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MACROMOLECULAR COMPOUNDS AND POLYMERIC MATERIALS

New Germanium- and Tin-Containing Polysalicylideneazomethines Derived from Tetraamines

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Abstract—Polysalicylideneazomethines containing Ge and Sn atoms in the polymeric chain were prepared by polycondensation of N,N',N'',N'''-tetrasalicylidene-3,3',4,4'-tetraaminodiphenyl ether with germanium or tin tetrachloride or tetraethoxide. Spectroscopic examination showed that the polymers exhibit nonclassical polyconjugation and belong to a new class of semiconductor polytransannular-conjugated polymers.

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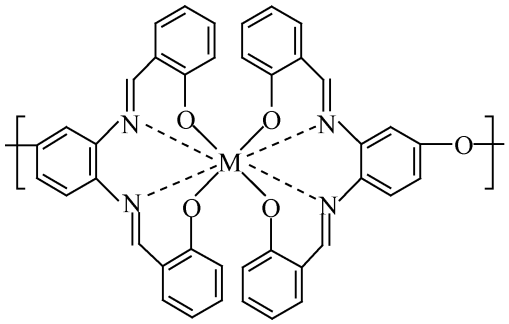
Previously by polycondensation of N,N',N'',N'''-tetrasalicylidene -3,3',4,4'-tetraaminodiphenyl ether (TSDPE) and N,N',N'',N'''-tetrasalicylidene-3,3',4,4'-tetraaminodiphenyl (TSDP) with silicon tetrachloride we prepared polytetrasalicylideneazomethines with Si atoms in the backbone: catena-poly[silicon(μ-N,N',N'',N'''-tetrasalicylidene-3,3',4,4'-tetraiminodiphenyl-O,N,O',N':O'',N'',O''',N''')] and catena-poly[silicon(μ-N,N',N'',N'''-tetrasalicylidene-3,3',4,4'-tetraiminodiphenyl oxide-O,N,O',N':O'',N'',O''',N''')] [1, 2]. We found that the Si-containing polymers, despite break of the conjugation chain (presence of Si–O–Si bonds), are electroactive polymeric semiconductors.

This fact was accounted for from the standpoint of nonclassical electron density delocalization. This concept, applied previously to interpretation of properties of organometallic polymeris such as poly(dialkylsilyl-*p*-xylylidenes) [3, 4], consists in assuming formation of a "nonclassical" conjugation system in the polymer by donor–acceptor interaction of valence shells of the heteroatoms (metalloid and nitrogen) separated by a nonconjugated fragment (e.g., methylene group). The backbone of silicon-containing polymers also contains both donor (nitrogen atoms of azomethine bond) and acceptor (Si) atoms, which creates prerequisites for the formation of intramolecular donor–acceptor charge-transfer complexes (CTCs). Such a transannular donor–acceptor (DA) interaction should be accompanied by efficient charge transfer from the donor to the acceptor, which will lead to polarization of the polymer and hence impart to it electro- and photophysical properties.

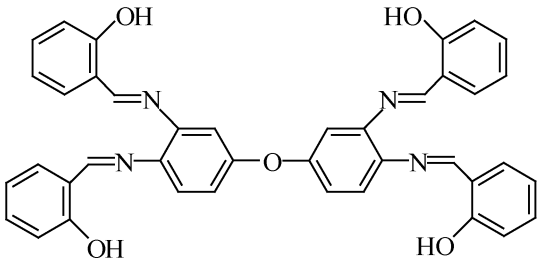
As this study is a logical continuation of the previous studies, it seemed interesting to synthesize and examine polymers of similar structure but containing the Ge and Sn atoms as chemical analogs of Si:



M = Ge (P1-Ge); Sn (P2-Sn)

EXPERIMENTAL

In synthesis of the polymers, we used as comonomers N,N',N'',N'''-tetrasalicylidene-3,3',4,4'-tetraaminodiphenyl ether (M1)



and germanium or tin tetrachloride or tetraethoxide.

N,N',N'',N'''-Tetrasalicylidene-3,3',4,4'-tetraaminodiphenyl ether was prepared by the reaction of salicylaldehyde with 3,3',4,4'-tetraaminodiphenyl ether. The aldehyde : tetraamine molar ratio was 4 : 1.

The polymers were prepared in DMF by polycondensation of the corresponding salicylidene derivatives of the tetraamines with germanium or tin tetrachloride or tetraethoxide. The polymers were isolated by precipitation into diethyl ether. The characteristics of the polymers prepared from the tetraethoxy derivatives of Ge and Sn are given in the table and in Figs. 1–3.

Synthesis of P1-Ge and P2-Sn. To a stirred solution of 0.006 mol of M1 in 15 ml of DMF, we added dropwise 0.006 mol of germanium tetrachloride. The reaction was performed at room temperature under dry argon for 8 h, after which the mixture was concentrated on a rotary evaporator and the dry residue was dissolved in methanol. Polymer P1-Ge was isolated by precipitation into diethyl ether from a methanol solution. Yield 86%.

P2-Sn was prepared similarly (yield 91%).

Elemental analysis of the comonomers and polymers was performed in a LECO CHNS(O)-932 CHN analyzer. The Ge and Sn content was determined with a REAN X-ray fluorescence analyzer. Consistent analytical data were obtained.

The ^{1}H NMR spectra of solutions of the monomers and polymers (4–5 wt %) in deuterated DMF were recorded with a Bruker Avance 200 NMR spectrometer at a frequency of 200 MHz; the UV spectra of solutions in methanol or isopropanol, with an SF-2000 spectrophotometer in the wavelength range 200–700 nm; and the IR spectra of the comonomers and polymers (KBr pellets), with

Spectral characteristics and molecular weight of metal-containing polymers

Polymer	UV spectrum, nm	IR spectrum, cm^{-1}	^{1}H NMR spectrum, ppm	M_n
M1	366s, 398 sh	1614 (C=N), 1577(C_{ar}–C_{ar})	9.2 (s, CH=N), 7.0–7.5 (C_{arp}–H)	–
P1-Ge	363 s, 378 sh, 432 s, 456 sh, 598 w	1610 (C=N), 1597 (C_{ar}–C_{ar})	9.6 (s, CH=N), 6.9–7.5 (C_{ar}–H)	10000
P2-Sn	357 s, 391 sh, 433 s, 464 sh, 603 w	1611 (C=N), 1598(C_{ar}–C_{ar})	9.8 (s, CH=N), 6.9–7.6 (C_{ar}–H)	8000

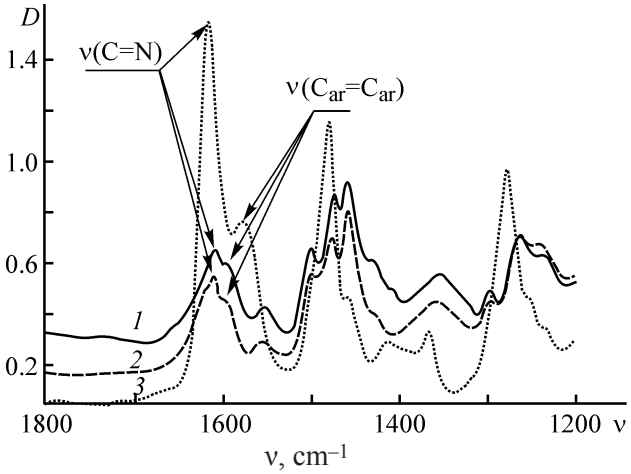


Fig. 1. IR spectra of (*1*) P2-Sn, (*2*) P1-Ge, and (*3*) M1. (*D*) Optical density and (ν) wavenumber.

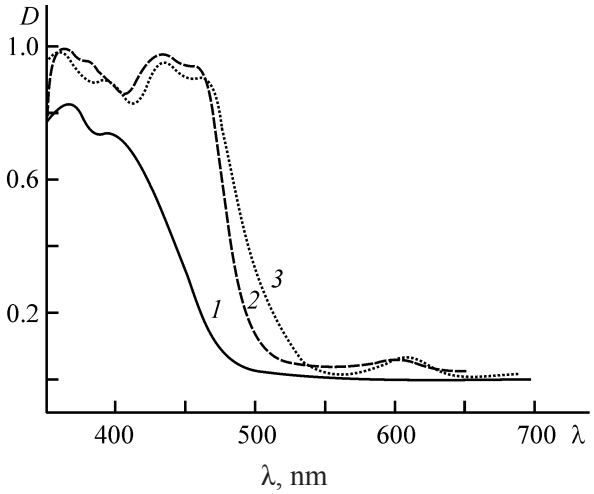


Fig. 2. UV spectra of (*1*) M1, (*2*) P1-Ge, and (*3*) P2-Sn. (*D*) Optical density and (λ) wavelength.

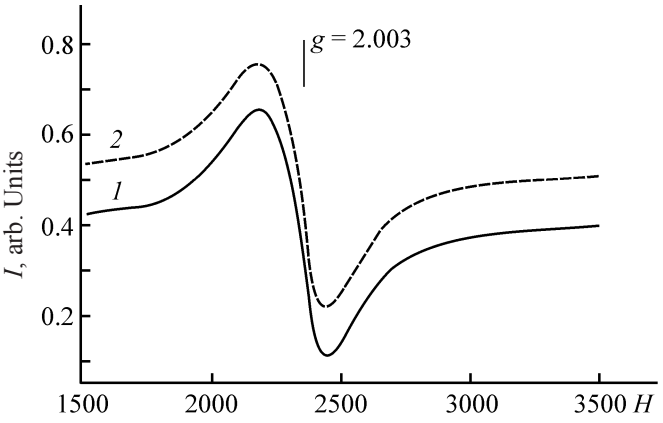


Fig. 3. ESR spectra of polymers (*1*) P1-Ge and (*2*) P2-Sn. (*I*) Signal intensity and (*H*) field intensity.

a Bruker Vertex Fourier IR spectrometer in the range 400–4000 cm^{-1}. The bands were assigned in accordance with published data [5–7].

The ESR spectra of the polymers were taken with a modified RE-1306 radiospectrometer of the 3-cm range.

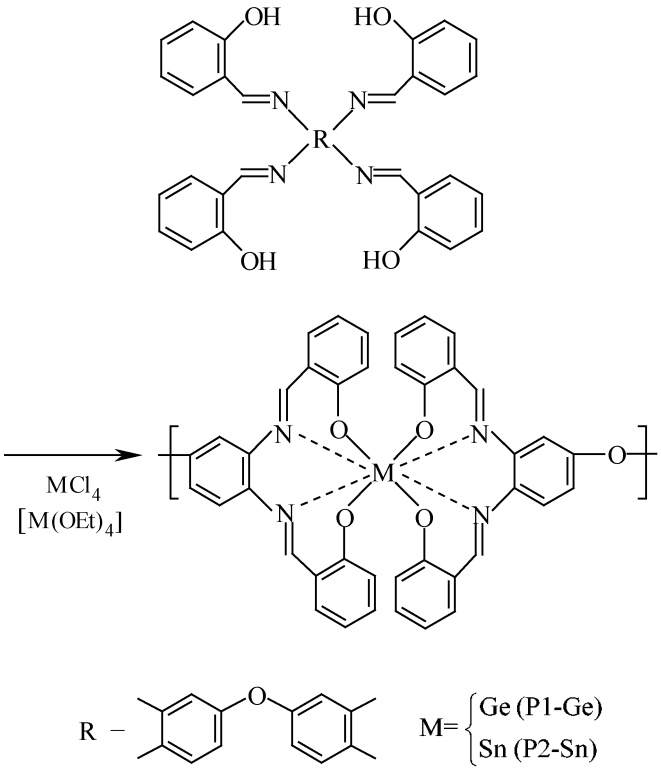
The number-average molecular weight M_n and the degree of polymerization of the polymers X_n were estimated by ^{1}H NMR spectroscopy from the content of residual terminal hydroxy groups which, in turn, was evaluated from the ratio of the integral intensity of the signal of azomethine protons, chosen as reference, to that of the signal of residual terminal hydroxyl protons:

$$X_n = \frac{I_{C=N}}{I_{OH}},$$

$$\overline{M}_n = \overline{X}_n M_{\underset{\text{unit}}{\text{monomeric}}} = \frac{I_{C=N}}{I_{OH}} M_{\underset{\text{unit}}{\text{monomeric}}}.$$

The donor–acceptor interactions were studied for low-molecular-weight complexes of silanes with various organic polydentate ligands. In particular, reactions of dialkyldichlorosilanes with salen-type ligands [salen = *N,N*'-ethylenebis(salidylidenimine)] have been described [4–9]. Data on synthesis of low-molecular-weight CTCs suggested that replacement of monosalicylidene derivatives by tetrasalicylidene ones would allow preparation of polymeric CTCs. In our case, polycondensation should occur, firstly, via nucleophilic substitution of a phenolic proton in M1 molecule by a germanium or tin atom and, secondly, via DA interaction N → M, as this interaction leads to the formation of a thermodynamically favorable six-membered ring, which should significantly stabilize the forming segment of the polymer chain.

Polymers P1-Ge and P2-Sn were prepared by polycondensation of salicylidene derivatives of tetraamines (M1) with germanium and tin tetrachlorides or tetraethoxides. The comonomers were taken in 1 : 1 molar ratio:



The major factor governing the yield and molecular weight of the polymer is how exactly the equimolar ratio of the reactants is observed. The other significant factors are the solvent, monomer concentration, and temperature. As solvent we chose DMF which well dissolves the starting monomers and the forming polymer and can also act as an acceptor of hydrogen chloride released in the process.

As germanium and tin tetrachlorides are highly reactive, to suppress side reactions (hydrolysis of Ge and Sn tetrachlorides followed by tetracyclization) and increase the probability of more complete replacement of the phenolic proton by the metal atom, we performed the polycondensation at 20–25°C. Another way to decrease the contribution of undesirable processes such as hydrolysis of germanium and tin chlorides consisted in replacement of chloro derivatives by their ethoxy analogs, which are less reactive and less susceptible to

hydrolysis. Since in the latter case the leaving group in the polycondensation is the ethoxy group, for its more complete removal the reaction was performed at a higher temperature, 85–90°C.

The presence of germanium and tin in the polymers was confirmed by X-ray fluorescence analysis (XPA). In the X-ray fluorescence spectrum of P1-Ge, there are two bands of Ge atoms, corresponding to the K_α band at 9.9 keV and K_β band at 10.9 keV. In X-ray fluorescence spectrum of P1-Sn, there are two bands of Sn atoms, corresponding to the L_α band at 3.4 keV and L_β band at 3.7 keV.

The main problem in spectroscopic analysis of the polymers obtained is to elucidate the structure of the monomeric unit, i.e., to prove the presence of a six-membered ring formed by the N → M coordination interaction. This interaction should be accompanied by a shift of the electron density from the donor to the acceptor, which, in turn, should affect the spectral characteristics of the objects. According to published data, in the case of low-molecular-weight salicylidene complexes, significant changes in the IR spectra are observed for both the donor and acceptor molecules [8]. The vibration frequencies of the donor are shifted toward longer wavelengths, and those of the acceptor, toward shorter wavelengths. The absorption band intensities also change. Changes are also observed in the ^{1}H NMR spectra: Proton signals of the donor are shifted downfield [9]. In our case, the strongest changes should be expected for the azomethine group, because specifically this group directly participates in the electron density redistribution in the monomeric unit in formation of an intramolecular CTC.

An interesting feature of the IR spectra of the polymers is a change in the intensity ratio of the stretching vibration bands of the azomethine groups (C=N) and aromatic rings (C_{ar}–C_{ar}). Comparison of the intensities of the bands at 1608 (C=N stretching vibrations) and 1595 cm^{-1} (stretching vibrations of aromatic ring) shows that the intensity of the former band in the spectrum of the monomer is considerably higher than that of the aromatic ring, whereas in the spectrum of the polymer the difference is less pronounced (Fig. 1). This fact may be due to a decrease in the extinction coefficient of the azomethine band as a result of DA interaction. Thus, the ratio of the integral intensities of these bands can be considered as a criterion of the efficiency of formation of donor–acceptor bonds N → M.

There are also some other changes in the IR spectrum in going from the monomer to the polymer. The $\nu(C_{ar}–N)$ band is shifted toward longer wavelengths by approximately 20 cm^{-1}, with its intensity decreasing by a factor of ~5. The phenolic band $\nu(C_{ar}–O)$ is shifted toward longer wavelengths by 10 cm^{-1}, with its intensity decreasing by a factor of ~3. One of the stretching vibration bands $\nu(C_{ar}=C_{ar})$ of the phenylene group of the amine, the so-called pulsation vibration band at 1480 cm^{-1}, also changes the position and intensity.

The ^{1}H NMR spectra of the polymers contain signals of aromatic ring protons at 6.9–7.7 ppm. The pattern is poorly resolved, which does not allow the signal assignment to particular aromatic groups. In the ^{1}H NMR spectra of the polymers, the azomethine signal is in an untypical position, at 9.2 ppm (in salicylidene complexes, this signal is usually observed at 8.3–8.9 ppm). This fact confirms the occurrence of efficient DA interaction between the lone electron pairs of the nitrogen atoms and unoccupied *d* orbitals of the Ge and Sn atoms, leading to the downfield shift of the signal by ~1 ppm. This position of the azomethine proton signal in the ^{1}H NMR spectra of the polymers confirms the formation of an intramolecular DA complex.

Figure 2 shows the electronic absorption spectra of the monomers and polymers. Considerable bathochromic shift (50–70 nm) accompanied by a hyperchromic effect and appearance of additional long-wave bands in the range 500–600 nm in going from the monomers to the polymers unambiguously confirm once again the formation in the polymeric chain of multiple CTCs and hence an increase the conjugation length.

Interesting results were obtained by ESR spectroscopy. In the ESR spectra of polysalicylidenes (Fig. 3), a narrow singlet appears with the g-factor close to that of the free electron, which indicates that the polymers under consideration belong to a new class of semiconductor polytransannular-conjugated polymers.

CONCLUSIONS

(1) New Ge- and Sn-containing polysalicylideneazomethines were prepared: catena-poly[germanium (μ-N,N',N'',N'''-tetrasalicylidene-3,3',4,4'-tetraiminodiphenyl oxide-O,N,O',N':O'',N'',O''',N''')] and и catena-poly[tin (μ-*N*,*N*',*N*'',*N*'''-tetrasalicylidene-3,3',4,4'-tetraiminodiphenyl oxide-O,N,O',N':O'',N'',O''',N''')].

(2) Spectroscopic studies revealed the occurrence of intramolecular donor–acceptor interaction in the

polymers, leading to the formation of a charge-transfer complex in the backbone. This fact suggests that these polymers, like their Si-containing analogs, should exhibit semiconductor properties.

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