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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Synthesis and Spectral Characteristics of Silicon-containing Poly(Salicylidene Azomethines) Derived from Aromatic Di- and Tetraamines

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Abstract—New silicon-containing poly(salicylidene azomethines) were prepared by polycondensation of di- or tetrasalicylidene derivatives of aromatic di- or tetraamines. The spectral data suggest the occurrence of noncovalent transannular donor–acceptor interaction N→Si providing “nonclassical” conjugation.

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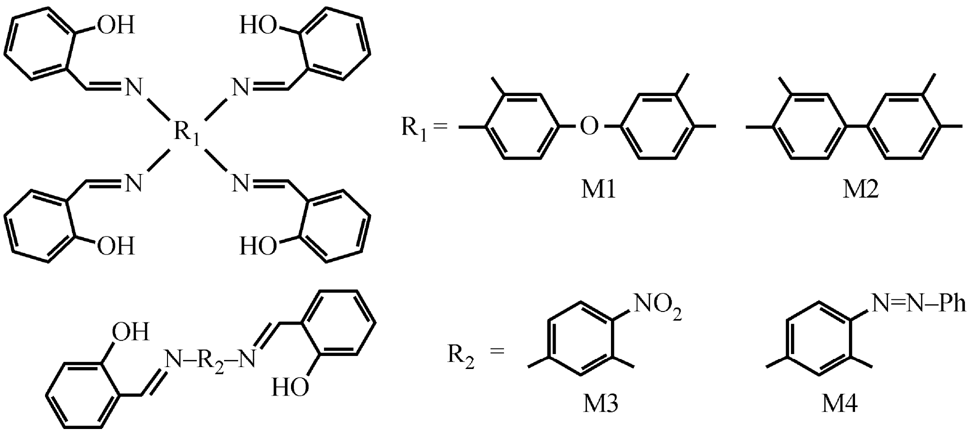
The goal of this study was to develop a procedure for preparing a new class of polymers, Si-containing poly(salicylidene azomethines) containing donor nitrogen atoms and acceptor silicon atoms in the chain, which creates prerequisites for the formation of intramolecular donor–acceptor charge-transfer complexes (CTCs) in the polymer chain. Such kind of complexation should be accompanied by effective charge transfer, which will polarize the polymers and hence impart to them specific electro- and photophysical properties.

EXPERIMENTAL

As comonomers we used *N*,*N*',*N*'',*N*'''-tetra-salicylidene-3,3',4,4'-tetraaminodiphenyl ether (M1), *N*,*N*',*N*'',*N*'''-tetrasalicylidene-3,3',4,4'-tetraaminodiphenyl (M2), 1,3-bis(salicylidenimino)-4-nitrobenzene (M3), and 2,4-bis(salicylidenimino)azobenzene (M4):



The monomers were prepared by reactions of salicylaldehyde with 3,3',4,4'-tetraaminodiphenyl and 3,3',4,4'-tetraaminodiphenyl ether in 4 : 1 molar ratio or with 4-nitro-1,3-diaminobenzene and 2,4-diaminoazobenzene in 2 : 1 ratio.

The polymers were prepared in a DMF solution by polycondensation of the corresponding salicylidene derivatives of tetraamines and diamines with tetrachlorosilane or tetraethoxysilane (Vekton, bp 57 and 168°C, respectively). Polycondensation of disalicylidene de-

Characteristics of the polymers obtained

Polymer	UV, λ, nm	IR, ν, cm^{-1}	NMR, δ, ppm	M_n
P1	236, 289, 314, 444, 461	1610 (C=N), 1597 (C_{ar}–C_{ar}), 1110 (Si–O)	9.3 (C=N), 6.9–7.6 (C_{ar}–H)	11 000
P2	230, 295, 315, 430, 455	1606 (C=N), 1596 (C_{ar}–C_{ar}), 1110 (Si–O)	9.4 (C=N), 6.9–7.6 (C_{ar}–H)	8000
P3	230, 323, 349, 421	1613 (C=N), 1595 (C_{ar}–C_{ar}), 1112 (Si–O)	9.0 (C=N), 6.9–7.5 (C_{ar}–H)	12 000
P4	242, 270, 347, 428	1603 (C=N), 1582 (C_{ar}–C_{ar}), 1100 (Si–O)	9.3 (C=N), 6.8–7.5 (C_{ar}–H)	9000

rivatives of aromatic diamines was performed with dimethyldiethoxysilane prepared from dimethyldichlorosilane and sodium ethylate. The polymers were isolated by precipitation into diethyl ether. The characteristics of the polymers are listed in the table.

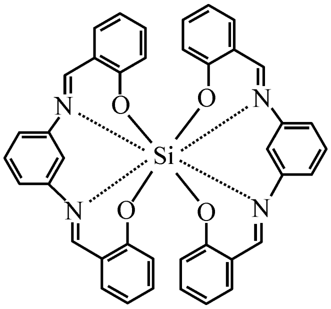
Polymers P1 and P2. To a solution of 0.006 mol of M1 in 15 ml of DMF, 0.006 mol of tetrachlorosilane was added dropwise under agitation. The reaction was performed at room temperature in an inert atmosphere (dry Ar) for 8 h, after which the reaction mixture was concentrated on a rotary evaporator and the dry residue was dissolved in methanol. Polymer P1 was isolated by precipitation from methanol solution into diethyl ether. Yield 94%.

Polymer P2 was prepared similarly.

Polymers P3 and P4. To a solution of 0.011 mol of M3 in 20 ml of DMF, we added 0.011 ml of dimethyldiethoxysilane under agitation. The reaction was performed in an inert medium (dry Ar) for 6 h at 80°C, after which the mixture was concentrated on a rotary evaporator and the dry residue was dissolved in methanol. Polymer P3 was isolated by precipitation from methanol solution into diethyl ether. Yield 89%.

Polymer P4 was prepared similarly.

The model compound necessary for identifying the spectra of the synthesized polymers was prepared by condensation of 1,3-bis(salicylidenimino)benzene with tetraethoxysilane in 2 : 1 molar ratio:



An elemental analysis of the monomers was performed on a LECO CHNS(O)-932 dewvice, and consistent results were obtained.

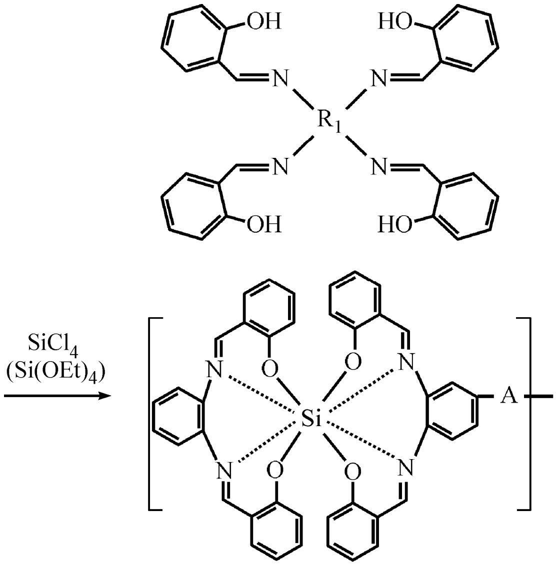
The ^{1}H NMR spectra of 4–5 wt% solutions of the monomers and polymers in DMF-*d*–7 were recorded on a Bruker Avance 200 NMR spectrometer operating at 200 MHz; the UV spectra, on an SF-2000 spectrophotometer in methanol or isopropanol in the wavelength range 200–700 nm; and the IR spectra, on a Vertex IR Fourier spectrometer (Bruker) from KBr pellets in the 400–4000 cm^{-1} range. The bands were assigned taking into account published data [1–3] and data obtained for the model compound.

The ESR spectra were measured at 35 GHz with the magnetic field varied in a wide range.

The number-average molecular weights and degrees of polymerization of the polymers were estimated by NMR spectroscopy from the ratio of the integral intensity of the signal of terminal hydroxy groups to the total integral intensity of the signals of aromatic protons or to the integral intensity of the signal of the azomethine proton.

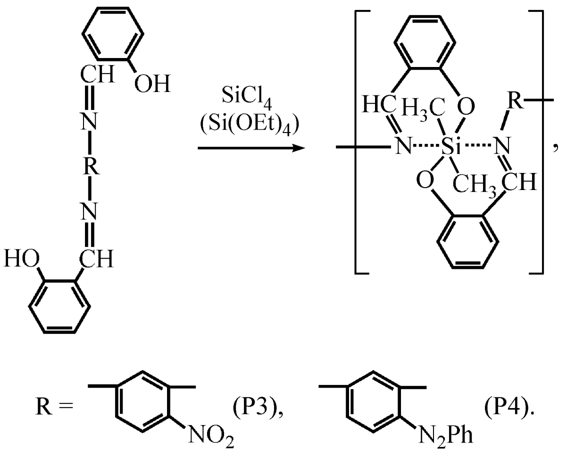
Donor–acceptor interactions are well understood for “low-molecular-weight” reactions of silanes with various organic polydentate ligands. In particular, reactions of dialkyldichlorosilanes with salen-type ligands [salen stands for *N,N'*-ethylenebis(salicylidenimine)] have been reported [4–9]. These data on the synthesis of low-molecular-weight CTCs give grounds to expect that replacement of mono- with di- and tetrasalicylidene derivatives will allow synthesis of polymeric CTCs. In our case, the polycondensation should involve, firstly, nucleophilic substitution at the silicon atom and, secondly, N→Si donor–acceptor interaction with the formation of a stable six-membered ring, which should significantly stabilize the corresponding segment of the forming polymer chain.

Polymers P1 and P2 were prepared by polycondensation of salicylidene derivatives of tetraamines M1 and M2 with tetrachloro- or tetraethoxysilane in a 1 : 1 molar ratio by the following scheme:

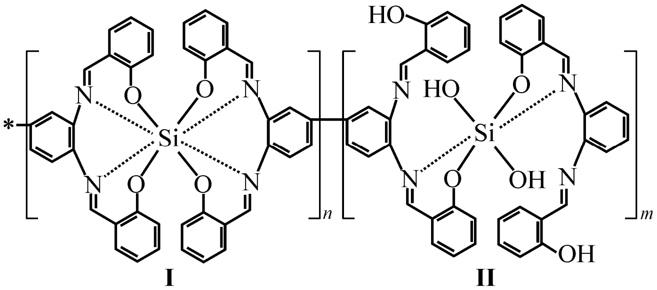


A = –O– (P1), – (P2).

Polymers P3 and P4 were prepared from bis(salicylidenimino) derivatives and dimethyldiethoxysilane, also in a 1 : 1 molar ratio:



The major factor determining the yield and molecular weight of the product is the strict observance of the equimolar ratio of the reactants. It is also important to properly choose the solvent, monomer concentration, and temperature. As solvent we chose DMF, which well dissolves the starting monomers and the forming polymer and can also serve as acceptor for the hydrogen chloride released in the reation. To prepare poly-[tetra(salicylidene azomethines)], it is appropriate to take the starting monomers as dilute (5–10%) solutions, because the probability of formation of disubstituted fragments **II,** along with the desired tetrasalicylidene fragments **I,** increases at high concentrations :



I **II**

Because chlorosilanes are highly reactive, to suppress side reactions (hydrolysis of chlorosilanes, followed by tetracyclization) and raise the probability of more complete substitution at silicon (i.e., to raise the relative content of tetrasalicylidene units **I**), the polycondensation should be performed at low temperature (20–25°C). Another way to suppress the contribution of undesirable processes, such as hydrolysis of chlorosilanes, is their replacement with ethoxysilanes, which are less reactive and less susceptible to hydrolysis. However, in the latter case, the leaving group in the polycondensation is the ethoxy group, and therefore, to ensure its complete removal, the reaction should be performed at 85–90°C.

The main spectral problem in analysis of the polymers obtained is to confirm the structure of the monomeric unit, i.e., to confirm the presence in polymer chians of a six-membered ring formed by N→Si coordination interaction. This interaction results in a shift of the electron density from the donor to the acceptor, which, in turn, should affect the spectral characteristics of the substance.

According to published data, the formation of low-molecular-weight complexes is accompanied by pronounced changes in the IR spectra of both donor and acceptor molecules [10]. The vibration frequencies of the donor are shifted toward higher frequencies, and those of the acceptor, toward lower frequencies. The intensities of the absorption bands also change. In the NMR spectra, the signals of the donor are shifted downfield [11]. In our cases, the strongest changes should be expected for the azomethine group, because this group is directly involved in the coordination bonding. Indeed, the intensity ratio of the stretching vibration bands of the azomethine groups (C=N) and aromatic rings (C_{ar} –C_{ar}) in the IR spectra of the samples examined changes upon complexation. Comparison of the intensities of the bands at 1610 and 1597 cm^{-1} shows that,

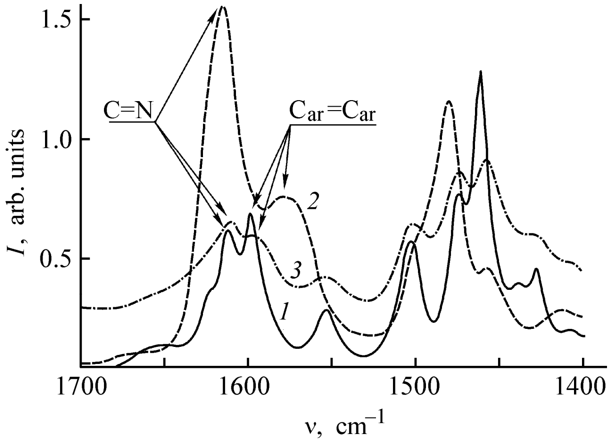


Fig. 1. IR spectra of (*1*) model low-molecular-weight compound, (*2*) M1, and (*3*) P1 (1700–1400 cm^{-1}). (*I*) Intensity and (ν) wavenumber; the same for Fig. 2.

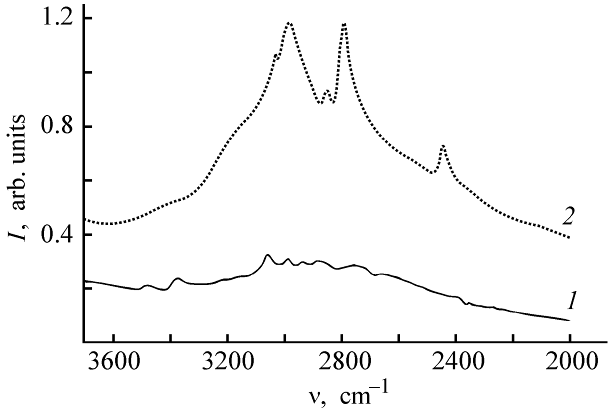


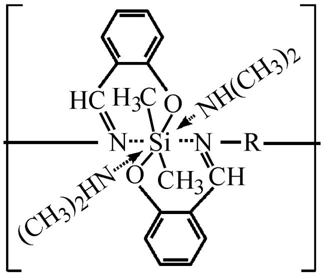
Fig. 2. IR spectra of (*1*) M2 and (*2*) P2 (3600–2000 cm^{-1}).

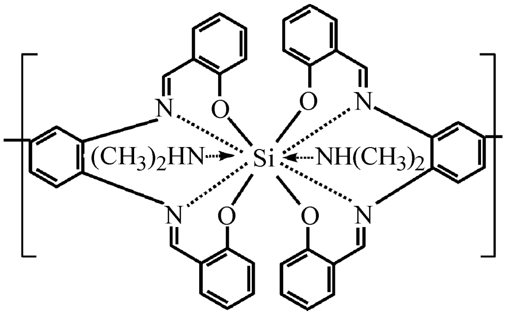
in the spectrum of the monomer, the intensity of the first band (C=N groups) is considerably higher than that of the second band (stretching vibrations of the ring), whereas in the polymer, the intensity of the first band decreases and for the model compound, it becomes even lower than that of the C_{ar}–C_{ar} band (Fig. 1).

These differences may be due to a decrease in the extinction coefficient of azomethine groups as a result of donor–acceptor interactions. Thus, the intensity ratio of these bands can serve as a criterion of the efficiency of N→Si donor–acceptor bonding.

Along with the above features, strong absorption in the range from 2000 to 4000 cm^{-1} engages attention (Fig. 2). According to the previously described polymerization scheme, the amount of OH groups directly is involved in the formation of the polymer chain should decrease in the course of the synthesis. Thus, a decrease in the absorption in the range of stretching vibrations of hydroxy groups whould be expected. However, by contrast, a series of strong bands at 2978, 2780, and 2439 cm^{-1} appear in the spectrum. These bands cannot be assigned to absorption of the polymer and suggest that DMF is involved in side processes accompanying the polymerization. In polycondensation of salicylidene derivatives and chlorosilanes, the release of hydrogen chloride favors decomposition of the solvent. The decomposition products, primarily dimethylamine, are capable of binding with the polymer by donor–acceptor interaction with vacant *d* orbitals of the Si atoms.

In the process, the N atom of the amine competes with the N atoms of azomethine groups, thereby decreasing the effective conjugation length. The forming complex is apparently so stable that the amine cannot be removed by simple reprecipitation. To eliminate the above-described side processes, eses we replaced DMF with a more inert dioxane in further synth.





Figures 3a and 3b show the absorption spectra of the monomers and the synthesized polymers. A considerable bathochromic shift (50–70 nm) accompanied by a hyperchromic effect and the appearance of additional long-wave bands in going from the monomers to the polymer suggest that multiple CTCs are formed in the polymer structure and the conjugation length increases.

The absorption spectra of 1,3-bis(salicylidenimino)-4-phenylazobenzene (M4) and its silicon-containing polymer P4 are markedly different. The strong

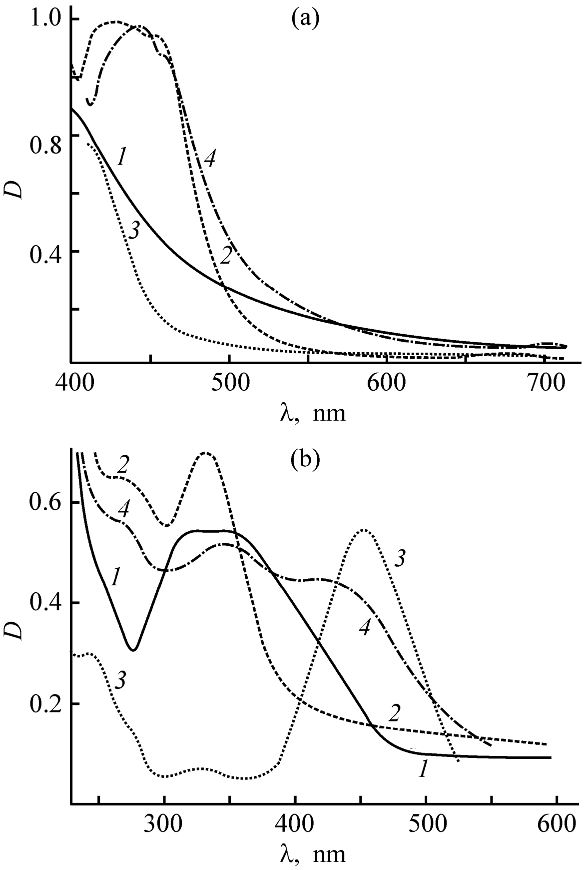


Fig. 3. UV spectra of monomers and polymers derived from (a) tetra- and (b) di(salicylidene azomethines). (*D*) Optical density and (λ) wavelength. (a) (*1*) M2, (*2*) P2, (*3*) M1, and (*4*) P1; (b) (*1*) P3, (*2*) M3, (*3*) M4, and (*4*) P4.

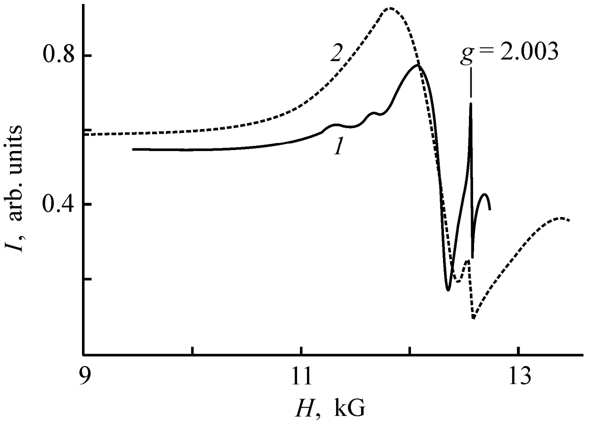


Fig. 4. ESR spectra of polymers (*1*) P1 and (*2*) P3. (*I*) Intensity and (*H*) magnetic field intensity.

absorption band of the azo group present in the spectrum of the monomer ($\lambda = 470$ nm, Fig. 3b, curve *3*) disappears in the spectrum of the polymer (Fig. 3b, curve *4*), suggesting this group is involved either in specific donor–acceptor interaction, or in a polymer-analogous transformation in the reaction with the released hydrogen chloride.

The position of the azomethine proton signal in the ^{1}H NMR spectrum also suggests a strong coordination interaction of the lone electron pair of nitrogen with the *d* orbitals of the Si atom.

Interesting information is furnished by ESR spectra. In the ESR spectra of polysalicylidene derivatives (Fig. 4), there is a narrow singlet with the *g*-factor close to that of the free electron, which suggests conjugation in the polymer chain.

CONCLUSION

In the silicon-containing poly(salicylidene azomethines) prepared, there is intramolecular donor–acceptor interaction resulting in the formation of charge-transfer complexes in the polymer backbone.

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