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# Polyorgano-polysiloxane Block Copolymers

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The literature data on the principal methods for the synthesis of polyorgano-polysiloxane block copolymers incorporating carbochain and heterochain organic fragments are examined and surveyed. It is shown that the microphase separation, associated with the differences between the chemical natures of the blocks, exerts a decisive influence on the morphological, physicochemical, and mechanical properties of such block copolymers. The wide scope of the applications of polyorgano-polysiloxane copolymers is demonstrated.
The bibliography includes 229 references.

CONTENTS

I. Introduction 1079
II. Methods of synthesis of polyorgano-polysiloxane block copolymers 1079
III. Structural characteristics and physicochemical properties 1084
IV. Applications 1090

## I. INTRODUCTION

One of the problems in polymer chemistry of current interest involves the development of methods of synthesis and the study of the properties of a relatively new class of polymeric materials—block copolymers. Linear copolymers having the structure $(AB)_n$, in which the contributions by blocks of different nature create a set of specific properties, are of considerable interest in this connection. On the other hand, the introduction as one of the blocks into such copolymers of a polyorganosiloxane, which is characterised by a low glass point, good chemical, hydrolytic, radiation, and thermal stabilities, a high permeability to gases, a weak temperature dependence of its physicochemical properties, a low surface tension, a pronounced hydrophobic character, and a high frost resistance, makes it possible to obtain materials with properties of practical value.

The thermodynamic incompatibility of the organic and organosilicon blocks leads to the appearance in such systems of microphase separation, which makes it possible to regard them as pseudo-filled systems. The physical network arising under these conditions increases the deformation-strength characteristics and influences the physicochemical properties of block copolymers. The above features of polyorgano-polysiloxanes permit the segregation of these block copolymers as a separate group of polymers.

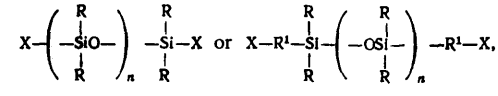
Polyorgano-polysiloxane block copolymers are of special interest for biology and medicine. The stability of these materials in biologically active media is high, they are readily sterilised, exhibit high haemo- and tissue compostibility, are resistant to ageing and the action of microorganisms, are optically transparent, and are permeable to vapours and gases. Such block copolymers can be used as implants of different rigidity, which can be achieved by regulating the composition of the copolymer.

In the reviews devoted to block copolymers published hitherto,[1-5] siloxane-containing copolymers incorporating carbochain and heterochain organic fragments have been examined. However, these publications deal with only certain individual examples of the synthesis and investigation of the properties of linear polyorgano-polysiloxane systems. We thought it timely to survey in the present review the available literature data on siloxane-containing block copolymers.

## II. METHODS OF SYNTHESIS OF POLYORGANO-POLYSILOXANE BLOCK COPOLYMERS

Two main methods of synthesis of block copolymers containing siloxane fragments have now been proposed.

1. Polycondensation of organic oligomers, synthesised beforehand, with silicon-containing oligomers having the structure



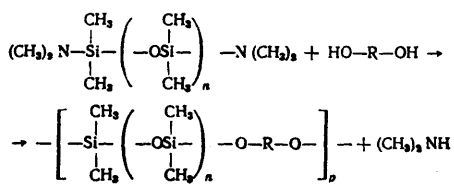
where R,R′ is a carbon containing group and X is a functional group (hydroxy-, halogeno-, amino-, aminoalkyl, carboxy-, etc.).

2. Methods based on the use of cyclic organosiloxanes.

The principal methods of synthesis of linear oligomers and cyclic organosiloxanes have been examined in detail in monographs.[6-8] Depending on the nature of the initial components, block copolymers containing Si–C, Si–O–Si, Si–O–C, and Si–N interblock linkages have been described.

### Polycondensation with Participation of αω-Bis(dialkylamino)-oligosiloxanes

The commonest method of synthesis of polyorgano-polysiloxane block copolymers involves the interaction of αω-bis-(dimethylamino)oligodimethylsiloxanes with organic oligomers in organic solvents in accordance with the mechanism



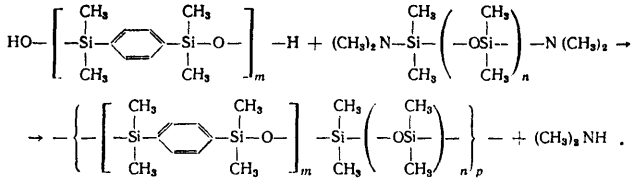
The structure of the organic blocks in the copolymers obtained and the reaction conditions are indicated in Table 1.[9-26] The polycondensation results in the formation

of regularly alternating block copolymers in which the molecular weight of the blocks is equivalent to the average molecular weight of the oligomers.

The dimethylamine evolved is readily removed and the reaction is therefore simple and effective and can be used to synthesise copolymer blocks of different lengths. However, the dimethylamine evolved can induce side reactions in the synthesis of copolymers containing ester linkages. It has been noted[11,25,27] that, when oligomers with a sufficiently high molecular weight are used, it is not possible to ensure reliably the equimolar reactant ratio, which leads to the formation of block copolymers with low molecular weights and a broad molecular weight distribution. In order to obtain block copolymers with a high molecular weight, it has been suggested that one of the components be gradually injected into the reaction zone; the character of the end groups and blocks of the copolymer then depends on the specific stoichiometry of the reaction. In order to avoid hydrolysis and homocondensation of alkylaminosiloxanes, the solvents must be carefully dried. The process temperature varies from 25° to 108 °C depending on the nature of the organic oligomer and the solvent employed.

When oligomers with aliphatic OH groups are used, the above reaction is much slower than with aromatic OH groups, as has been demonstrated in relation to dihydroxymethylstyrenes.[25,26]

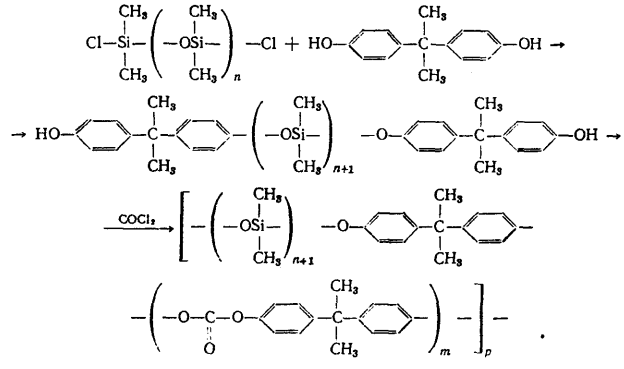
Dimethylaminosiloxanes have successfully used recently for the synthesis of polyblock polytetramethyl-*p*-silphenylene-siloxane-polysiloxane copolymers with a regular alternation of blocks:[28]



In the above example both oligomers contain silicon. However, it is useful to consider such systems in the present review because the principal features of polyorgano-polysiloxanes mentioned above can in fact be observed in them also.

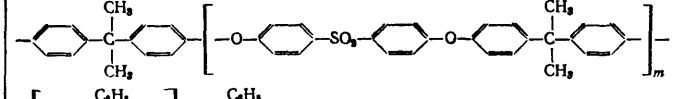
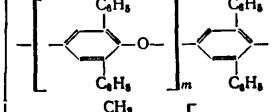
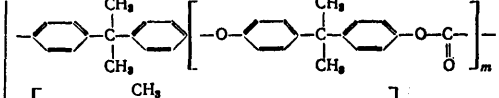
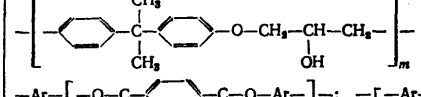
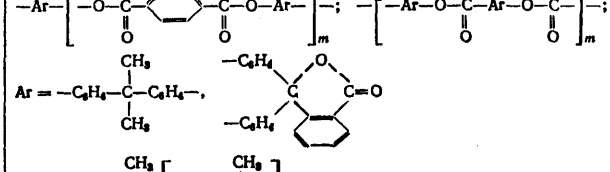
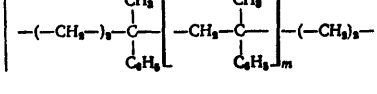
## Polycondensation with Participation of αω-Dichloro-oligosiloxanes

Oligodimethylsiloxanes with terminal chlorine atoms are used mainly to synthesise polycarbonate-polysiloxane block copolymers. It has been noted[29–31] that the reaction of αω-dichloro-oligosiloxane with an excess of a bisphenol in solution in chlorinated hydrocarbons in the presence of a hydrogen chloride acceptor results in the formation of a αω-dihydroxy-derivative, which is treated with phosgene in the presence of an excess of the bisphenol until the attainment of the maximum viscosity of the reaction mixture:

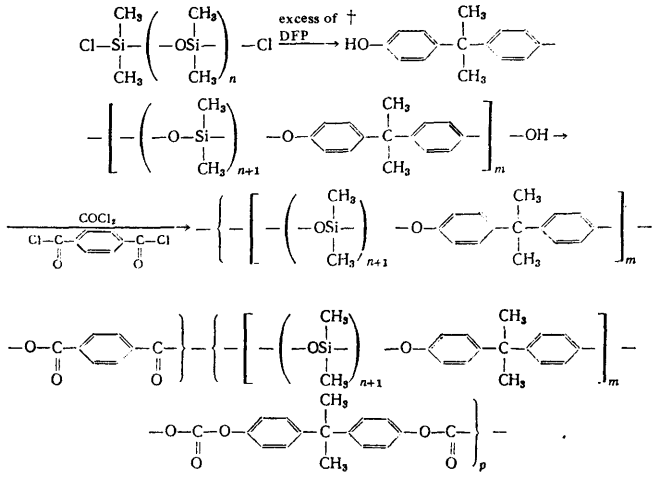


The resulting copolymer consists of statistically alternating polydisperse blocks and has a low molecular weight.

**Table 1.** The structure of the organic block and the conditions in the synthesis of polyorgano-polysiloxane block copolymers.

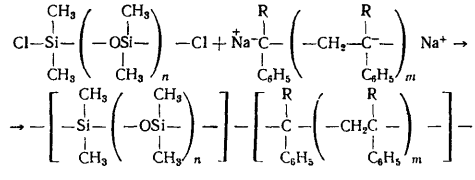
| Organic block | Structure | *T*°, C | Solvent | Refs. |
|---|---|---|---|---|
| Polysulphone |  | 25–120 | Chlorobenzene, THF | [9–14] |
| Poly(phenylene oxide) |  | 130 | Chlorobenzene | [15–17] |
| Polycarbonate |  | | Chlorobenzene | [18–20] |
| Polyhydroxyester |  | 40–130 | Methylene chloride, THF, chlorobenzene | [21] |
| Polyarylate |  | 120–180 | Trichlorobenzene | [22–24] |
| Poly-α-methylstyrene |  | 120–180 | Chlorobenzene, *o*-dichlorobenzene | [25–26] |

The synthesis of a polyester-polysiloxane containing fragments of organic acids together with polycarbonate units has been described in a patent: [32]



In order to obtain block copolymers with a regular structure, it has been suggested that αω-dichloro-oligodimethylsiloxanes be condensed with oligomeric dihydroxycarbonates in solution in chlorobenzene in the presence of a tertiary amine (pyridine, triethylamine). [33–36] The molecular weights of the copolymer synthesised are $10^5$.

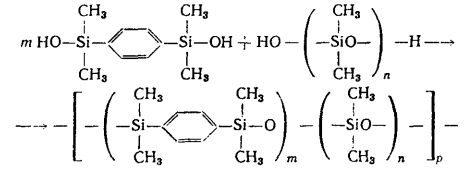
It has been shown[37,38] that the interaction of oligodimethylsiloxanes having terminal chlorine atoms with the disodio-derivatives of styrene, α-alkylstyrene, or α-phenylstyrene in solution in tetrahydrofuran (THF) at room temperature can yield linear block copolymers:



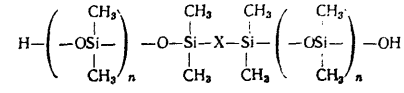
## Polycondensation with Participation of αω-Dihydroxy-oligosiloxanes

The high mobility of the hydrogen atom in the hydroxy-group in dihydroxyoligosiloxanes makes it possible to use them for the synthesis of a whole series of block copolymers: polysilarylene-polysiloxanes, polyurethane-polysiloxanes, polyamidepolysiloxanes, and polyimide-polysiloxanes.

The synthesis of polysilarylene-polysiloxane block copolymers proceeds in accordance with the scheme

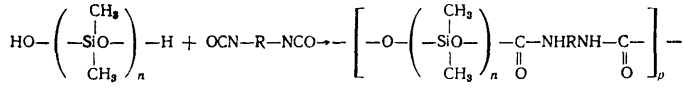


The reaction is carried out in solution in aromatic hydrocarbons at elevated temperatures in the presence of catalysts which do not cause a redistribution of units between siloxane blocks of different type, for example, tetramethylguanidine-bis-2-ethylhexanoate, *N*-hexylamine-2-ethylhexanoate, or a salt of formic acid and t-butylamine. [39–41] Since both initial components have the same functional groups, the condensation is statistical and the resulting high-molecular-weight copolymer contains blocks whose average length depends both on the ratio of the initial substances and on the molecular weight of the oligodimethylsiloxanes. Similar block copolymers with a more ordered structure have been obtained[42] by the reaction of diols having the formula



[$n$ = 0–1; X = 1,3 or 1,4-phenylene or the Y–Z–Y fragment, where Y = 1,3- or 1,4-phenylene and Z = O or OC(O)O] with phosgene in solution in pyridine.

Polyurethane-polysiloxanes can be obtained by polyaddition:



The reaction is carried out in two stages: in the first stage, the hydroxylated oligodimethylsiloxane reacts with the organic diisocyanate, while in the second stage a "chain lengthening agent"—an organic diol or diamine—is introduced into the reaction mixture. [43,44]

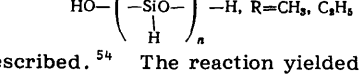
Prepolymers with terminal NCO groups, based on di- and poly-isocyanates and organic diols, can also be used as the organic component. [43,45,46]

It has been shown that the reactivity of oligosiloxane-glycols in urethane formation reactions is higher than that of aliphatic glycols, [47] which made it possible to synthesise successfully polyurethane-siloxane block copolymers containing alkylene bridges between the organic and organosilicon blocks. [48] Diamines, [49] organic oligodiols and oligodithiols, [50] as well as 1,3-bis(4-hydroxybutyl)tetramethyldisiloxane[51] have been used as the "chain lengthening agents".

Polyester-siloxane-urethanes with polyester and polydimethylsiloxane blocks alternating statistically in the chain have been obtained; [52] the synthesis was carried out in one stage by introducing the intermonomer [di(4-isocyanatophenyl)methane or 2,2′-di-(*p*-isocyanatophenyl)hexafluoropropane] into a mixture of oligodiols [poly(ethylene glycol) or poly(ethylene glycol adipate) and αω-bis(β-hydroxyethoxymethyl)oligosiloxane] at elevated temperatures in solution in chlorobenzene in the presence of tin dibutyl-laurate as the catalyst.

Polyblock polyamide-polysiloxanes have been obtained by the reaction of dihydroxyoligodimethylsiloxane with an excess of terephthalic acid chloride and subsequent condensation of the resulting polyester with hexamethylenediamine; [53] however, it was not possible to achieve a high molecular weight of the polymer, whose intrinsic viscosity did not exceed 0.3 dl $g^{-1}$.

A method for the modification of polycaprolactam in the synthesis of polyamide by polyorganosiloxane compounds having the structure



has been described. [54] The reaction yielded block copolymers containing siloxane linkages in the carbamide groups; an increase of the content of the organosilicon component in the

†Excess of DFP (in Russian; Ref.32 states $Me_3N$ in $CH_2Cl_2$) (Ed. of Translation).

reaction mixture above 2 wt.% inhibits the polarisation of caprolactam and impairs the physicomechanical characteristics of the block copolymer.

Treatment of a mixture of αω-bis(3-propoxy)oligodimethylsiloxane, di(hydroxyphenyl)propane, and terephthalic acid chloride in solution with phosgene afforded high yields of block copolymers with a high molecular weight.[32] The attempts to use oligosiloxanes with terminal hydroxypropyl and hydroxybutyl groups to synthesise polycarbonate-polysiloxanes by direct treatment with phosgene of a mixture of the oligosiloxane and di(hydroxyphenyl)propane under the conditions of interfacial condensation led to the formation of block copolymers with a statistical alternation of blocks and the degree of conversion of the oligodimethylsiloxane was low. Investigations[20,55] led to the discovery of the need for the preliminary treatment of the organosilicon oligomer with phosgene in order to obtain block copolymers having a high molecular weight and a high content of the organosilicon blocks. It is therefore useful to use the bischloroformates of oligomeric organosilicon diols in order to obtain polyorganopolysiloxanes by heterophase polycondensation.

### Polycondensation with Participation of αω-Bis(chloroformato-organo)oligosiloxanes

The heterophase method of synthesis of block copolymers based on αω-bis(chloroformatoethoxymethyl)oligodimethylsiloxanes makes it possible to obtain high yields of regularly alternating polycarbonate-polysiloxanes[56] and polycarbonate-urethane-polysiloxanes with a unimodal molecular weight distribution (Fig.1) in accordance with the scheme[57,58]

### Polycondensation with Participation of αω-Diamino-oligosiloxanes

These oligomers react readily at room temperature in solution or under the conditions of interfacial polycondensation with aliphatic and aromatic acid dichlorides[64] to produce high yields of high-molecular-weight soluble polyamide-polysiloxanes.

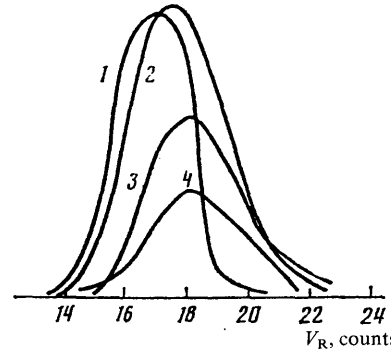
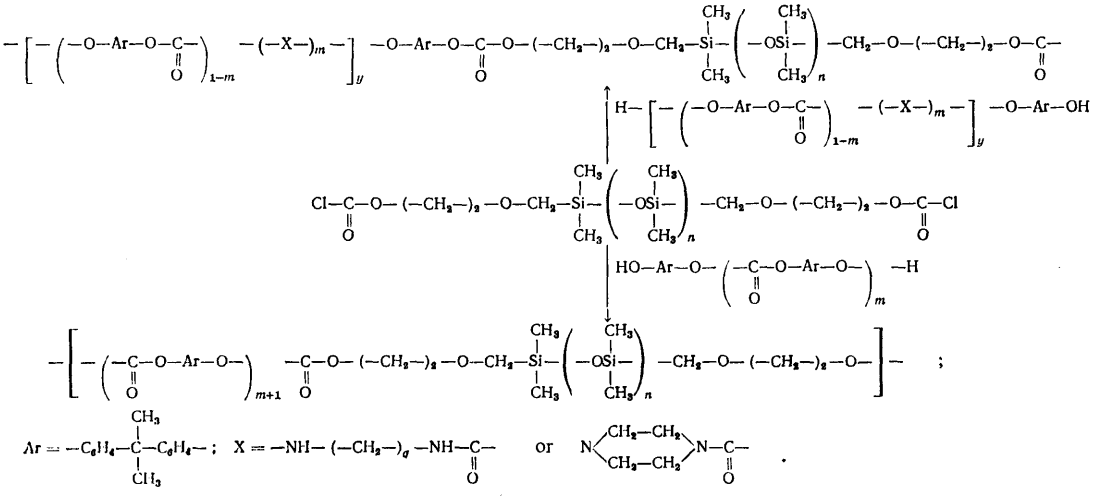


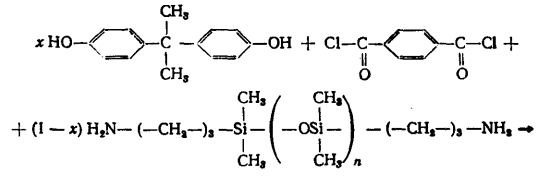

**Figure 1.** Chromatograms of polycarbonate-urethane-polysiloxanes with different compositions $N_{Si}:N_{CU}$: 1) 45:6; 2) 45:10; 3) 45:3; 4) 45:2; $N_{Si}$ = number of siloxane units, $N_{CU}$ = number of carbonate-urethane units, and $V_R$ = volume of eluent (one count = 2.5 ml).[58]

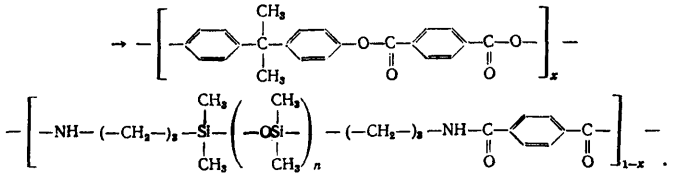


The bischloroformatosiloxanes presented in the scheme were used to obtain polyurethane-siloxanes in a heterophase system[59] and also copolymeric siloxane-carbonates[60] and siloxane-urethanes[61,62] with a statistical distribution of organic and organosilicon blocks.

Polyarylate-polysiloxanes have been synthesised by interfacial polycondensation to form αω-bis(chloroformato-organo)-oligosiloxanes and oligoarylate diols from phenolphthalein and di(hydroxyphenyl)propane.[63]

Polyamide-polysiloxanes containing polyarylate fragments have been obtained by the reaction[65]



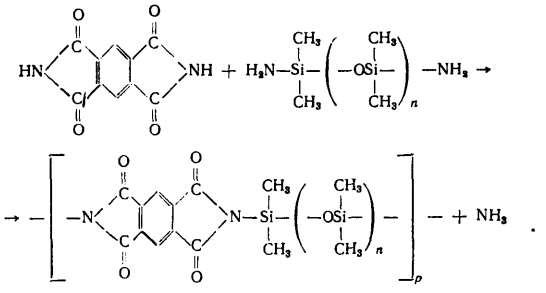


The yield of the target product is 80–90% and the intrinsic viscosity is 0.89 dl $g^{-1}$.

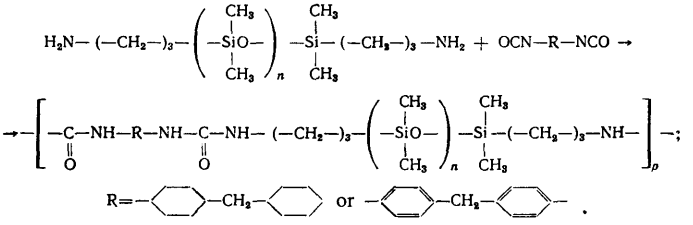
The reaction of oligodimethylsiloxane having terminal $NH_2$ groups with *N*-carboxyanhydrides of aminoacids of the type of DL-phenylaniline or γ-benzyl-L-glutamine in solution in chloroform at 200 °C leads to the formation of block copolymers of polysiloxane with polypeptides.[66]

Soluble polyimide-polysiloxanes have been synthesised by heating a prepolymer based on an excess of an aromatic dianhydride and an aromatic diamine[67] or the dianhydride of benzophenonetetracarboxylic acid[68] with aminoalkyl-containing oligodimethylsiloxanes.

The synthesis of polyimide-polysiloxanes whose nitrogen atoms are linked directly to silicon atoms has been described in a patent:[69]

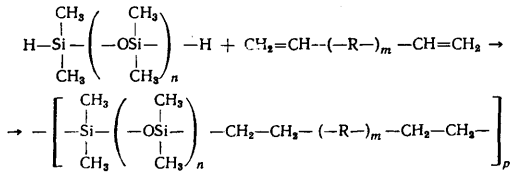


αω-Bis(aminopropyl)oligodimethylsiloxanes interact with an organic diisocyanate in 2-ethoxyethyl ether or THF with formation of polysiloxane-urea:[70]



## Polycondensation with Participation of Oligosiloxanes having Terminal Silicon Hydride Groups

Copolymers with regularly alternating blocks have been obtained from oligodimethylsiloxanes having H–Si groups by the hydrosilylation reaction:



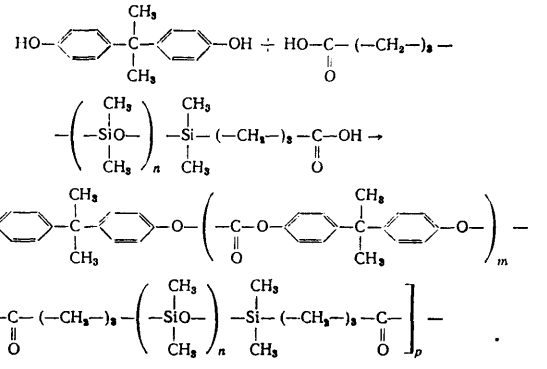
The polysulphone-polysiloxane,[71] polystyrene-polysiloxane and poly-α-methylstyrene-polysiloxane,[72,73] and polyurethane-polysiloxane[74,75] block copolymers have been synthesised by this method.

Despite the fact that the condensation conditions rule out side reactions and make it possible to obtain block copolymers with a high molecular weight, the reaction has not as yet found extensive application owing to the complexity and the multistage nature of the synthesis of the initial vinyl-containing organic oligomers and the need to employ expensive catalysts.

## Polycondensation with Participation of Other Oligosiloxanes

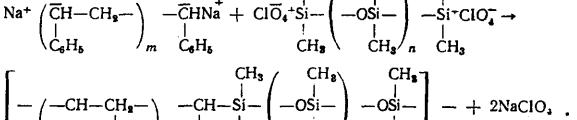
There are literature data on the synthesis of polyorganosiloxane block copolymers using oligodimethylsiloxanes having terminal acetoxy-groups. The process consists in the condensation of the terminal hydroxy-groups of polyester-urethanes obtained beforehand with the terminal acetoxy-groups of the oligosiloxane.[76]

The possibility of obtaining polyester-polysiloxanes by the heterophase condensation based on αω-bis(carboxypropyl)-oligosiloxanes in accordance with the scheme[77]



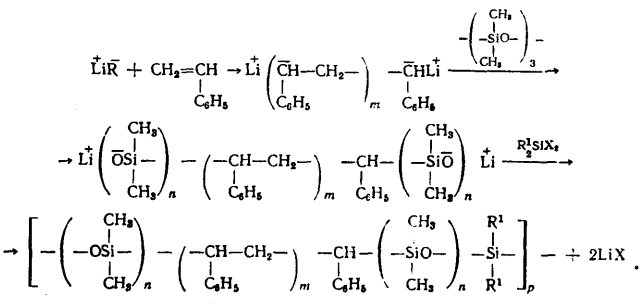
has been demonstrated. The authors note the need for the preliminary treatment of the oligosiloxane with phosgene to convert it into an acid chloride in order to increase the yield and the molecular weight of the copolymer.

Polystyrene-polysiloxane block copolymers containing regularly alternating blocks have been synthesised by the reaction of the oligostyrene anion with the oligomethylsiloxane cation in solution in THF:[78]



## Reactions with Participation of Cyclic Organosiloxanes

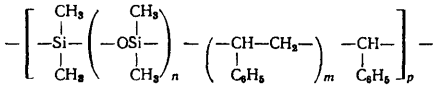
Polystyrene-polysiloxanes have been obtained by the joint anionic polymerisation of organosilicon cyclic compounds and styrenes:



The process includes the following stages: the polymerisation of styrene with a lithium initiator in the presence of a solvent (THF, benzene, or toluene) until "living chains" are formed, the introduction and polymerisation of hexamethylcyclotrisiloxane on such chains, and the joining together of the resulting blocks with bifunctional alkylsilanes.[79–83]

There is no chain termination in this process, which makes it possible to obtain a copolymer with a narrow molecular weight distribution. The block copolymer contains virtually no homopolymers nor cyclic compounds which failed to react. Dialkyldichlorosilane,[79–81] diacetoxydiphenylsilane,[82] and difluoromethyltrifluoropropylsilane[83] can be used as cross-linking agents.

In a modified synthetic scheme, the polysiloxane-polystyrene copolymer with terminal lithium atoms is treated with hydrochloric or acetic acid[81,84] to form blocks with terminal silanol groups. On further dehydropolycondensation in the presence of tin octanoate or caprylate, block copolymers having the following structure are obtained:



The copolymers of poly-α-methylstyrene with polydimethylsiloxane, containing short polystyrene[85] or α-alkylstyrene[86,87] blocks, have been obtained by analogous methods.

Polycarbonate-urethane-polysiloxane block copolymers can be obtained by the condensation in the melt of the oligocarbonate prepolymer with methylphenylcyclotrisiloxane in the presence of alkali metal hydroxides at 200–220 °C with subsequent interaction of the product with tolylene diisocyanate at 70–90 °C.[88]

Treatment of the oligocarbonate-siloxanediol synthesised in the first stage with methylphenylcyclotrisilazane in the melt at 180 °C yields polycarbonate-silazasiloxane block copolymers.[89] However, the process is complicated by the formation of isocyanate groups in side reactions, which are particularly vigorous for low molecular weights of the polysiloxane blocks. As a result of this, the block copolymers contain urethane linkages together with the polycarbonate and silazane blocks and have a branched or a cross-linked structure.

All the methods of synthesis of siloxane-containing block copolymers described above make it possible to obtain linear soluble products of different types with a predictable structure. The choice of particular conditions of synthesis permits the variation of the size of the blocks, the order in which they alternate, the molecular weight, the molecular weight distribution, and ultimately the properties of the polymers.

## III. STRUCTURAL CHARACTERISTICS AND PHYSICOCHEMICAL PROPERTIES

### 1. The Morphology of Polyorgano-polsiloxanes

The chemical structure of the macromolecule influences the temperature dependent transitions, the chemical stability, the thermal stability, and the permeability of the block copolymers. However, the specific properties of elastoplastics, namely the elasticity, strength, and rheology of the solutions and melts, are determined by the morphology of the block copolymer and are the result of its structural heterogeneity, i.e. the incompatibility of the blocks leading to their separation into microphases.

The fundamental morphological model of silicon-containing block copolymers can be represented by a continuous matrix formed by a flexible siloxane block in which rigid blocks, associated into dispersed formations (domains) chemically linked to the continuous matrix, are distributed in a discrete fashion. The domains fulfil the function of the nodes of a chemical network or filler.[1]

The appearance of a two-phase supermolecular structure and the degree of separation into phases depend on the structure of the copolymer macromolecule and are determined by the degree of incompatibility of the components forming the blocks. A quantitative characteristic of the degree of incompatibility may be the difference between the solubility parameters of the constituent blocks of the polymer. The dependence of the degree of separation on the difference between the solubility parameters is illustrated by the quantitative correlation[90] between the solubility parameters of segments of polyorgano-polysiloxane block copolymers and their capacity for being worked in the melt (Table 2).

Table 2. The rheological characteristics of the block copolymers.[90]

| Organic block | Δ* | Mouldability |
|---|---|---|
| Poly-α-methylstyrene | 1,3 | Good |
| Polystyrene | 1,6 | Good |
| Polycarbonate | 2,2 | Satisfactory |
| Polyarylate | 2,6 | Satisfactory |
| Polysulphone | 3,3 | Poor |

*The difference between the solubility parameters of the blocks.

Table 2 shows that the smaller the difference between the solubility parameters of the rigid and flexible blocks of the copolymer, the more easily can it be worked in the melt. The explanation is that a large difference between the solubility parameters promotes an appreciable phase separation of the system even as far as the retention of a physical network in the melt, which significantly impairs the capacity of the copolymer for being worked. Microphase separation is also promoted by the increase in the molecular weight of the blocks and by the tendency of the rigid block to crystallise.

Despite the large number of methods at the disposal of investigators (transmission and scanning electron microscopy, large- and low-angle X-ray scattering, reversed gas chromatography), which makes it possible to determine the shape and size of the domains, the distance between them, and the nature of the interfaces, only certain classes of polyorgano-polysiloxane block copolymers have been investigated in detail owing to the difficulty of interpreting the results.

The composition and method of preparation of the specimen influences decisively the supermolecular structure of the block copolymer.

The studies of the supermolecular structures of polyorgano-polysiloxanes containing rigid amorphous blocks, comprising polycarbonate-polysiloxanes,[91–97] polyarylate-polysiloxanes,[98,102] polystyrene- and poly-α-methyl styrene-polysiloxanes[82,103,104] polyimide-polysiloxanes,[105] and polyamide-polysiloxanes[105] made it possible to put forward a morphological model of the block copolymer (Fig.2) in which certain rigid blocks are associated into domains, which act as a physical network, while the matrix consists of polysiloxane blocks, whereupon

there is a possibility of partial interpenetration of the phases. When their content is low, the rigid blocks form a discrete phase, for intermediate contents both components form part of the continuous phase, and, for a high content of the rigid blocks, the polydimethylsiloxane aggregates into a discrete phase.

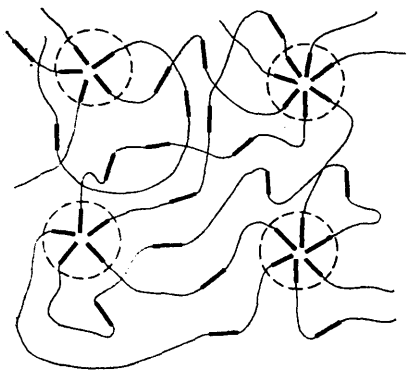



**Figure 2.** A morphological model of an amorphous polycarbonate–polysiloxane block copolymer.[91]

Depending on the composiiton of the block copolymer, the conditions in the preparation of the specimen, and the chemical nature of the organic blocks, the size of the domains formed by the latter varies over the range 30–350 Å.

The domains formed by the rigid blocks are separated by a distance of approximately 300 Å and the number of blocks in the domain may reach 800. With decrease in the molecular weight of the organic block, the presence of the mixed phase is manifested to a greater extent and the content of the polydimethylsiloxane component within the rigid domains increases. It has been noted that polycarbonate domains can contain up to 11 wt.% of the polydimethylsiloxane blocks.[95]

The statistically alternating block copolymers in which both blocks are polydisperse have a less ordered morphology than the block copolymers with a regular alternation of fragments. It has been suggested[94] that, in the formation of domains in such copolymers, long blocks are initially aggregated and small blocks are aggregated on the latter, which function as seeds. For this reason the short blocks "draw" the flexible polydimethylsiloxane blocks into the interior of the domain in the course of the formation of the structure.

When the content of the organic or the organosilicon blocks in the copolymer changes, the sizes of the domains can alter. Thus the surface area of the polycarbonate domains can be calculated from reverse gas chromatographic data,[96,97] and it has been shown that the area of the domains diminishes significantly with increase in the fraction of the carbonate block. The authors attribute this to the transition from the structure containing many small dispersed spherulites with a large surface area to a structure with close-packed folded domains.

A change in the method of preparation of the specimen for the same composition of the block copolymer results in a significant alteration of its structure. The supermolecular structure of film specimens then depends on the type of solvent and reflects the nature of the molecular associated species in solution. It has been shown[103,106,107] that, even in solutions of polyorganopolysiloxanes in selective and sometimes also in general solvents, the appearance of supermolecular formations and of a network between the domains has been observed, the microphase separation becoming more pronounced with increase of solvent selectivity. The most sensitive structural parameters under these conditions are the dimensions of the particles and the distance between them. For example, for polyarylate-polysiloxanes, increased selectivity of the solvent with respect to polydimethylsiloxane (enrichment of the solution in hexane) leads to a decrease in both the size of the domains themselves and in the distance between them. An analogous decrease of the distance between the domains occurs also for other methods of increasing the solvent selectivity and of altering the previous history of the specimen.

When the film is obtained from a solution in chloroform in an atmosphere of saturated xylene vapour with a gradual change in solvent composition as the xylene condenses and the chloroform evaporates, the distance between the domains decreases from 215 to 165 Å.[100]

Films based on polystyrene-polysiloxanes, obtained from toluene (common solvent), have a structure in which the polystyrene blocks produce agglomerates in the form of spaghetti-like microphases 282 ± 15 Å in diameter. The polydimethylsiloxane blocks give rise to a continuous matrix in which the polystyrene formations are separated by a distance of 170 ± 20 Å and the interpenetration of the phases is observed. With increase in the content of the polystyrene blocks, the agglomerates form cylindrical domains and there is a possibility of phase inversion.

Phase inversion has been achieved by choosing selective solvents for the same composition of the block copolymer. The toluene–cyclohexane (solvent for polydimethylsiloxane) mixture "displaces" polystyrene first on evaporation of the solvent, while films containing a discrete polydimethylsiloxane phase have been obtained from a toluene–bromobenzene (solvent for polystyrene) mixture.[103] Heat treatment of both blocks in the vicinity of the glass point promotes a better phase separation of the domain structures.[104]

Whereas the amorphous copolymers examined above exhibit some compatibility of the flexible and rigid blocks in both the continuous and discrete phases, the ability of the rigid blocks to crystallise leads to phase separation with a distinct interface.

Morphological studies of polysilphenylene-polysiloxanes revealed a two-phase structure, with a discrete phase comprising the crystallised silarylene block and an amorphous phase, consisting of non-crystallised polysilarylene and polydimethylsiloxane blocks, which is fully excluded from the crystal lattice regardless of the content of this phase in the copolymer.[108,109] The morpholigical model of the copolymer consists of lamellae alternating with the less ordered amorphous phase (Fig.3).

The degree of crystallinity depends on the amount of the polydimethylsiloxane component and diminishes from 53 to 15% with increase of the content of polydimethylsiloxane from 10 to 70 wt.%.[110] The temperature at which the maximum rate of growth of the crystals is observed diminishes with decrease in the content of the polysilarylene block.[111]

The morphology and cohesion between the phases in the block copolymer is influenced significantly by the solvent, temperature, conditions, and the time of formation of the structure.[112]

Thus the degree of microphase separation of polyorganopolysiloxane block copolymers is determined mainly by the composition of the copolymer, the method of preparation of the specimen, and also by the capacity of the rigid block for crystallisation.

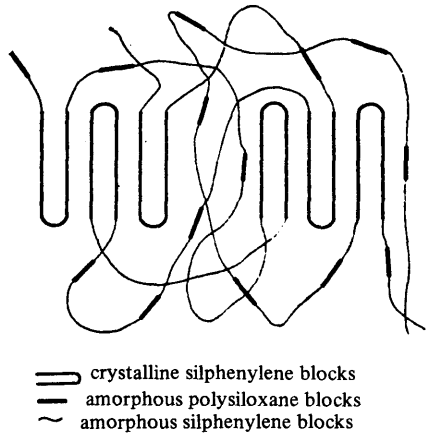



**Figure 3.** A morphological model of a crystalline polysilphenylene-polysiloxane block copolymer.[110]

## 2. The Temperature Dependent Transitions in Polyorganopolysiloxane Block Copolymers

The most characteristic feature of polyorgano-polysiloxanes, which follows from their ability to form morphological structures discussed above, is manifested by the presence of two glass points, reflecting the individual properties of each block (Table 3). Microlayer formation and the appearance of two glass points caused by it are observed for polyorganopolysiloxanes, starting with relatively low (3000–5000) molecular weights of the rigid block, which has been attributed to the large difference between the solubility parameters of the organic and polydimethylsiloxane blocks.

**Table 3.** Transition temperatures of polyorgano-polysiloxanes.

| Organic block | $T_c$, °C | Transition temperatures of the block copolymer, °C | | | Refs. |
|---|---|---|---|---|---|
| | | $T_c$ | $T_{g1}$ | $T_{g2}$ | |
| Polysulphone | +160 | −55 | −110÷−120 | +140÷+160 | [11 113] |
| Polycarbonate | +149 | — | −110 | +37÷+104 | [114] |
| Polycarbonate-urethane | — | −53÷−66 | −105÷−110 | +36÷+70 | [58] |
| Polyarylate | +320 | −50 | −110÷−120 | +320 | [24 100] |
| Polystyrene | +88 | −40÷−45 | −108 | +83 | [81] |
| Poly-α-methylstyrene | +130 | −45 | −105÷−120 | +80÷+130 | [25] |

The majority of investigators claim (Table 3) that the temperature dependent transition, which is attributed to glass formation by the polydimethylsiloxane block ($T_{g1}$) occurs at lower temperatures (−105 to −120 °C) and is almost independent of the molecular weights of the polydimethylsiloxane and organic blocks for all the block copolymers considered (Fig.4). Its temperature is close to the glass point of polydimethylsiloxane rubber (−120 °C).

The independence of $T_{g1}$ of the molecular weight of polydimethylsiloxane for comparatively short lengths of the blocks (2000–3000) is probably associated with the appreciable flexibility of the polydimethylsiloxane chain and hence with the small length of the kinetic segments responsible for the glass forming processes.

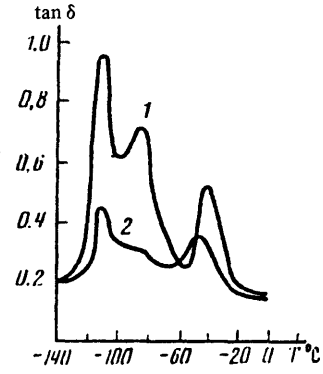



**Figure 4.** Temperature variation of the tangent of the mechanical loss angle (tan δ) for polyarylate-polysiloxane specimens having different compositions $N_{Si}:N_{Ar}$: 1) 420:20; 2) 200:20; $N_{Si}$ = number of siloxane units and $N_{Ar}$ = number of arylate units.[24]

However, a sharp increase[89,115] or decrease[116] of $T_{g1}$ in polyorganopolysiloxanes compared with homopolyorganosiloxane has been noted in certain investigations. The authors were unable to give an unambiguous explanation, suggesting that such anomaly may be associated both with the change in the character of the packing of organosiloxane blocks and with the high degree of interpenetration of the phases during their segregation.

An increase of $T_{g2}$ (the temperature dependent transition associated with glass formation in the rigid block) increases both with increase in the molecular weight of this block and with increase in the length of the polydimethylsiloxane block for constant lengths of the rigid block, which has been explained[25] by the increasing degree of phase separation. However, in polyarylate-polysiloxane[99] and polystyrene-polysiloxane,[82] $T_{g2}$ hardly differs from the glass point $T_g$ of the homopolymer over the entire range of compositions of the block copolymers investigated. The results obtained indicate, according to the authors, a more complete phase separation in these copolymers.

X-Ray diffraction studies have shown that the domains formed by silphenylene units have a high degree of crystallinity and the changes associated with glass formation by the rigid block are therefore very slight in these copolymers.[117]

Studies of polyarylene-polysiloxanes by differential scanning calorimetry also showed that there is a melting point of the silarylene blocks. With increase in the number of silarylene-siloxane units, the melting point increases and the decreased content of siloxane units also causes an increase in the melting point of the silarylene-siloxane domains.[115,118]

The decreased melting points of the silarylenesiloxane and polydimethylsiloxane blocks compared with the melting points of the corresponding homopolymers can probably be accounted for by the fact that, although the structures of the crystal

lattices of the domains of the homopolymers and the block copolymers are identical (their X-ray diffraction parameters are the same), the lattices of the domains in the block copolymers are more defective,[117,119] since the development of crystallisation processes is limited by the incomplete segregation of the individual sections of the macromolecules to form domains.

It is of interest to note that amorphous polyorgano-polysiloxanes, for example, polycarbonate-polysiloxanes,[120] can be crystallised by being kept in the vapours of chlorinated hydrocarbons. The degree of crystallinity determined by the crystallisation of the polycarbonate component of the block copolymer diminishes with increase in the content of the siloxane component in the copolymer. The maximum attainable degree of crystallinity (up to 45%) for block copolymers with any silicon content is higher the greater the length of the siloxane fragment.

The crystallisation of systems containing high-molecular-weight polydimethylsiloxane blocks has been noted at a temperature $T_c$. The degree of crystallinity depends little on the length of the rigid block and is close to the degree of crystallinity of the pure polydimethylsiloxane rubber.[121]

The temperature dependent transitions are an important characteristic of block copolymers, since they in fact determine the temperature ranges within which these materials can be worked and used.

### 3. Deformation-strength Properties

The mechanical characteristics of elastoplastics are determined by the properties of the continuous phase and by the frequency of the physical cross links and they therefore depend on the same factors as the supermolecular structure: the composition of the copolymer and the method of preparation of the specimen.

**Table 4.** The deformation-strength properties of polyorgano-polysiloxane block copolymers.

| Organic block | $c$, wt.% | $\sigma$, MPa | $\varepsilon$, % | $E$, MPa | Refs. |
|---|---|---|---|---|---|
| Polysulphone | 55 | 17 | 350 | 140 | [11] |
| Poly(phenylene oxide) | 49 | 18 | 450 | — | [17] |
| Polycarbonate | 51 | 21 | 150 | — | [114] |
| Polycarbonate-urethane | 56 | 25 | 500 | — | [58] |
| Polyarylate | 60 | 15 | 180 | — | [90] |
| Polysilarylene | 50 | 13 | 750 | $10^3$—$10^4$ | [111,118] |
| Poly-α-methylstyrene | 52 | 13 | 370 | 500 | [25] |

Notation: $c$ is the content of the polydimethylsiloxane blocks, $\sigma$ the breaking tensile stress, $\varepsilon$ the relative elongation on rupture, and $E$ the modulus of elasticity.

The main characteristic of the mechanical properties of the copolymers is the relation between the breaking tensile stress and the relative elongation on rupture. This relation determines the modulus of elasticity of the system, its strength, and its deformability.

With increased content of the polydimethylsiloxane component, the properties of all the polyorgano-polysiloxane block copolymers vary from those of rigid materials, which are difficult to deform, to flexible elastomeric compositions, which is well illustrated by Fig.5 for polycarbonate-urethane-polysiloxanes.[58]

The different conditions in the preparation of the specimens and in the tests preclude quantitative estimation of the influence of the chemical structure of the rigid block on the deformation-strength properties of the copolymer. However one may note that the presence in the block copolymer of fragments with an increased tendency towards crystallisation [poly(phenylene oxide), polysilarylene] or capable of forming interchain hydrogen bonds (polycarbonate-urethane) increases its deformability (Table 4).

It is essential to note that the molecular weight of the block copolymer has an appreciable influence on its deformation-strength properties (Fig.5).

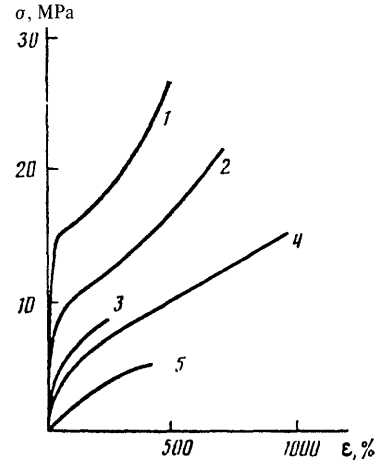



**Figure 5.** The influence of the composition and molecular weight of polycarbonate-urethane-polysiloxanes on the breaking tensile stress $\sigma$ and the relative elongation on rupture $\varepsilon$; content of polydimethylsiloxane blocks (wt.%); 1) 56; 2) 62; 3) and 4) 67; 5) 77; $\bar{M}_w$: 3) $5 \times 10^4$; 4) $11 \times 10^4$.[58]

The deformation-strength properties of films based on a block copolymer of one composition can be varied within wide limits by altering the method of their preparation. On passing from a common to a selective solvent, the properties of the film approach those of the component with respect to which the solvent is selective, which is associated with the different character of structure formation in the solution from which the film is obtained.[115,122,123]

It has been shown in relation to polyarylate-polysiloxane[122] that the change in strength is manifested to a greater extent in systems enriched in the rigid block (the polyarylate) and the change in deformability is manifested more in systems enriched in polydimethylsiloxane. The influence of the solvent and of the method of formation of the film is particularly marked in systems with similar weight fractions of the components.

The expansion of the region of high elasticity occurs, as can be seen from Table 5, when the film is obtained via a gel stage, compared with the film obtained from the same solvent via the solution stage or after swelling the film in a medium in which it forms a gel and is then dried.[100]

A distinctive feature of almost all polyorgano-polysiloxane block copolymers is their ability to be worked in the melt at temperatures above the glass point of the rigid blocks. In

thermal moulding, the material is usually oriented, which leads to an appreciable increase of strength.[124]

**Table 5.** Dependence of the deformation-strength properties of a polyarylate-polysiloxane on the nature of the solvent and the method of preparation of the film.[100]

| Solvent | Solvent selectivity | $\sigma$, MPa | $\varepsilon$, % | $E$, MPa |
|---|---|---|---|---|
| Chloroform | common | 13.0 | 160 | 66.0 |
| Tetrachloroethane | polyarylate | 19.0 | 95 | 100.0 |
| Xylene | polydimethylsiloxane | 3.0 | 220 | 7.5 |
| Chloroform–hexane (60–40) | » | 9.5 | 280 | 10.0 |
| Chloroform–toluene (70–30) | » | 9.0 | 420 | 29.0 |
| Chloroform–hexane (60–40*) | » | 10.5 | 375 | — |
| Xylene (from the gel) | » | 9.5 | 270 | — |

*Film obtained from solution in chloroform, swollen in a chloroform–hexane mixture, and dried.

## 4. Thermal and Thermo-oxidative Stability

The thermal and thermo-oxidative degradation of polyorgano-polysiloxanes has been investigated to determine the temperature and conditions for their processing and to estimate the possibility of using these materials at elevated temperatures.[11,27,63,125–127] In the first place, it is essential to note that the high energy and ionic character of the siloxane bond are responsible for the appreciable thermal stability of polysiloxane. The Si–O–C bond is more vulnerable in this respect.[128] Since the rigid blocks of the copolymers investigated also exhibit a high thermal stability, it follows that, as was to be expected, the block copolymers are stable up to high temperatures (Table 6).

**Table 6.** Thermal stability of polyorgano-polysiloxanes.

| Organic block | Temperature of 10% weight loss, °C | | Refs. |
|---|---|---|---|
| | in air | in nitrogen atmosphere | |
| Polysulphone | 475 | 510 | [11] |
| Polycarbonate | 400 | 450 | [127] |
| Polycarbonate-urethane | 350–400 | — | [58] |
| Polyarylene | 420 | 480 | [11] |
| Polysilarylene | — | 427 | [129] |
| Polyimide | — | 500 | [66] |

As a rule, the weight content of the blocks in the copolymer changes and no appreciable alteration of the thermal stability is observed.[127,129] The reason for this is probably that the stability of the macromolecule is determined by its weakest bonds, which are located at the sites of contact between the blocks (the Si–C or Si–O–C bonds). Polyarylene-polysiloxanes, whose thermal degradation takes place preferentially with rupture of the Si–O–Si linkage whereupon the thermal stability of the copolymer diminishes with increasing content of the polysiloxane block,[130] and polysulphone-polydimethylsiloxane copolymers where the polydimethylsiloxane blocks are the first to undergo thermal degradation with formation of linear and cyclic oligodimethylsiloxanes,[131] are exceptions.

The change in the chemical structure of the rigid block (within the framework of a single class) is reflected in the thermal stability of the block copolymer.[80,129,132,133] The poly-α-methylstyrene-polysiloxane block copolymers, for example, exhibit a better thermo-oxidative stability than polystyrene-polysiloxanes having the same composition.[80] Whereas heating of polystyrene-polysiloxane in air for 80 h at 150 °C diminishes its strength by a factor of 2, this is not observed for poly-α-methylstyrene-polysiloxane.

The study of the time variation of the weight losses at 305–385 °C by polyarylate-polysiloxanes based on phenolphthalein and phenolfluorene terephthalates[133] showed that the thermal stability of the latter copolymer is higher; this has been attributed to the absence from it of the thermally unstable lactone group. As has been frequently noted,[129,134] copolymers without Si–O–C bonds in the main chain show a higher thermal stability.

## 5. Hydrolytic Stability

The resistance of polyorgano-polysiloxane block copolymers to hydrolysis is one of the principal indices indicating the retention of the properties of polymeric articles under the real conditions of their use. The hydrolytic stability of polyorgano-polysiloxanes is lower than that of homopolymeric polysiloxane and the degradation of the polymer takes place as a rule at the bonds between the organic and organosilicon blocks or within the organic block.

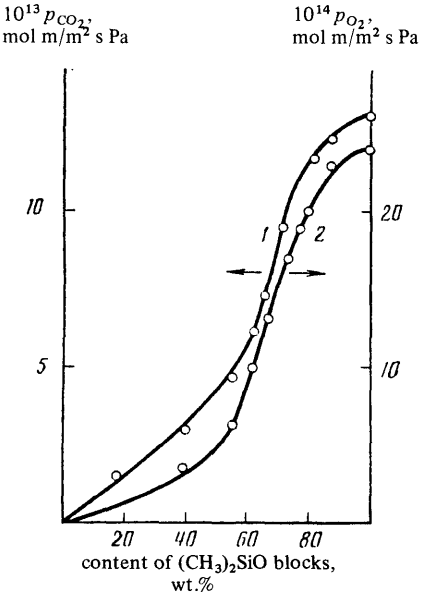



**Figure 6.** Dependence of the coefficient of gas permeability to $CO_2$ ($P_{CO_2}$) (curve *1*) and $O_2$ ($P_{O_2}$) (curve *2*) on the composition of polycarbonate-polysiloxane at 20 °C.[114]

It has been shown[135] that the heterogeneous hydrolytic degradation of polyarylate-polysiloxane in argon takes place to an appreciable extent at 160 °C, while the hydrolysis of

polydimethylsiloxane under analogous conditions does not begin until 220 °C. It has been noted that the hydrolysis proceeds preferentially at the Si—O—C linkage and that the rate of hydrolysis increases with increase in its concentration per unit volume.

The stability of polysulphone-polysiloxanes containing the Si—O—C bond can be increased by introducing large hydrophobic silicon-containing segments into the main chain of the macromolecule.[136] As a result of this, steric hindrance arises in the hydrolysis of the Si—O—C bond and the concentration of such bonds in the copolymer falls. The hydrolytic stability of polyorganopolysiloxanes can be raised also by introducing polyester-urethane[76] fragments into the siloxane chain.

An increase in the hydrolytic stability of the block copolymers can be achieved by replacing the hydrolytically vulnerable Si—O—C bond between the blocks by the Si—C bond.[58,63,66,137]

Estimation of the hydrolytic stabilities of various polysiloxanes showed[138] that the replacement of the methyl groups in polydimethylsiloxane by sterically more bulky substituents (phenyl, ethyl, and trifluoropropyl groups) increases the hydrolytic stability of homo- and co-polysiloxanes. One can therefore assume that the synthesis of block copolymers from such polysiloxanes would make it possible to increase their hydrolytic stability.

## 6. The Resistance of Polyorgano-polysiloxanes to UV Radiation

In connection with the possibility of using organosiloxane block copolymers as transparent materials without a filler such as carbon black, studies have been made of the resistance of these polymers to UV radiation. The block copolymers of polyorganosiloxane and polystyrene showed satisfactory photostability.[139] However, the stability of copolymers containing aromatic rings in the main chain proved to be limited.[11,140]

The study of the photodegradation of polyarylate-polysiloxane showed that the degradation takes place mainly in the polyarylate block and that the most unstable structures in relation to UV radiation are the ester bond and the phthalide ring. The siloxane block does not absorb UV radiation but does undergo degradation with evolution of methane, which has been attributed to the occurrence of secondary radical reactions.[140] The presence of oxygen appreciably accelerates the degradative processes.

## 7. The Permeability of Polyorgano-polysiloxanes to Gases

Polyorganosiloxanes are known[141] to be distinguished by a high permeability to gases owing to the high flexibility and mobility of the Si—O—Si bonds and also to the weak intermolecular interaction between such macromolecules.

An advantage of the two-phase polyorgano-polysiloxane block copolymers is that strong thin film membranes can be obtained from them without chemical cross-linking or the use of a filler. The presence of the highly permeable siloxane block therefore entails prospects for an important application of the block copolymers considered as gas separating membranes.

The permeability of such membranes to gases is up to 80% of the permeability of siloxane rubber and increases with increasing content of the polydimethylsiloxane blocks in polyarylate-polysiloxanes,[63,142] polycarbonate-polysiloxanes,[114] polycarbonate-urethane-polysiloxanes,[58] and polysulphone-polysiloxanes.[143]

The study of the influence of the composition of polycarbonate-polysiloxane on the gas-permeability to $CO_2$ and $O_2$, carried out by the gas-chromatographic method on film specimens,[114] revealed the S-shaped character of the dependence of the gas-permeability coefficient on the content of the polydimethylsiloxane blocks (Fig.6). The sharp increase in this coefficient in the region where the content of the polydimethylsiloxane blocks is up to 50—60 wt.% suggests that phase inversion takes place for this composition of the copolymer.[114]

The selectivity of the gas separation ($CO_2/O_2$) remains approximately 6 regardless of the composition of the copolymer. This has been attributed[114] to the fact that the properties of the siloxane phase depend little on the composition of the copolymer. It has also been noted that a characteristic feature of the membranes in the region of compositions investigated is the virtual absence of a temperature dependence of the permeability to $CO_2$ in the range 20—90 °C as a function of the ratio of the block lengths. This has been explained by the mutual compensation of the activation energies for the diffusion of $CO_2$ and the heat of solution of $CO_2$ in the block copolymer.

Since the permeability to gases is determined by the content of the siloxane component regardless of the nature of the rigid blocks constituting the relatively impermeable phase, comparison of the block copolymers having different organic blocks[144] showed that they are to a large extent analogous in their gas separating properties. For this reason, in selecting polymeric materials for gas separating membranes, the criterion to be used as a guide should probably be their physicochemical characteristics, their resistance to degradation, and the technological feasibility of their preparation.

Analysis of the literature data permits comparative estimation of the properties of polyorgano-polysiloxane block copolymers containing different rigid elements (Table 7).

**Table 7.** Comparative characteristics of the properties of polyorgano-polysiloxane block copolymers*.

| Rigid block | Deformability | Upper temperature limit of operating range | Thermal stability | Hydrolytic stability | UV stability | Mouldability | Thermoweldability | Atmospheric stability |
|---|---|---|---|---|---|---|---|---|
| Polysulphone | * | * | + | + | * | − | − | − |
| Poly(phenylene oxide) | + | + | − | * | * | − | − | − |
| Polycarbonate | * | * | * | * | * | * | − | * |
| Polyarylate | * | + | + | * | * | * | − | * |
| Polysilarylene | + | + | * | * | * | − | − | * |
| Polystyrene | * | − | * | * | + | + | − | + |
| Poly-α-methylstyrene | * | − | * | * | − | + | − | − |
| Polyurethane | + | * | * | + | − | * | − | * |

Notation: "*"—presence of given property; "−"—absence of given property (or information about it); "+"—advantage in terms of the given property.

The Table shows that such block copolymers have a set of useful properties. The choice of the material for each specific application is determined by the property which should predominate.

It is noteworthy that, since modern economic trends are characterised by a tendency towards further growth of prices of petrochemical raw materials and energy, the manufacture of organosilicon products and materials based on them will be one of the most promising branches of chemical

industry due to the relatively low consumption of raw materials and energy per unit output.[145]

## IV. APPLICATIONS

Polyorgano-polysiloxane block copolymers can be used for the modification of homopolymers whose structure is analogous to that of the rigid fragment. Small amounts of added block copolymer (approximately 5%) impart new and unexpected properties to the homopolymer. The possibility of such modification follows from the two-phase morphology and the specific properties of the polyorganosiloxane block.

Thus the introduction of 5 wt.% of polysulphone-polysiloxane into the polysulphone homopolymer increases its impact strength by a factor of 20; this is also accompanied by an increase in the resistance to cracking.[9,126] Such behaviour can be explained by the solubility of the polysulphone fragment of the block copolymer in the chemically identical homopolymer matrix and by the segregation of the polysiloxane blocks into a discrete phase. This leads to the effective dispersion of the copolymer in the matrix and a high degree of interfacial adhesion.

A characteristic feature is that the modification is observed only after the introduction of a copolymer exhibiting a two-phase morphology.[14] The increased deformation following the rupture of polycarbonate-(polycarbonate-siloxane-urethane) blends compared with the deformations of the two components of the blend can be accounted for by analogous causes.[146]

Another possible type of modification involves the decrease in the wettability and of the coefficient of friction of the surface of the homopolymer by introducing into the latter a certain amount of the block copolymer.[63,147]

It has been shown by X-ray photoelectron microscopy[148,149] and electronic spectroscopy for chemical analysis[150] that the surface of the block copolymer and of the homopolymer–block copolymer blend is always enriched in the component with the lower surface energy, i.e. in the polysiloxane,[151] which ensures the modifying effect.

The principal applications of polyorgano-polysiloxane block copolymers are determined by the ability of these copolymers to effect highly productive selective separation of gases.[152]

Films based on polyarylate-polysiloxane are used as membranes for the enrichment of natural gas in helium[153] and for the isolation of helium from petroleum gas,[154] for the separation of the "carbon dioxide–hydrogen" or "oxygen–nitrogen" gas mixtures,[62,137,144,155] and for the isolation of sulphur dioxide from mixtures.[156] Polycarbonate-polysiloxane is used for the isolation of oxygen from "nitrogen–oxygen" mixtures.[157,158] Gas- and water-permeable coatings are obtained from polystyrene-polysiloxane.[159]

Ultrathin membranes,[160,161] thermostable films,[162] and films with thermal shrinking for the packing of food products[15] can be obtained by processing polysiloxane block copolymers. These materials are suitable for coatings with improved dielectric properties[66,163,164] and for non-shrinkable coatings with improved strength characteristics.[165] These coatings adhere to metallic surfaces,[166] exhibit a satisfactory resistance to the action of light and weather,[139] and, by virtue of their hydrophobic nature, prevent the icing of glass.[167]

The block copolymers of the given type are believed to be effective stabilisers of polymers[168] and are used as part of compositions with high impact strength,[169–172] thermal stability,[173] and effective adhesion properties[174] and as part of soil compositions.[175]

Polyorgano-polysiloxane block copolymers exhibit a satisfactory fire resistance,[176–179] which increases with increasing content of the siloxane blocks. This has been explained by the formation during combustion of varieties of coke-containing silicon, which increases the resistance of the material to oxidation.[180] Depending on the chemical structure of the organic fragment, the first resistance increases in the sequence polycarbonate based on di(hydroxyphenyl)propane = polycarbonate based on di(hydroxyphenyl)fluorene > polystyrene-poly(2,6-diphenyl-1,4-phenylene oxide).[181]

These materials have found applications in electrical engineering[182] as electrically insulating materials and in electronics[183,184] as coatings for transistors, resistors, and integrated circuits. They retain their useful properties at both elevated[185] and reduced[186] temperatures.

Laminated materials, in which the inner adhesive layer is a polycarbonate-polysiloxane,[29,187,188] as well as technical filaments made of polymethylstyrene-polysiloxanes[189] have been described.

A promising field in which polysiloxane block copolymers may be used currently is medicine.[190,191] Among all the synthetic polymers used in medicine in the USSR, organosilicon compounds are the commonest.[192] All the siloxane elastomers are used as vulcanised materials, reinforced by a filler, which are readily sterilised. However, their main disadvantage, which significantly restricts their applications, is their low mechanical strength and low anticlotting activity.

It is striking that the anticlotting properties of filled silicone rubber are determined not by the chemical nature of the rubber but by the presence on its surface of a filler—silicon dioxide, whose silanol groups are capable of forming hydrogen bonds with plasma proteins and inducing the coagulation of blood.[76,193] The use of polyorgano-polysiloxane block copolymers for medical purposes permits the elimination of these disadvantages. It was shown above that their strength can vary within wide limits and can surpass the strength of siloxane rubber by a factor of 2–3.

The copolymer containing 90 wt.% of polyester-urethane and 10 wt.% of polydimethylsiloxane is used nowadays as a blood-compatible material, having the necessary set of formation-strength characteristics.[76,150,194] Auxiliary devices for the maintenance of cardiac activity, intra-aortal balloons, and various types of pumps for ensuring the circulation of blood and made from this material.

Polyorgano-polysiloxane block copolymers are used as biomaterials,[73,77] medical hermetic sealing compounds,[195] and optical contact lenses correcting astigmatism.[196]

The possibility of obtaining selective gas-permeable films from copolymeric materials permitted their use as the membrane element in different types of "artificial lung" apparatus.[190]

The polyorgano-polysiloxane block copolymers examined in this review represent a new class of materials with a set of useful practical properties determined by their microheterogeneity. Detailed investigation of the factors permitting a fine regulation of the supermolecular structure of these copolymers will assist in the creation of materials with properties specified beforehand.

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During the preparation of this review for printing, new communications concerning research into polyorgano-polysiloxanes were published.

The synthesis of linear soluble block copolymers based on αω-diepoxyoligosiloxanes and the diglycidyl ether of di(hydroxyphenyl)propane at 60 °C in dioxan in the presence of stoichiometric amounts of piperazine has been examined.[197]

The interaction of diepoxy-derivatives of oligosiloxane with αω-di(hydroxyphenyl)oligosulphones in concentrated solution at elevated temperatures resulted in the formation of polysulphone-polysiloxanes,[198] but the molecular weights of the block copolymers synthesised proved to be low.

A number of publications deal with questions of the synthesis and modification of polyamide-polysiloxanes,[199,201] polyurea-polysiloxanes,[202,203] and polyimide-polysiloxanes[204–207] with participation of αω-diaminosiloxanes. High-molecular-weight polyamide-polysiloxanes have also been obtained by the copolymerisation in the melt at 130 °C of oligodimethylsiloxane having terminal anhydride groups with ε-caprolactam in the presence of an anionic initiator.[208]

The methods of synthesis of polyester- and polyurethane-polysiloxanes using organic functional group-substituted αω-dihydroxy(carboxy)oligosiloxanes[202,203,209,210] and αω-di(chloroformyloxymethyl)oligosiloxanes[211] and the hydrosilylation reaction[212,213] in the synthesis of polysulphone-polysiloxanes are being developed.

The detailed study of the physicochemical properties of polyorganopolysiloxanes is being continued. The composition and structure of block copolymers,[214,215] their microheterogeneity characteristics,[216–222] their surfaces,[223,224] the molecular mobility at the interface,[225] processes involving the transport of gases across membranes made of such block copolymers,[226,227] their biodegradation,[228] and their operating properties[229] have been analysed by different methods in recently published studies.

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