, and dried. Dark-turquoise powdered complex was obtained in a yield of 0.182 g (91%).

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