

Synthesis and Properties of Modified Polycarbonates by Organosilazasiloxanes

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Modification of the polycarbonate based on "bisphenol A" by organosilazasiloxanes has been carried out. Modification obtained via interaction of the silazasiloxy-fragments into the polycarbonate main chain and by addition of small amounts of polyorgano-silazasiloxyarylenes. The composition and structure of the polysilazasiloxanecarbonates have been studied. The properties of modified polycarbonates have been investigated.

Key Words: Polycarbonate, Organocyclosilazane, Oligocarbonate diol, Mechanism.

INTRODUCTION

Polycarbonates (PC) are well-known heterochain polymers. They are used in the medicine, optical and other industrial branches (carbon nanotubes, coatings, capacitor dielectrics, photo- and thermal-stable films for non-linear optics, fire-resistant materials, polyethylene-imine grafted polycarbonates as biodegradable polycations for gene delivery, etc.)¹⁻⁶. In spite of many valuable properties they are difficult to process. In the end products, they show high internal stresses, which limits the areas of their application. These deficiencies can be overcome by using the modified polycarbonates with organic-inorganic main chains⁷⁻¹¹, which combine the good optical and elastic properties with a high thermal stability. One of the representatives of modified polycarbonates was probably, the polysiloxanecarbonates obtained by the reported methods^{7,8}. The literature reported described to obtain the of modified polycarbonates by interaction α,ω -dichlorooligodimethylsiloxanes with the excess of "bisphenol A" in solution in presence of *tert*-amines as HCl acceptor and with consecutive reaction with phosgene⁸. To obtain polysiloxanecarbonates, dihydroxy-oligoarylcarbonates, synthesized by telomerization of cyclic carbonates by diphenols, were also used⁹. As the result of such modification, the copolymers with a high enough molecular mass ($m_n = 3.6 \times 10^4$) were prepared. The copolymers were able to form the optically transparent films^{8,10}.

The modification of polycarbonate based on "bisphenol A" have been carried out: (I) via interaction of the silazasiloxy-fragments into the polycarbonate main chain¹²⁻¹⁴ and (II) by addition of the polycarbonate a small amount of polyorgano-silazasiloxyarylenes¹⁵.

EXPERIMENTAL

Synthesis of polysilazasiloxycarbonates was carried out by combine polymerization-condensation method^{13,16}

Infrared spectra were obtained on the spectrophotometer SPECORD. Thermogravimetric and differential-thermal analysis (TGA and DTA) was performed on a derivatograph (Paulic, Paulic and Erdey) at the speed of the heating $10^\circ\text{C min}^{-1}$. Thermomechanical analysis was performed on the Kargin Scale (Moscow, INEOS RAS) at the speed of the heating 5°C min^{-1} . Wide-angle X-ray diffractograms have been obtained by DRON-2 instrument ("Burevestnik", Petersburg, Russia). $\text{Cu K}\alpha$ was measured without a filter; the motor angular velocity was $\omega \approx 2^\circ\text{deg min}^{-1}$.

RESULTS AND DISCUSSION

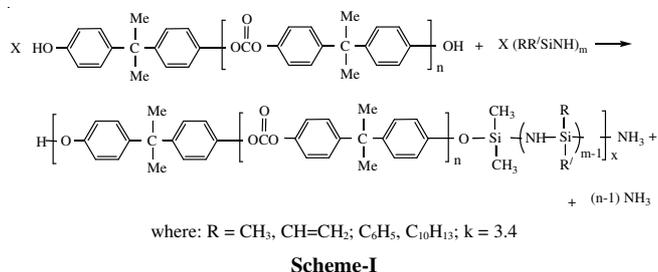
Synthesis and properties of polysilazasiloxycarbonates:

For the chemical modification of polycarbonate chains, we used the combine polymerization polycondensation reaction of diorganocyclosilazanes with oligocarbonate diols (OCD)¹³⁻¹⁷. Cyclosilazane with tricyclodecanyl radical ($\text{C}_{10}\text{H}_{13}$) at the silicon atom (1,3,5-trimethyl-1,3,5-tris(tricyclodeceny)cyclotrisilazane) synthesized by reaction of the ammonolysis of the corresponding dichlorosilane¹⁴.

As the initial monomers for synthesis of polysilazasiloxycarbonates we have chosen organocyclosilazanes in consideration on their high reactivity and the availability¹⁴. The quantitative removal of the side product of the polymerization polycondensation reaction-ammonia also take place without any special additives. We carried out the reaction in mass and in CHCl_3 , which well dissolves oligocarbonate diols. In the both

cases, the equimolar ratio of the initial compounds was used (Table-1).

The oligocarbonate diols based on "bisphenol A" with molecular masses 2.260 ($n = 8$, OCD-8), 3.280 ($n = 12$, OCD-12) and 4.290 ($n = 16$, OCD-16) was used in present studies. General equation of the reaction is given (**Scheme-I**).



Apart from the reaction of organocyclosilazanes with "bisphenol A"¹⁴, the reaction with oligocarbonate diol in the mass proceeds at higher temperatures. The reaction rate (Fig. 1), the physical state and properties of obtained polymers (Table-1) depend, mainly, on the length of the main chain of the oligocarbonate diol and structure of the organic radicals at the silicon atom of the heterocycle. In all cases, the polymers based on organocyclosilazanes, including 1,3,5-trimethyl-1,3,5-tris(tricyclodeceny)cyclotrisilazane are solid products, dissolved in chloroform, have limited solubility in aromatic hydrocarbons and are insoluble in alcohols and in the saturated hydrocarbons. On the metal (steel) and glass surfaces, after the solvent evaporation, optically transparent in the visible area of the spectra films are formed. The maximal transparency was found at $\lambda = 550\text{-}670$ nm.

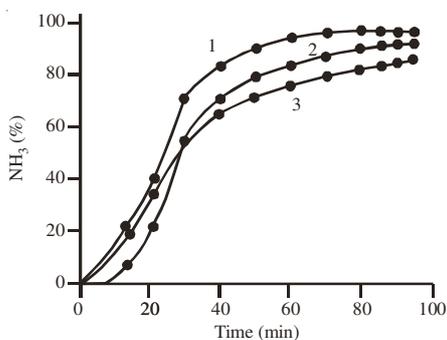
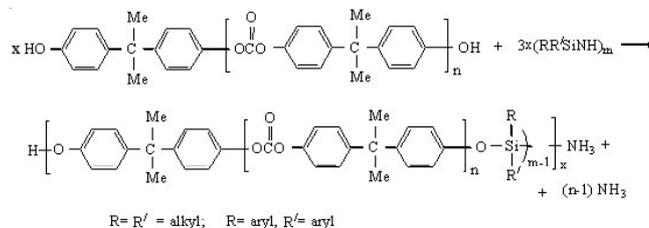


Fig. 1. Curves of ammonia separation in time at interaction of organocyclosilazanes with OCD-8 (in mass): (1) [Me₂SiNH]₃-OCD-8; (2) [MePhSiNH]₃-OCD-8; (3) [Me₂ViNH]₃-OCD-8 (Table-1)

At treble-molar excess of the oligocarbonate diol compared with cyclosilazane, the glass-like brittle products of the siloxyarylenecarbonate structure with a relatively small molecular mass are formed (Table-1). Apparently, as it was noted in our earlier works^{13,18}, there is a quantitative substitution of NH-groups in the polymer chain by the diol fragments in the course of formation of silazasiloxyarylenecarbonate intermediate macromolecular chains according to the general reaction (**Scheme-II**):



The structure of the polymers (Table-1) was determined based on the UV (Fig. 2) and IR-spectra. In the IR spectra, together of absorbency bands related to Si-CH₃ (1420 cm⁻¹) Si-C₆H₅ cm⁻¹ (1440 cm⁻¹), Si-CH=CH₂, CH₃, C₆H₅, CH=CH₂, C₆H₅, CHalk, CHvin, CHar and NH (1270, 1620, 810, 1595, 2970, 3050, 3100, 1580 and 3340 cm⁻¹, correspondingly) the following absorbency bands were also found: at 923-915 cm⁻¹ (for the Si-NH-Si bonds) and at 1000-998 cm⁻¹ (for the Si-O-C_{ar} bonds). It has to be noted that in the spectra of polymers based on OCD-8, obtained in mass at elevated temperatures at equal molar ratio of the initial compounds (Table-1), extremely weak absorbency bands at 957-963 cm⁻¹, related with the tretsilyl groups, were found¹⁶.

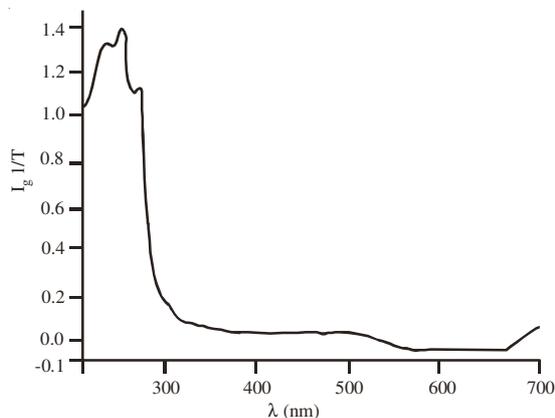


Fig. 2. UV-visible spectrum of the polymer-6 (Table-1)

TABLE-1
POLYCONDENSATION OF ORGANOCYCLOSILAZANES WITH OLIGOCARBONATEDIOLS (OCD)

| No. | Organocyclo-silazan | OCD (m) | Reaction conditions | Reaction temp. (°C) | Reaction time (h) | NH ₃ /cycl (mol/mol) | η _{max} ** (dl/g) |
|-----|-------------------------------------|---------|------------------------|---------------------|-------------------|---------------------------------|----------------------------|
| 1 | [Me ₂ SiNH] ₃ | 8 | In mass | 130-140 | 0.8 | 0.98 | 0.30 |
| 2 | [MeViSiNH] ₃ | 8 | In mass | 140-150 | 1.8 | 0.91 | 0.25 |
| 3 | [MePhSiNH] ₃ | 8 | In mass | 170-180 | 1.6 | 0.88 | 0.45 |
| 4 | [Me ₂ SiNH] ₃ | 12 | In mass | 190-200 | 2.5 | 0.78 | 0.33 |
| 5 | [Me ₂ SiNH] ₃ | 16 | In mass | 220 | 3.0 | 0.71 | 0.22 |
| 6 | [MeTSiNH] ₃ | 8 | In mass | 150-160 | 2.0 | 0.80 | 0.10 |
| 7 | [Me ₂ SiNH] ₃ | 8 | 15 % CHCl ₃ | 60 | 26 | 1.02 | 0.72 |
| 8 | [MePhSiNH] ₃ | 8 | 15 % CHCl ₃ | 60 | 26 | 0.42 | 0.62 |

*Me: methyl, V: vinyl, Ph: phenyl, T: tricyclodeceny; **In CHCl₃, T = 298 K.

Taking into account the kinetic calculation for the model systems (organocyclosilazane: phenol)^{13,14} and also some experimental results (for example, existence of the induction period on the kinetic curves, ability to structure formation of polymer at elevated temperatures, high yield of NH₃) for the mentioned systems, we calculated several variants, describing the possible mechanism of the polymerization condensation of [CH₃(R)SiNH]₃ with oligocarbonate diol and "bisphenol A"¹⁴. The simplest mechanism, including the stage of the heterocycle opening on the Si-N bond and the consecutive heterofunctional polycondensation of the intermediate end ≡Si-NH and HO-X-groups, does not lead to any satisfactory approximation at the extreme task solution. The consecutive incorporation of the elementary stages, indicated below indicated below and the calculation of each of the assumable mechanisms has shown that at the given preciseness of the experiment, the most acceptable from the point of view of minimizing the average deviation (Fig. 3) are the combination of the following stages, including along with the basic stages of formation of the intermediate complex and its decomposition on oligomers with the end groups Si-NH₂ and HO-(k_{1,2})¹⁴: (i) The stage of heterofunctional condensation of the end Si-NH₂ with the HO-groups of the intermediate oligomers (diol) (k₃), (ii) The stage of equilibrium ...-R-OH + NH₃ ↔ -R-ONH₄(k₄); (iii) The stage of the *tert*-silyl group formation (branching) (k₅); (iv) The stage of the transamination (k₆).

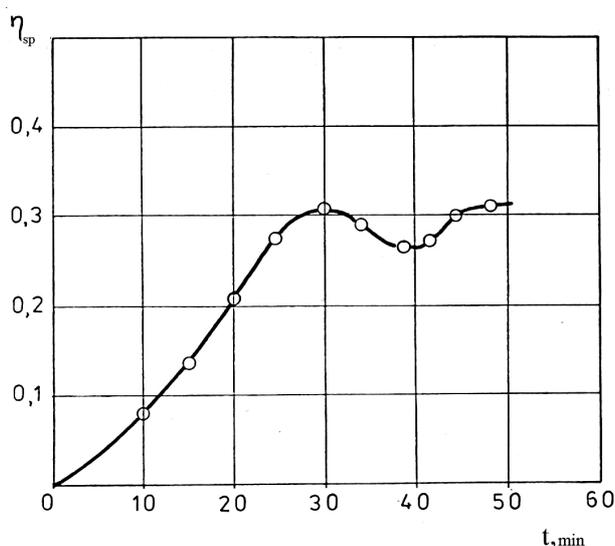


Fig. 3. Change of the characteristic viscosity of the polymerization condensation product in the reaction of [(CH₃)₂SiNH]₃ with OCD-8 in mass at their equimolar ratio, temperature 140 °C

The stages can occur in the conditions of the reaction, in particular, at high temperature, in the mass (Table-1).

The constants of the elementary stages of the polymerization polycondensation were calculated according to the method, described in the works^{14,19}. In the calculations, the amount of separating ammonia was taken in the molar fractions.

The analysis of the rate constant of the elementary stages calculation showed that as in the case of the model system¹³, the lowest rate constant in the both cases -[CH₃(R)SiNH]₃ + "bisphenol A" (1) and [CH₃(R)SiNH]₃ + OCD-8 (2) (R-tricyclodeceny)-is for the stage of the *tert*-silyl group

formation. Besides the rate constant of the stage (k₅) for the system (2) is approximately four times lower compared with the one for the system [(CH₃)₂SiNH]₃ + OCD-8 and it is 1.961 × 10⁻¹ min⁻¹. The structure of the organic radical at silicon atom affects the value of k_{1,2} and k₅ (Table-2)¹⁴.

| Initial compounds | k _{1,2} | k ₅ |
|---|--------------------------|-------------------------|
| [Me ₂ SiNH] ₃ + OCD-8 | 64.01 × 10 ⁻¹ | 6.94 × 10 ⁻¹ |
| [MeTsiNH] ₃ + OCD-8 | 46.83 × 10 ⁻¹ | 1.80 × 10 ⁻¹ |

The character of the viscosity change in time (Fig. 3) and also the careful analysis of the IR-spectra of the products of the polymerization polycondensation of [CH₃(R)SiNH]₃ with oligocarbonate diol in mass, determined in the course of the reaction, confirms the more complicated character of the reaction compared with the reactions of organocyclosilazanes with the relatively simple diols, such as "bisphenol A"¹³.

In the IR spectra of polymers 1 and 6 (Table-1) obtained in the course of the process at 160-180 °C, appears the weak absorbency bands with the maximum at 2285 cm⁻¹ that are characterized for the isocyanate group. These absorbency bands disappear after certain conversion (60-70 % based on the separated ammonia). This fact allows to assume that not all of the NH₂ groups, which appear on the beginning stages of the reaction by the heterocycles opening, enter in the condensation with HO-groups of oligocarbonate diols and the intermediate oligomers. However, some of the NH₂-groups interact with the OC(O)O bond of the oligocarbonate macrochain according to the **Scheme-III**, with the further transformation urethane groups into oligomer with the end isocyanate groups. The isocyanate groups can react again with HO- and H₂N-groups of the products forming in the course of the reaction. This will provide also the system viscosity rise (Fig. 4). However, this is difficult to take into account at the calculation of the polymerization polycondensation mechanism.

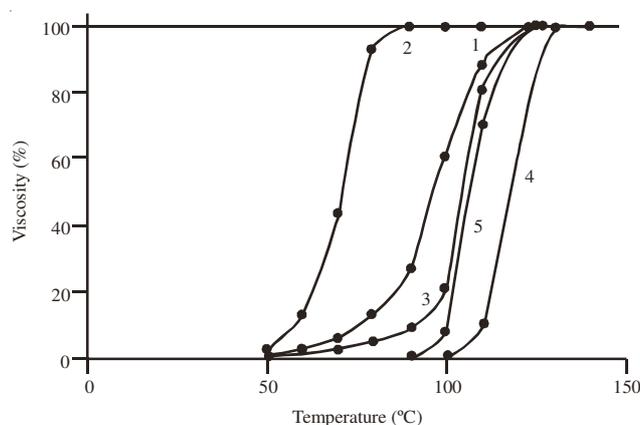
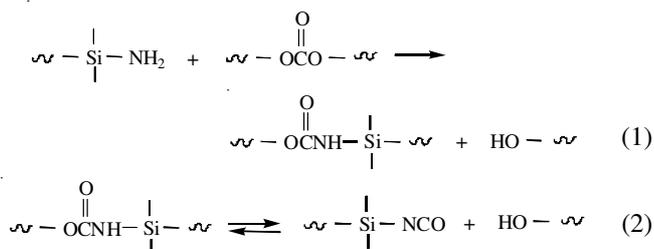


Fig. 4. Thermomechanical curves of the polymers: (1) polymer 1; (2) polymer obtained from [(CH₃)₂SiNH]₃ and OCD-8 (1:1); (3) polymer 6; (4) polymer 5; (5) polymer 3 (Table-1). The heating rate, 4-5 °C/min; loading, 100 g



Scheme-III

The occurrence of the side reactions of the polycarbonate-silazane blocks fragmentation is also confirmed along with the IR-spectroscopy by the relatively low values of (the molecular masses (MM) of the polymers (Table-1, η_{ch} values), obtained in mass at elevated temperatures compared with molecular masses of the polymers obtained in chloroform.

The thermo-mechanical properties and the thermal oxidative stability of the synthesized polymers have been investigated. As it is seen from the thermo-mechanical curves in Fig. 4, their glass transition temperatures are shifted towards the lower temperatures compared with the ones of the non-modified polycarbonate. The T_g depends on the heterocycle structure and the length of the oligocarbonate diol chain. The thermal-oxidative stability of the synthesized polymers was studied by the methods of DTA and TGA (Fig. 4). It is seen from the TGA curves that the modified polycarbonates show high enough thermo-oxidative stability. The basic process of the thermo-oxidative destruction occurs above 400-450 °C and the temperature interval of the destruction shifts towards right on the abscissa with the Si-NH groups content in the macrochains of polycarbonatesilazane increase. The polymer with the siloxyarylenecarbonate structure shows also the high enough thermal-oxidative stability for this class of polymers. Thus, the TGA data show that the mentioned polymer has the mass loss at 320 °C less than 3-4 % (Fig. 5, curve 3).

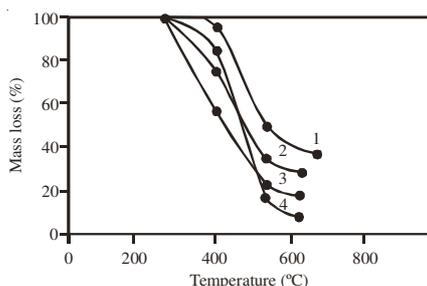


Fig. 5. TGA curves of polymers: (1) polymer 3; (2) polymer 5; (3) polymer obtained from $[\text{CH}_3(\text{T})\text{SiNH}]$ and OCD-8 (1:1); (4) polymer 6 (Table-1). The heating rate, 5 °C/min (air)

The data of the wide angle X-ray analysis confirm the one-phase and amorphous structure of the modified polycarbonates¹³.

The studies are carried out in the direction of the synthesis of polycarbonatesilazasiloxiarylene block-copolymers containing silazane, siloxane and carbonate fragments simultaneously¹⁹. For the obtaining such polymers we used the combine polymerization condensation process organo-cyclosilazanes with oligocarbonatsiloxane diols (OCS D) with polyblock structure of the main chain (Table-3).

| No. | Methylsiloxane linkes' number | Containing of the PC-block in the PCSS main chain (%) | Yield of the PCSS (%) | η_{ch} (dl/g) |
|-----|-------------------------------|---|-----------------------|---------------------------|
| 1 | 2 | 69.0 | 86 | 0.43 |
| 2 | 12 | 57.5 | 76 | 0.62 |
| 3 | 18 | 49.0 | 74 | 1.10 |
| 4 | 30 | 39.0 | 74 | 1.66 |
| 5 | 60 | 24.0 | 70 | 1.50 |
| 6 | 120 | 14.0 | 69 | 1.65 |

The molecular masses of the polymers formed undergo changes to the reverse conversion in terms of ammonia depending upon the length of the siloxane part of oligocarbonatsiloxane diols macromolecule elementary link. This occurring at a high concentration of functional groups, *i.e.*, the amount of released ammonia exceeds its rated value at low m-values in oligocarbonatsiloxane diols. Both these data and the IR analysis data (absorption bands appearing with the maximum of 2285-2280 cm^{-1} which is typical of the NCO-groups) indicate that the reaction of oligocarbonatsiloxane diols and cyclic silazane is ambiguous and the macromolecule structure comprises also isocyanate groups, like in **Schemes I** and **II**. The equilibrium of reaction 2 will shift rightwards if the oligocarbonatsiloxane diols hydroxyl groups react with the silazane link not only in a cycle, but also in a linear chain.

The latter reaction proceeds more readily at a higher hydroxy group concentration, *i.e.*, at a lower m-value in oligocarbonatsiloxane diols and in the presence of an anion-type catalyst which forms as a result of reaction between the hydroxyl groups and the released ammonia¹⁸.

At high m-values, the rate of reaction between hydroxy groups and silazane links an linear chain (reaction 3) is significantly lower, the Si-NCO-group forming reaction equilibrium (reaction 2) is shifted left wars; hence, higher molecular masses of the and polymers are achieved.

The branching and binding mechanism in reacting system can be shown schematically as: Thus, the scheme of PCSS formation seems to be an ideal one, because the resulting block-copolymers, containing not only polycarbonate and silazasiloxane blocks, but also urethane groups in a chain, have branched macromolecular structure. Table-3 shows some data for synthesized polymers in consider of the relation of siloxane and polycarbonate blocks.

The data showed the elemental analysis correspond with the probability formulae of the polymers' elementary ring (**Scheme-IV**).

As it seen from Fig. 6, quantity of evaluated NH_3 depends on the length of siloxane components of oligocarbonatsiloxane diols. When the length of siloxane components is small, quantity of evaluated NH_3 is more than calculated quantity, while when length of siloxane components' chain increases, conversion of NH_3 reduces to 0.8-0.9 mol per each 1 mol of initial cycle.

Molecular mass of resulting polymers changes by inverse relation, during the conversion, according to the dependency on the length of siloxane block of macromolecule's elementary

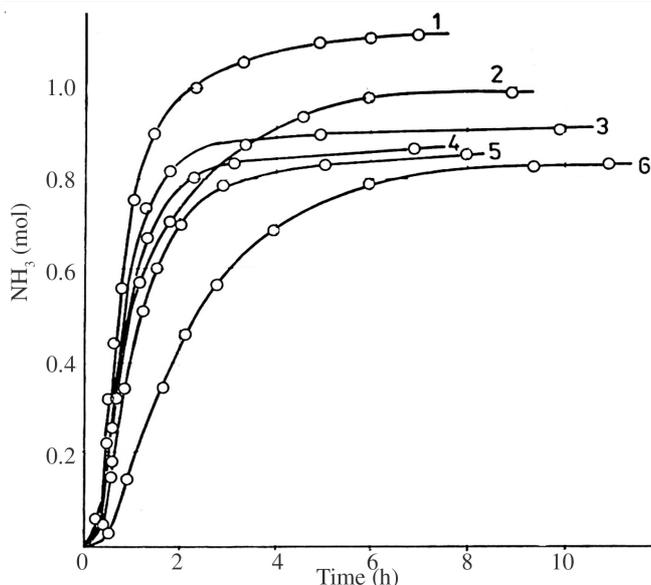
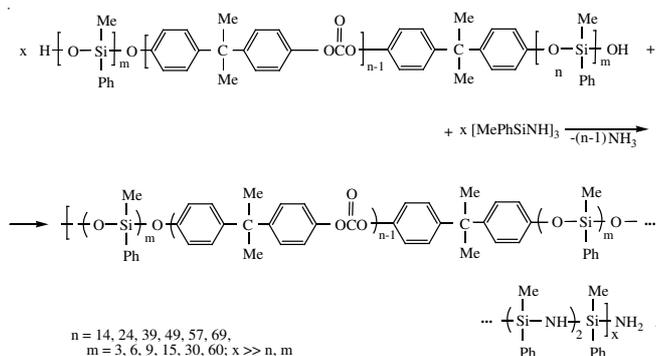


Fig. 6. Kinetical curves of the isolation of the ammonia during the polycondensation of OCSD-s with the TMTPhCTS (in mass, at 180 °C) (Table-3)



Scheme-IV

ring (Fig. 7). It is noteworthy that the fact that at reaction temperatures reactive system reveals certain inclination to the process of structurization (cross-linking). This tendency reveals with high degree in those polymers, in which content of siloxane components is high. Polymer with $m = 60$ transforms into non-fusible insoluble state within 14 h after the beginning of reaction.

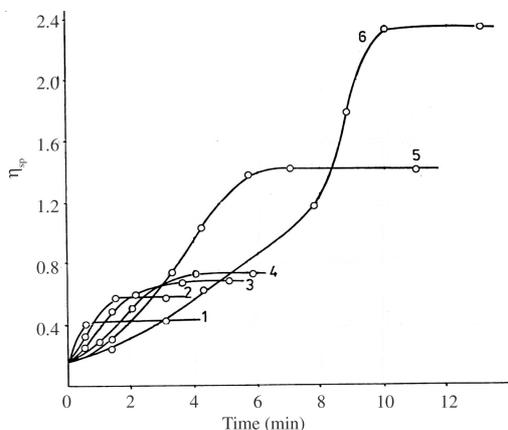
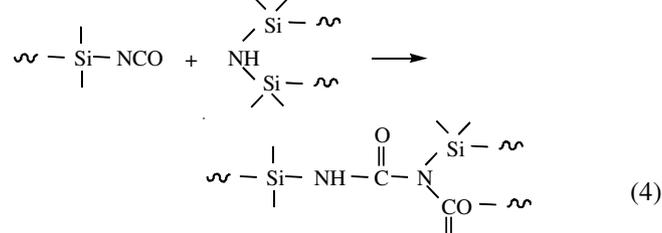
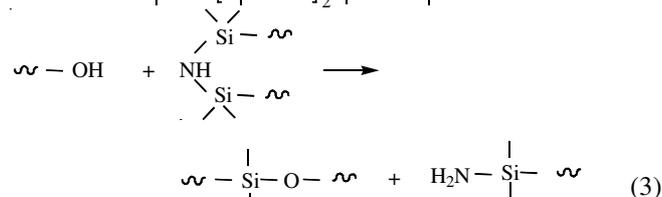
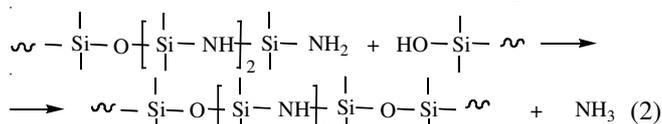
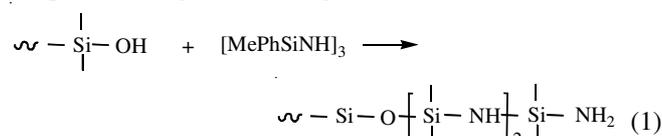


Fig. 7. Change of the values of the specific viscosity of the reaction product during the polycondensation the OCSD with the TMTPhCTS (in mass, at 180 °C) (Table-3)

Reaction of simultaneous polymerization polycondensation of trimethyltriphenylcyclotrisilazane (TMTPhCTS) with oligocarbonatsiloxane diols is carried out in the mass, at 180 °C, until full termination of ammonia evolution¹⁴. In the course of reaction curves of time dependence of evaluated NH₃ and reduced viscosity is shown in the Figs. 6 and 7.

Intensity of absorption band distinctive for OCN-group in the IR spectrum of the polymer, with maximum of 2285 cm⁻¹, reduces rapidly depending on the m magnitude. When $m = 15$, this band is almost invisible in the spectrum. During variation of m from 0-3, intensity of this band reduces twice. In the course of considered reaction the formation of isocyanate group runs by the same way, as it occurs during the polycondensation reaction (3 and 4) of oligocarbonate diol and organocyclosilazane (Scheme-V). In the reaction 4 balances will be displaced to the right in the case when the group interacts not only with the Si-N bond of the silazane cycle, but also with the Si-N bonds of macrochains, formed during the reaction. According to the reaction (5), for small value of m the rate of reaction is high enough and that increases the conversion of NH₃ and content of end OCN-group in the polymer. When value of m increases reaction mixture is more saturated with organosiloxane components. But when rate of reaction (5) decreases, balance in the reaction (4) displaces to the left and as a result we receive final product with big molecular mass and with high content of lateral groups. Quantity of evaluated ammonia (%), in comparison with theoretical is fewer, since the part of nitrogen atoms migrates in the urethane bonds^{14,18}.



Scheme-V

Polymer formed as a result of reaction may become branched and "sewed" at the expense of the reaction of transamination. According to experimental data, the inclination to the structurization process, during increase of siloxane components' length, as well as simultaneous reducing of concentration of NH- and NH₂ groups testifies the low specific part of this reaction. More

suitable is to represent the possible mechanism of branching reaction in the following form:

It is also possible to represent the mechanism of reaction in the form of other such reactions, which are specific and distinctive only for compound containing urethane groups^{13,18}. Rate of reaction (6) and its specific part in the total process is getting bigger, when molar ratio of these groups is close to stoichiometric. Thus, the system is close to this ratio for high magnitudes of m , during increase of concentration of urethane groups.

Some physical-chemical properties of received polycarbonate-siloxanes are studied. Results of electron-microscopic research confirm that received polymers represent two-phase system, with established molar ratio of carbonate-silazane and siloxane components. It was established that against the background of continuous matrices there is chaotic disposition of aggregates, which are close to spherical by their form and that is typical for two-phase polyblock systems¹⁸. The noteworthy fact is that the spherical aggregates have large size (50-60 nm), which significantly exceeds the size which is distinctive for block polymers and doesn't correlate with the contour length of neither carbonate, nor silazane components. Wide-angle X-ray graphical studies also confirm the two-phase construction of received PCSS (with carbonate and siloxane blocks)¹⁸.

For certain ratio of initial components, interpretation of the results obtained by X-ray-graphical methods involves some problems. The point is that the magnitude $2\theta = 2.97 \times 10^{-1}$ rad ($d = 0.5$ nm) corresponds to basic diffraction maximum of amorphous siloxane block, at the same time $2\theta = 3.67 \times 10^{-1}$ rad ($d = 0.42$ nm) corresponds to the second diffraction maximum of polymethylphenylsiloxane. Since all these maximums are wide enough, their partial covering is presumable. Typical diffractogram of PS (57.5 % of PC) is shown on Fig. 8.

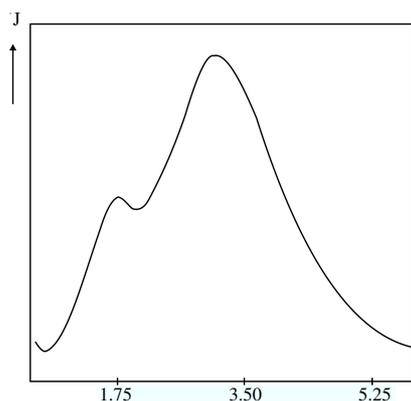


Fig. 8. X-Ray pattern (diffractogram) of the synthesized PCSS with the containing 57.5 % polycarbonate block

Basic diffraction maximum, which is distinctive for siloxane ($2\theta = 1.75 \times 10^{-1}$ rad, $d = 0.8$ nm) and carbonate ($2\theta = 2.97 \times 10^{-1}$ rad, $d = 0.5$ nm) components of amorphous block-copolymer are clearly seen on the diffractogram (Fig. 8). Similar diffractograms will be received for all synthesized PCSS. The values of interplanar distance, which are received on the basis of diffractograms, are given below. It is also determined, that for PCSS, which contains 49 % and more per cent of PC, such

diffraction maximums are characteristic, which are in good correlation with carbonate (0.5 nm) and siloxane (0.83 nm) blocks. Existence of these maximums on the diffractogram allow us to conclude, that PCSS, in which content of PC exceeds 49 %, will have two-phase structure¹⁸.

It is quite difficult to make clear conclusion about phase state of such PCSS, in which the content of PC is less than 49 %, because of the fact, that basic diffraction maximum, which is characteristic for PC, is not seen on the diffractogram. It is possible that it is covered by the second diffraction maximum of polysiloxane component or doesn't exist at all. Displacement of the second diffraction maximum confirms detection of basic maximum of PC, which is revealed for PCSS containing 39 % of polycarbonate fragments.

By further increase of the concentration of polycarbonate-siloxane component location of maximum remains unchangeable ($d = 0.83$ nm) (Table-4). At the same time corresponding diffraction maximum of PC-component is revealed better.

| PC molar ratio (%) | 0 | 14 | 24 | 39 | 49 | 57,5 | 69 | 100 |
|--------------------|------|------|------|------|------|------|------|------|
| d_1 | 0.83 | 0.80 | 0.74 | 0.73 | 0.83 | 0.83 | 0.83 | – |
| d_2 | 0.42 | 0.41 | 0.42 | 0.45 | 0.51 | 0.51 | 0.52 | 0.50 |

It was determined on the basis of considered data that change of PCSS phase state should occur in case of 40-50 % content of PC. It was also determined that for more than 50 % content of PC continuous matrix is constructed from fragments enriched by carbonate components¹⁸.

Dependence of temperature of glazing of synthesized PCSS, which is determined by thermomechanical method, upon the inverse value of molecular mass of siloxane component is given (Fig. 9). As it seen from the Fig. 9, a polymer glass temperature (T_g) raises by increase of PC content in the copolymer. Within 50 % content of PC or in the same range, where qualitative changes of diffractogram character take place, it is revealed the cinked curve of dependence of glazing temperature upon the inverse value of molecular mass, that fact testifies the abrupt changes of polymer's appropriate state.

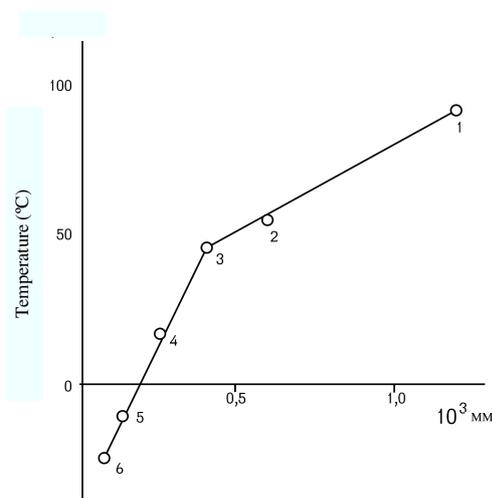


Fig. 9. Dependence of the glass-transition temperature of the synthesized PCSS on the content of the molecular mass of the siloxane block

TABLE-5
 PROPERTIES OF THE MODIFIED POLYCARBONATE BASED ON "BISPHENOL A"

| Composition | Melting index ($I_{\text{melt.}}$) | Change of strength characteristics during of ageing, σ kG/cm ² /ε | | | | ρ , 10 ⁶ (hz) | $T_g \delta$, 10 ⁶ (hz) | E (kV mm) |
|---|--------------------------------------|---|--------------|---------------|---------------|-------------------------------|-------------------------------------|-----------|
| | | Before ageing | After 5 days | After 10 days | After 30 days | | | |
| Polycarbonate (PC) | 1 | 605/80 | 635/70 | 630/50 | 535/30 | 3.1×10^{16} | 0.0080 | 23.5 |
| PC + 5 % fluoroplast | 2 | 567/91 | 580/85 | 555/71 | 515/50 | 4.5×10^{16} | 0.0092 | 21.2 |
| PC + 1 % [Me ₂ SiOMe ₂ SiNHMe ₂ OSiMe ₂ ORO] _n | 8 | 631/93 | 646/93 | 640/95 | 630/80 | 4.4×10^{16} | 0.0076 | 24.0 |
| PC + 1 % [MeEtSiNHMeEtSiOR'O] _n | 3 | 620/100 | 602/95 | 612/86 | 560/81 | – | – | – |
| PC + 1 % [Me ₂ SiOMe ₂ SiORO] _n | 8 | 628/99 | 639/88 | 636/62 | 626/60 | 2.2×10^{16} | 0.0078 | 23.0 |
| PC + 1 % [Me ₂ SiOMe ₂ SiOR'O] _n | 2 | 600/102 | 610/88 | 606/80 | 602/78 | 2.4×10^{16} | 0.0072 | 23.3 |
| PC + 1 % [Me ₂ SiO] ₄₈ R'O] _n | 4 | 560/72 | 603/70 | 602/66 | 560/52 | 4.1×10^{16} | 0.0095 | 22.5 |
| PC + 1 % [MeButSiNHMeButSiOR'O] _n | 3 | 665/93 | 650/90 | 648/80 | 632/80 | 2.3×10^{16} | 0.0090 | 21.0 |

Modification of polycarbonate by polyorganosilazasiloxiarylenes: Polycarbonates (macrolon, diphlon and others) are characterized by remarkable physical and chemical properties and are widely used for preparation of constructional materials and various elements. Treatment of polycarbonates by high efficiency method is complicated by necessity of high viscosity of their melts, as well as by necessity of maintenance of high temperatures during its treatment in the narrow temperature range.

In the products, manufactured from polycarbonates, it is indicated a high level of residual internal stresses, as a rule, which is caused by chain rigidity and low rate of relaxation processes. This fact causes cracking of products manufactured from polycarbonate in the treatment process and because of it their use is limited.

Well known polycarbonatesiloxane elastomers represent polycarbonates copolymers with polyorganosiloxanes¹⁸. Main defect of such elastomers is their low heat stability and very low mechanical solidity, in comparison with common polycarbonates.

Polymeric composition manufactured on the basis of polycarbonates contains aromatic polycarbonates and polyorganosiloxanes with various viscosities-polydimethyl-siloxane and polymethylphenylsiloxane. Polycarbonate dissolved in methylene chloride is added to liquid organosiloxanes. Films (webs) are taken from the formed solution. Compositions received by this method are characterized by low liquidity, while during their exploitation at high temperatures their mechanical solidity reduces. For the purposes of increase of above-mentioned compositions liquidity and their mechanical solidity polyorganosilazasiloxiarylenes are used as modifiers instead of polyorganosiloxanes^{12,14}. Polyorganosilazasiloxiarylenes (0.1-3.0 mm) used for the same purposes are capable to penetrate not-reversibly into disordered areas of polycarbonates supramolecular structure, don't initiate their swelling or opening and increase shear capacity of structural units. This fact provides acceleration of relaxation processes and lowers the level of residual stress in the product^{14,15}.

It is established, that the insertion of alloying additions doesn't require any special accommodating, doesn't complicate technology of polycarbonates receiving and allows to improve polymers treatment capacity, reduces treatment temperature by 30-60 °C. Polycarbonates (PC), obtained on the basis of diphenylolpropane and phosgene (which are manufactured with molecular mass from 25000-45000) are used.

As it seen from Table-3, insertion of certain amount of polyorganosilazasiloxiarylenes as alloying additions in polycarbonate increases its liquidity from 2 to 7 times, at the same time, limit value of solidity during tension and given limit value of extension coefficient during bruise are maintained for a long period of time, in the ageing process at 120 °C, while non-modified polycarbonates have no such capacity¹⁴.

It is established by the studies that index of polycarbonates melting ($I_{\text{melt.}}$) raises with increase of alloying addition content in the composition, at the same time its solidity characteristics worsen. Polycarbonate modification with above-mentioned alloying additions allows manufacturing such polymeric compositions, good technological properties of which are combined with increased indices of solidity. A composition prepared by this method has the wide use for producing of reinforcing constructions, electric and radio-technical details. Manufacturing of above-mentioned details from pure polycarbonate is complicated because of high viscosity of its melts and, respectively, because of low liquidity, that fact necessitates increase of melt's temperature. In this case, as a rule, cracking of products manufactured from polycarbonates, as well as polymers destruction and high level of residual stress are mentioned. Polycarbonates treatment capacity improves, its liquidity increases and treatment temperature lowers by 40-60 °C by insertion of silazasiloxiarylene alloying additions and that makes the application of these technology.

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