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Synthesis of Thermotropic Liquid Crystalline Polycarbosiloxanes and Manifestation of Nonclassical Conjugation in Polymer Backbone

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SUMMARY: Polysiloxanearylenes gain mesogenic ability by introduction of methylene joint group between Si-atom and phenylene core of rigid section as it was shown previously. The investigation of model compounds showed the existence of electronic interaction between Si-atom and β-carbon atom of the backbone known in siliconorganic chemistry as β-effect. The effect is considered as an example of nonclassical conjugation. An attempt to synthesize the polymer built from such segments led to obtaining of a nonclassicaly polyconjugated backbone. Preliminary characterization of polydimethylsilylxylilidene obtained as first example of nonclassicaly polyconjugated polymer is presented and mechanism of polyconjugation is proposed.

The basic idea in the synthesis of thermotropic main chain LC polymers is reasonable combination of rigid and flexible elements of the backbone. Second tool is the introduction of the side groups, their size and positions. The intra- and intermolecular forces such as hydrogen bonds, dipole-dipole interactions are also important factors influencing LC ordering.

This investigation is devoted to the problem of molecular engineering in organosilicon and related polymers.

Among the thermotropic main chain alternanting rigid-flexible (RF) polymers many siliconcontaining are known [1]. Introducing of flexible siloxane spacer of different length is widely used to reduce the transition temperatures, to broaden of interval of LC phase existence and to improve the solubility [1].

In a previous research we have synthesized series of RF polymers with dimethylsiloxane spacers of increasing lengths [2, 3]. At certain value of the length the expected transition temperature was determined lower than T_g. In our further study of the synthesis of new siliconorganic potentially mesogenic polymers the dynamics of polymer

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chain was also studied by dielectroscopy methods in parallel with the synthesis of new polymers [4].

Then we turn to more complicated and less studied polycarbosiloxanes. We have prepared polysiloxyarylenes like polymers synthesized by Lenz and Dvornik [5]. The polymers were obtained by polycondensation of corresponding dicarboxylic acid dichlorides and diphenols. The details of the synthesis and characterization data were published [6]. In no case LC polymers were obtained. According to molecular mobility parameters all the polysiloxyarylenes synthesized were flexible. In solid state they were amorphous. A special investigation of basic properties of these polymers in solution was prepared by V.Tsvetkov et al. [7]. The values of Kuhn segment of the polysiloxyarylenes were found a little bit higher than in usual RF alternating LC polymers but not higher than 40-50 A or less. The deviation from linearity of the backbone was deduced from analysis of the structure of the chain. The bending of the chain probably was caused from relatively rigid combination of flexible "spacer" group -Si-O-Si- with aromatic stiff sections.

In search of the LC polymers the most popular approach namely the introduction of flexible spacers into the backbone were used.

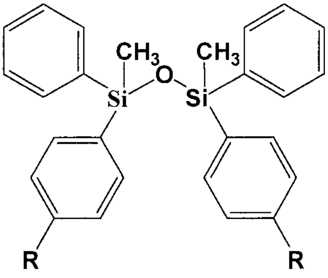
For this aim monomers were synthesized. Aromatic α,ω-diamines having methylene spacers of different length in the middle of rigid section were prepared. Polycondensation with basic dicarboxylic acid led to corresponding polyamides with spacers $(-CH_2-)_n$, n = 2, 3, 4 appear LC according to polarization microscopy, X-ray and DSC data [8].

Then the influence of modification of the structure of the main chain by introduction of methylene joint group between Si-atoms and aromatic sections was examined. Corresponding monomeric dicarboxylic acid and their chloroanhydrides were synthesized. The polycondensation of new monomer with several diphenols was carried out. The polyesters obtained all were crystalline or liquid crystalline. The interval of existence of LC phase was rather broad [3, 9].

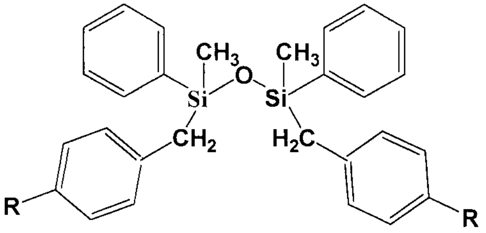
The dielectric study of molecular mobility of new polymers was continued. It was observed appreciable restriction of rotation in $Si-CH_2-Ph$ section in comparison with rotation about Si-Ph bond in corresponding polymers described earlier [6]. This result seems to be opposite to expected increasing of local mobility as consequence of introduction of joint group between Si-atom and rigid cyclic aromatic group as it was usually observed in practice of the synthesis of rigid polymers.

The explanation of the phenomenon observed is to drow from specific electronic structure of Si-atom. For a very long time so named β-effect of silicium is known [10]. This effect demonstrates the ability of Si-atom electronic shall to interact with electronic shall of carbon atom in β-position to Si-atom. The more pronounced effect was observed in reacting systems with positively charged carbon. The mechanisms of corresponding reactions were analyzed in comprehensive reviews [11, 12]. The situation in uncharged system is less studied, but for a long time some spectral data were interpreted as manifestation of β-silicon and carbon atoms interaction [10]. The restriction of rotation in benzylsilanes in comparison with carbon analogs was observed by T.Schaefer at al. [13]. In our case we have to do with geometrical consequences of electronic interaction, e.g. creation of ability to ordering. This steric aspect of the problem was not analyzed before. The corresponding analysis needs deep penetration into the mechanism of electronic effects under consideration. At present in theoretical organic chemistry two main mechanisms are proposed. These are hyperconjugation, or electronic interaction through ordinary bonds and homoconjugation meaning the electronic interaction directly through the space [11]. There are pro and contra by analysis of concrete systems and are many examples of more or less clear confirmation of validity of both mechanisms in different cases. We prefer homoconjugation mechanism and try to give more or less substantiate explanation of the effect in our case. For this aim several model compounds were synthesized and investigated.

The model compounds synthesized represent the section of the backbone where special electronic interaction manifest themselves



I

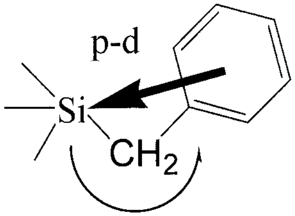


II

R= CH_3 , COOH

At first it is necessary to mention that the diacid II is stronger that I as it show the data of conductivity measurements in hexametapole solution in 1.6 times. This relation support the existence of special electronic interaction in acid II.

The next arguments are UV and Luminescent spectra of p-tolyl derivatives. UV spectra of II show batochromic shift of L_b aromatic band in comparison with I like that observed for trimethylbenzylsilane [13]. There are also additional bands with low intensity in spectra. The luminescence spectra also include these additional bands, which can be interpreted as manifestation of charge transfer in accordance with previous consideration. The interpretation was supported by study of solvatochromic behavior in nonspecific media. The strong batochromic shift (about 35 nm) by transition from I to II indicated the possibility the p-d interaction of silicon atoms with π-system of aromatic nuclei in II directly through the space. At the same time hyperconjugation can show itself.



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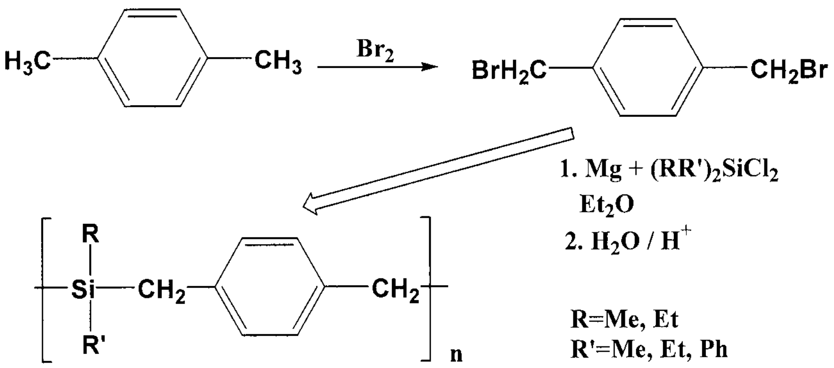
Consideration of the data obtained by investigation of model compounds and polymers lead to the idea to attempt synthetic preparation of polymers the whole backbone of which would be built by homoconjugated sections, e.g. to synthesize a conjugated polymer. This idea was realized in a following manner



The polycondensations were prepared by organomagnesium reaction under special conditions.

From the reaction mixture a solid product was isolated. The product was soluble only in the boiling 4,4'-dichlorobiphenylene. The purification of the product was achieved by repricipitation from dichlorobiphenyl into mixture of o-dichlorobenzene and n-oktanol (10:1). The purity of nonmeltable product obtained was controlled by thinlayer chromatography and elemental analysis.

The structure of the product was analyzed by several spectroscopic methods.

The fluorescence spectra of solid product show a band with maximum intensity at 420 nm. The soluble product (probably oligomers) also has this maximum of absorption. The lifetime of exited state of soluble products was determined and average value 800±100 picoseconds was obtained. The data obtained indicate the individual structure of the chromophore and the transition observed can be classified as singlet-singlet.

The maximum of emittence of the solid product is approximately 100 nm shifted to longer waves than observed in the spectra of luminescence of low molecular model compounds dimethyldibenzilsilane. This is the evidence of existence of continued conjugation and correspondingly of polymeric character of the product.

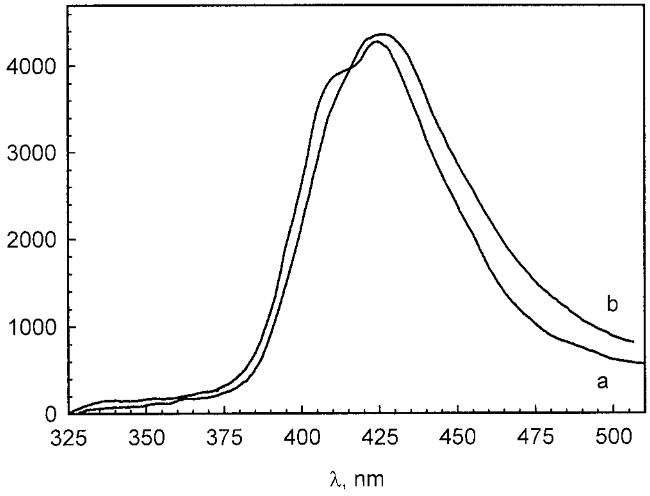


Fig.1. Emission spectra of solid polymers in optically homogenous LiF-glass for R_1R_2=Me(a) and R_1=Me, R_2=Ph(b).

The structure of the polymer obtained was confirmed by ^{13}C-NMR spectroscopy in solid state (see Fig.2). The signals of Si-CH_3 groups are shifted to strong field relatively of TMS indicate the excess of electronic density on Si-atoms and support the conclusion of manifestation of the conjugation along the chain of the polymer.

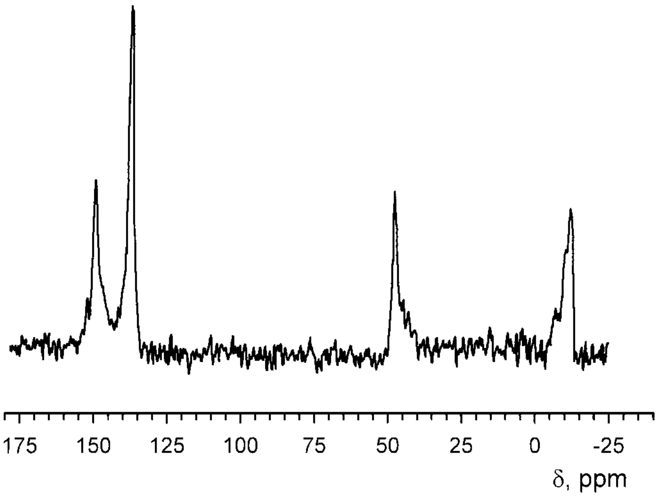
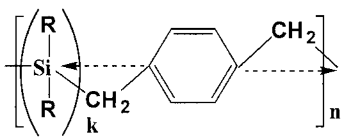


Fig.2. The ^{13}C-NMR spectrum in solid state of polymer with $R_1=R_2=Me$,

To our knowledge this is the first example of the polyconjugated polymer demonstrating nonclassical conjugation.



The results obtained can be generalized for derivatives of Ge, Sn having similar electronic shell as Si.

Note. Authors are aware of convention for using symbols as dotted lines etc. We can only refer to exiting review of R.Hoffman and P.Laczlo. "Representation in Chemistry" published in Angew. Chem., Int. Ed. 30, 1-112 (1991)

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