Activation of Si—C bonds and synthesis of silicon-functional polycarbosilanes

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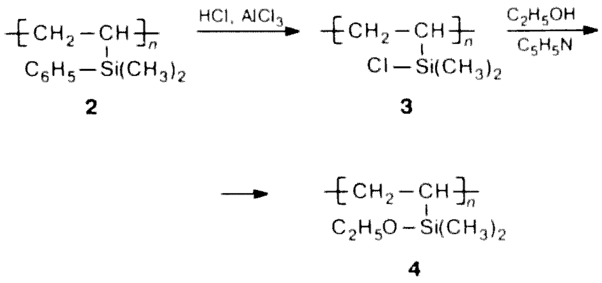
The functionalization of polycarbosilanes was studied using poly(vinyltrimethylsilane) as an example. The possibility of synthesizing of silicon-functional polycarbosilanes by the catalytic activation of Si—C-bonds involving catalytic systems based on compounds of metals of III, VI, and VIII groups was shown. Properties of the obtained polymers are discussed.

Key words: polycarbosilanes, functionalization, catalysts.

The introduction of functional groups to silicon atoms in polycarbosilanes (PCS) makes possible a wide variety of directed chemical modifications of their properties[1] and preparation of new polymer products from them. Various graft copolymers and cyclolinear polymers of a new type combining carbochain and siloxane regions in macromolecular chains can be obtained by polymer-analogous transformations involving functional groups.

It has been established in the study of the polymerization of organovinylsilanes of the general formula $VinRSiX_2$ (**1**, X = Cl, OAlk, NR_2) that the reactivity of vinyl groups in radical polymerization is low.[2,3] Therefore, the contribution of side chain transfer reactions, which limit the growth of macromolecules and distort their structure, is fairly high. The radical polymerization of compounds **1** results in the formation of only low-molecular products (MW = 8000—20000) with irregular structures characterized by the complex structure of the polymer chain.[4–6] The methods of ion polymerization cannot be applied to organovinylsilanes **1** because of possible reactions of the functional groups of the monomer molecules with ionic type initiators. Therefore, poly(vinyltrialkyl(aryl)silanes) without functional groups obtained by the anionic polymerization of the corresponding vinylsilanes are the most accessible high-molecular PCS. As is known, under these conditions, monomer molecules add to the active centers of the growing polymer chain in the "head-to-tail" fashion due to which the macromolecules formed have regular structures. This fact is of special interest for the creation of new methods for the chemical modification of polycarbosilanes by the selective introduction of functional groups and for preparation of macromolecules with a specified distribution of functional group along the polymer chain. One method of thus introducing functional groups into PCS macromolecules through cleavage of Si—C bonds was illustrated using high-molecular poly(dimethyl(phenyl)vinylsilane)[7] (Scheme 1).

Scheme 1



Although this method for preparing chloro- and alkoxyderivatives of PCS is of interest due to the comparatively easy cleavage of Si—Ph bonds, it has substantial restrictions, such as the necessity of using not easily available dimethyl(phenyl)vinylsilane, the multi-stage process of preparation of functionalized PCS, and the difficult control of the microstructure of the polymer chains in the case of copolymers with different contents of Si—Ph groups.

The method for synthesizing of reactive PCS from polyvinyl(trimethylsilane) (PVTMS) produced on the industrial scale is more promising. The purpose of this work is to study the possibility of preparing silicon-functional high-molecular polycarbosilanes based on PVTMS.

The chosen object of the study has a completely regular polymer chain structure, and the side frame contains organosilicon substituents, trialkylsilyl groups. In addition, the initial PVTMS contains Si—C bonds of different types, whose activation can occur at different

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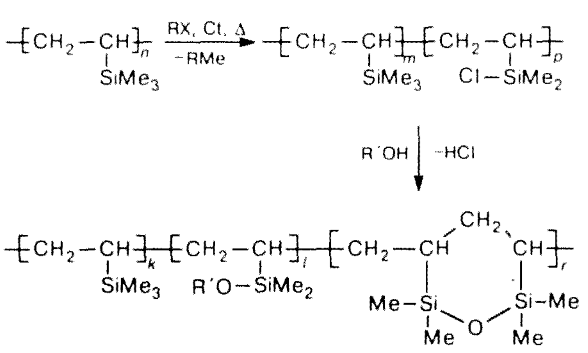
rates. In order to introduce functional groups to the Si atoms, we studied the polymer-analogous transformations occurring due to the activation of the Si—C bonds of PVTMS macromolecules under the effect of compounds of group III, VI, and VIII metals ($MoCl_5$, WCl_6, and H_2PtCl_6) and $AlCl_3$. The methods of metallocomplex activation used in this work have been previously suggested[8,9] for simpler systems in the alkylation of organic compounds involving organosilicon monomers and here they have been applied for the first time to high-molecular objects.

The transformations of PVTMS occurring due to the cleavage of the Si—C bonds under the effect of the studied metal compounds are presented in Scheme 2.

Scheme 2



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X = Cl; Ct = $AlCl_3$, catalytic systems based on Mo, Pt, and W

The reaction was carried out in a 5—15 % solution of PVTMS in an organic solvent (CCl_4, chloroform, toluene) under mild conditions at room temperature or with moderate heating (60—80 °C) for 2 to 10 h. Equimolar ($MoCl_5$, WCl_6) or catalytic ($[Ct] < 1$ wt. % for $AlCl_3$ and H_2PtCl_6) amounts of metal compounds were used in the reaction. It has been established that polycarbosilanes with the main chain framed by silyl substituents having reactive Si—Cl bonds are formed in high yields (60—80 %) under these conditions. In all cases, the products formed retained high solubility with the exception of the system in which the PVTMS : $MoCl_5$ ratio was 1 : 1, where an insoluble polymer was obtained. Reaction products **5** were isolated by reprecipitation into a twofold volume of methanol in the absence of an acceptor for the HCl formed. Further analysis of the obtained copolymers was performed by IR and NMR spectroscopies and elemental analysis.

The IR spectra of the isolated products contain new absorption bands at 1090 and 1025 cm^{-1} characteristic of Si—O—C and Si—O—Si bonds in carbocyclosiloxane fragments. The resemblance of the IR spectra of the obtained products to those of reference compounds confirms the existence of carbosiloxane fragments in the macrochain of polymer **5**.

The ^{29}Si NMR spectra of the isolated polymers contain a signal corresponding to the Si atom in the $-Si(CH_3)_3$ group typical of the initial PCS, and an additional signal at −21.3 ppm similar to the signal of Si atoms in the —SiOSi— group of the reference compound, six-membered 1-oxa-2,6-disilacyclohexane. The signal corresponding to the silicon atom in the SiOC group is not in the ^{29}Si NMR spectra probably due to the low concentration of these units and the necessity to use dilute solutions of the polymer for recording NMR spectra because of its high molecular weight and viscosity.

Thus, the combination of two methods of study, IR and NMR spectroscopies, makes it possible to elucidate in more detail the structure of the final polymer product. The existence of signals of the types considered above in the NMR spectrum of reaction products **5** indicates the absence of the elimination of the $(CH_3)_3Si$ groups from the main chain and a fairly high selectivity of chemical transformations of PVTMS under the studied conditions.

The available data show that the studied metal compounds can be arranged in the order $MoCl_5 = WCl_6 > H_2PtCl_6 > AlCl_3$ by their efficiency in reactions of the polymer-analogous transformation of PVTMS. The structure of the formed functional PCS and the dependence of the extent of substitution of $Si—CH_3$ groups in PCS on experimental conditions should be additionally studied.

Thus, the possibility of using catalytic systems based on compounds of group III, VI, and VIII metals for the selective activation of Si—C bonds and the target synthesis of silicon-functional polycarbosilanes was demonstrated for the first time.

Experimental

^{29}Si NMR spectra were recorded on a Bruker WP-200SY spectrometer (TMS as external standard). IR spectra were obtained on a Specord M82 spectrometer in thin layers on KBr.

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Chemiluminescence in the oxidation of Na_2S by oxygen in water solutions

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Chemiluminescence was observed in the the oxidation of Na_2S by oxygen in aqueous solution. One of the luminescence emitters was identified as the triplet state $(SO_2)^*$ (λ_{max} = 420 nm) generated without participation of free radicals at the first stage of oxidation of Na_2S to $Na_2S_2O_3$. Oxygen is a necessary reagent for CL and isa quenching agent. CL was shown to increase in the presence of $Ru(bpy)_3Cl_2$ as a result of the transfer of energy from $(SO_2)^*$ to form $Ru(bpy)_3^{2+*}$, which emits at λ_{max} = 593 nm.

Key words: chemiluminescence, catalysis.

Weak chemiluminescence (CL) has been observed previously in the oxidation of aqueous solutions of $NaHSO_3$ (in the presence of metal salts)[1] and Na_2SO_3[2] by oxygen. The associate $(O_2)_2^*$ is the emitter in the former reaction (λ_{max} = 480 nm); in the second case the emitter is not identified. CL reactions of O_3 with sulfur-containing organic compounds and O atoms with CH_3SH, CH_3SCH_3, SO are also known,[3] where the triplet state of the $(SO_2)^*$ (λ_{max} = 340 nm) is the emitter.

Chemiluminescence was observed in the oxidation of Na_2S (**1**) by oxygen in aqueous solutions. A freshly prepared solution of **1** in water (10^{-2} mol L^{-1}, V = 20 mL) emits light ($I_{max} = 1.7 \cdot 10^5$ photon/s · mL), the intensity of which decreases 50 % after 3 min. This auto-CL disappears when O_2 is removed by evacuation or by bubbling the solution with N_2. After the introduction of O_2 into the solution of **1** the intensity of chemiluminescence jumps up and then begins to slowly decrease. A more pronounced jump in CL intensity is observed if N_2 has been preliminarily bubbled through the solution (Fig. 1). Thus, O_2 in this system is both the initiator of CL and the "quencher" of the CL emitter.

Products of the oxidation of **1** by oxygen are SO_2, $Na_2S_2O_3$ and Na_2SO_4.[4] We established that CL arises at the first stage of the oxidation that results in $Na_2S_2O_3$ formation. Oxidation of $Na_2S_2O_3$ and Na_2SO_3 by oxygen under similar conditions is not accompanied by CL. In contrast to the CL that occurs during $NaHSO_3$ oxidation, which is attributed to the recombination of free radicals 2 $HO_2^{\cdot} \rightarrow H_2 + (O_2)_2^*$, and is inhibited by the addition of phenol,[1] we did not observe a decrease in CL intensity with the addition of phenol (up to 10^{-4} mol L^{-1}) to the oxidized solution of **1**. This allows us to assume that in Na_2S oxidation CL occurs generates without the participation of free radicals. The CL spectrum that was measured with the help of cut-off filters consists of three maxima (Fig. 2). The solutions of **1** before and after oxidation do not possess noticable photoluminescence PL (300 K). It can be assumed that one of the emitters of CL in Na_2S oxidation is the triplet state $(SO_2)^*$ (λ_{max} = 420±15 nm). The nature of the other maxima of the CL spectrum are not clear yet. According to the data,[5] oxidation of Na_2S can proceed both with and without the formation of elemental sulfur.

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