INORGANIC/ORGANIC POLYMERS FOR CONTACT LENSES BY THE SOL-GEL PROCESS

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ABSTRACT

The use of organoalkoxysilanes as network forming materials allows the introduction of organic groups into an inorganic network by the sol-gel process. This possibility, in addition to the inorganic network modification, opens a wide variability of material synthesis. Facing the desire for high performance materials for contact lenses, an attempt is made to meet the requirements of contact lens materials, as oxygen permeability and wetting. The paper shows the basic principles which can be carried out in order to taylor material for specific properties.

1 INTRODUCTION

In the field of material development an increasing demand for materials with special properties is obvious. Considering the properties of different types of materials like ceramics, metals, or organic polymers, one started very early to think about the combination of different properties in order to get materials for special applications which unify the desired different properties in one material. This led to the conception of composites. Examples of composites might be laminates (fig.1a) which are successfully used e.g. for windshields of cars, for skis, or to create protective surfaces; other examples are filled organic polymers (fig.1b), as they are used for tires of cars. From this point of view a ceramic material with a crystalline phase and a glassy phase as binder may be considered as a composite material, too; as a last example fibre reinforced materials may be cited (fig.1c). This type of composite is used e.g. with organic poly-

mers or inorganic materials like concretes. These examples represent composites where the combination of two materials is per-
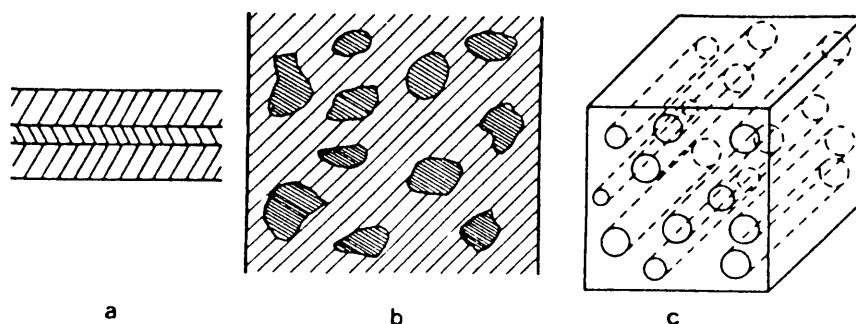

Fig.1a-c. Principle possibilities of composites.
(a) laminates; (b) filled organic polymers;
(c) fibre reinforced material

formed on a macroscopic scale. In order to process such materials, with a few exception, combination techniques have to be developed (mixing, sealing etc.). In the most cases this needs a more-step processing.

From this the question arises, if the principle of composites may be extended to the microscopic scale. In the field of material development one advantage might be (if such material are produced by the rules of chemistry) to apply an one-step processing. Another question is which technical means may be used in order to perform this.

A simple way could be to combine components on a molecular scale from which it is known that they cause different material properties. Examples might be components which lead to non-metallic inorganic networks on the one hand and organic substituents or organic polymers on the other hand; organic radicals might be functional groups or polymerizable components. In order to get a desirable combination of these materials, it seems to be necessary to develop a method where these two types of components may be linked together by well-defined chemical bonds like covalent ones. There might be considered two general possibilities. One is to build up an organic backbone and to link inorganic components to this backbone; this principle is realized in some organic polymers, so-called ionomers, as they are shown in fig.2.
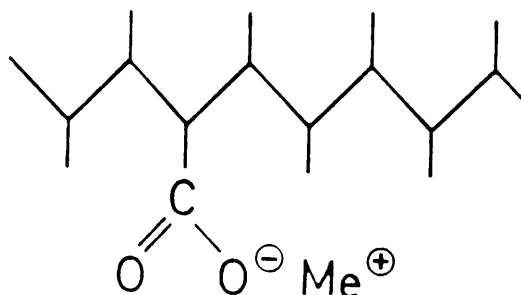
Me = metal

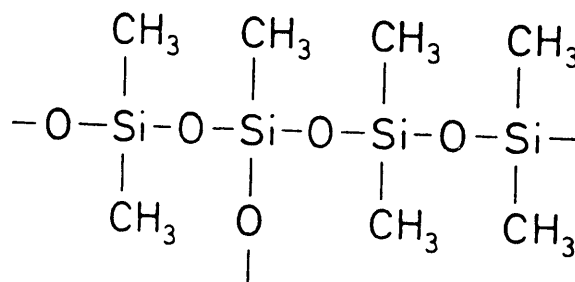Fig.2. Scheme of an organic ionomer

Fig.3. Scheme of a silicone polymer

The second possibility is to build up an inorganic (metal oxide) backbone which is partially realized in silicones (fig.3.).

Silicones normally are produced by hydrolsis and condensation of the proper chlorosilanes. In principle the preparation of this type of material is possible, too, by the means of the sol-gel process i.e. by the use of alkoxysilanes. The advantage of this route is that the steps of hydrolysis and condensation are

easier to be controlled because of the lower reactivity of the alkoxysilanes compared to the chlorosilanes [1-3]. The sol-gel process moreover enables the introduction of different other compounds like network forming elements into the material as it is described by Gulledge, Andrianov, and Noll [4-6]. An additional principle of modification is the use of organoalkoxysilanes, where the Si-C bond can be used to introduce organofunctional groups which may have special chemical properties or which can carry polymerizable ligands [7-11] according to equation (1).

$$Me^{IV}(OR)_4 + Si(OR)_4 + (RO)_m Si(\geq=)_{4-m} + (RO)_n Si(R'Y)_{4-n} \longrightarrow$$

$$
\begin{array}{ccccc}
 & \overset{|}{O} & \overset{|}{O} & \overset{|}{O} & \overset{|}{O} \\
-O-Me^{IV}-O & -Si-O & - Si-O & - Si-O- \\
 & \overset{|}{O} & \overset{|}{O} & \diagdown & \overset{R'}{Y} \\
 & | & | & &
\end{array}
\qquad (1)
$$
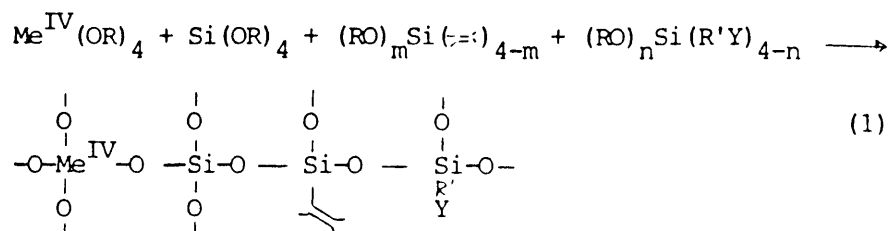
m = 3; n = 2

Me = metal e.g. Ti, Zr
R = alkyl, aryl
R' = alkylen, arylen
⋟= = polymerizable double bond
Y = organofunctional group e.g. $-NH_2$, $-CHO$

This conception leads to a very flexible system of material development. It was of high interest to find out, if this conception may be advantageously used in order to prepare special materials for contact lenses.

2 CONCEPTION OF MATERIAL DEVELOPMENT

2.1 Requirements for Contact Lenses

As a result of the special type of application (i.e. the material is in contact with the cornea) it is pretty well-known which requirements materials for contact lenses should fulfill [12]. The main requirements are listed in table 1. The wettability is necessary in order to maintain the lachrymal film between the material and the cornea; this wettability should not be lost, if the maerial is processed e.g. shaped by mechanical procedures. The oxygen permeability is necessary in order to supply the cornea with oxygen, since the cornea has no other supplying system. The mechanical properties have to be sufficient for a secure handling and the tendency of the surface not to deposit components of

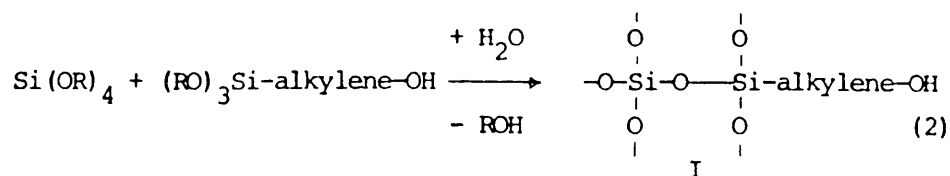Table 1. Main requirements for hard contact lens material

Wettability	contact angle with water 30° in the hydrated state,
O_2-permeability	permeability coefficient P = $10x10^{-11}$ ml $O_2.cm^2.ml^{-1}.s^{-1}.mm$ Hg^{-1},
Physical properties	density: 1.1-1.2 g cm^{-3}, sufficient flexibility, high hardness, good scratch resistance,
Optical properties	refractive index n^{20}_D = 1.43, transmission $\geq 98\%$,
Chemical properties	water absorbing capacity < 10 wt.%, low tendency of deposition of components of lachrymal fluid, chemical stability (no unlinked components of contact lens material; resistance to acids, bases, organic solvents, microorganisms, and UV-light).

the lachrymal film is necessary in order to avoid microbial contamination. The common polymers in the couple of special developments [12] are not able to unify all these requirements in one and the same material.

## 2.2 Possibilities of Realization

It seems to be useful in order to have a high oxygen permeability to use structure elements of silicones, since silicones have an oxygen permeability of P = $79x10^{-11}$ ml $O_2.cm^2.ml^{-1}.s^{-1}.mm$ Hg^{-1} [12]. But silicones are extremely hydrophobic. That means, the idea should be to build up a silicone-like network with hydrophilizing components incorporated. The hydrophilizing components have to be non-ionic in order to avoid deposition of components of the lachrymal fluid. Therefore alcoholic groupings are to be preferred.

In principle compounds of the type $(RO)_n Si(alkylen OH)_{4-n}$ should be useful in combination with another network forming Si compound like $Si(OR)_4$ [10]. Then the condensation reaction should follow equation (2), but there appears one complication, since, as proved by Voronkov et al. [14],transesterification reaction occurs very easily with mixtures of alkoxysilanes. Reaction according equation (3) may take place and lead to a decrease of hydro-
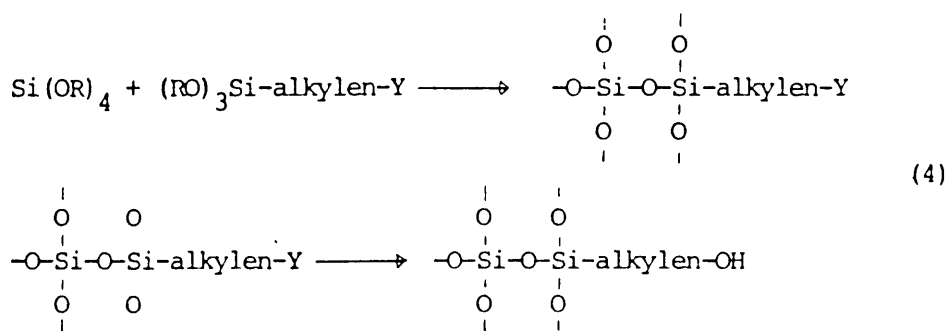
$$\text{Si(OR)}_4 + \text{(RO)}_3\text{Si-alkylene-OH} \xrightarrow[\text{- ROH}]{+ H_2O} \quad \begin{array}{cc} | & | \\ O & O \\ | & | \\ \text{-O-Si-O---Si-alkylene-OH} \\ | & | \\ O & O \\ | & | \\ & I \end{array} \qquad (2)$$

R = alkyl

philicity. Since equation (3) easily may occur under average con-
densation conditions, especially if one uses catalysts like pro-
tons, the complication has to be avoided. Measurements of alcoho-
lic solutions of compound I, equation (2), show that if the sol-
vent is evaporated to a high extent type II (equation (3)) oligo-
mers are formed. This was proved by mass spectrometric analysis.

$$\text{:Si-alkylene-OH} + \text{RO-Si:} \xrightarrow{-ROH} \text{:Si-alkylene-O-Si:} \qquad (3)$$
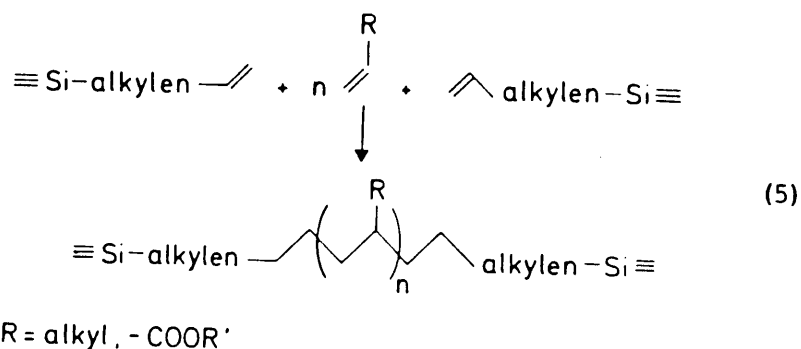$$\text{II}$$
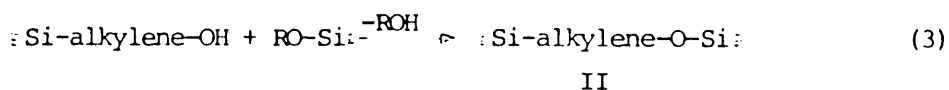
R = alkyl

In order to avoid this complication a better route should be
to use latent hydrophilic organic groupings which develop the
real hydrophilicity after the condensation process has taken
place. This principle should be performed according to equation
(4).

$$\text{Si(OR)}_4 + \text{(RO)}_3\text{Si-alkylen-Y} \longrightarrow \begin{array}{cc} | & | \\ O & O \\ | & | \\ \text{-O-Si-O-Si-alkylen-Y} \\ | & | \\ O & O \\ | & | \end{array}$$

$$\qquad (4)$$

$$\begin{array}{cc} | & | \\ O & O \\ | & | \\ \text{-O-Si-O-Si-alkylen-Y} \\ | & | \\ O & O \\ | \end{array} \longrightarrow \begin{array}{cc} | & | \\ O & O \\ | & | \\ \text{-O-Si-O-Si-alkylen-OH} \\ | & | \\ O & O \\ | & | \end{array}$$
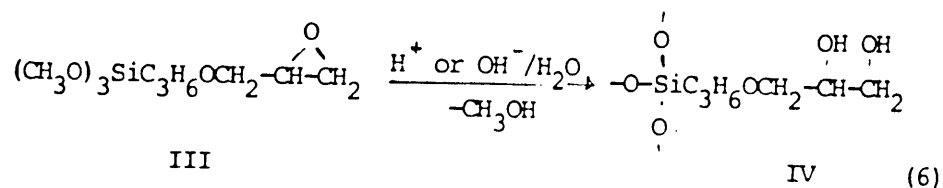
R = alkyl; Y = latent hydrophilic grouping

A technical possibility in order to realize this idea could be to
use the commercially available epoxysilane $(RO)_3Si \sim \overline{CHCH_2O}$(III).
A cocondensation of Si(OR)_4 with (III) should lead to highly cross-
linked and therefore to brittle materials. The influence of the
organic grouping on the network modification was unknown, and
therefore it was necessary to take care for building up suffi-
cient elasticity. If not, it will become necessary to incorporate
structure elements which lead to a more linear crosslinking. The
possibility for this is demonstrated in equation (5).

$$\equiv Si-alkylen \overset{}{\underset{}{}}\diagup\!\!\!\!/ \quad + \quad n \overset{R}{\underset{}{\diagup\!\!\!\!/}} \quad + \quad \diagup\!\!\!\!\diagdown alkylen - Si \equiv$$

$$\equiv Si-alkylen \overset{R}{\diagup\!\!\!\diagdown\!\!\!\diagup\!\!\!\diagdown_n\!\!\!\diagdown} alkylen - Si \equiv \qquad\qquad (5)$$

$$R = alkyl, -COOR'$$

3 RESULTS

3.1 Hydrophilicity

If water is added to the epoxysilane (III), the epoxide ring opens to the glycol grouping (IV) according to equation (6).

$$(CH_3O)_3SiC_3H_6OCH_2-\overset{O}{\overset{/\backslash}{CH-CH_2}} \quad \xrightarrow[-CH_3OH]{H^+ \text{ or } OH^-/H_2O} \quad -O-\underset{O}{\overset{O}{SiC_3H_6OCH_2}}-\overset{OH \; OH}{CH-CH_2}$$

III
IV   (6)

The reaction conditions under which this reaction can run are basically the same where hydrolysis and condensation may take place (alcoholic solutions, protons as catalysts, addition of water). The overall reaction according to equation (6) does not exclude a reaction according to equation (3), leading to a decrease of the hydrophilicity. The proof that the ring opening reaction takes place at the same time as hydrolysis and condensation was given by IR- and NIR-spectroscopy (fig.4). Investigations to which extent the reaction according to equation (6) decreases the hydrophilicity were not carried out, but another way
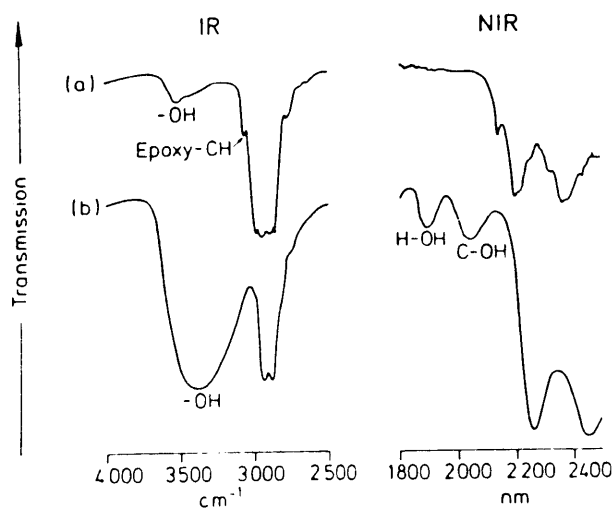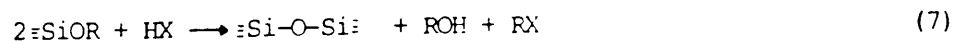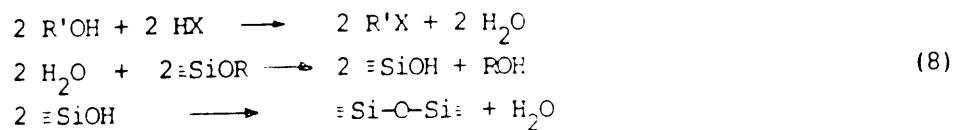
Fig.4. IR- and NIR-spectra of the epoxysilane III (a) before and
(b) after hydrolysis and condensation

which shows the good possibility to avoid this is given by Voron-
kov [12] as shown in equations (7) and (8). This "water-free"
condensation reaction was proved by IR- and NIR-spectroscopy
which showed that the epoxide ring was not opened and by mass
spectroscopy which proved the appearance of RX. By this, reaction
can be run to a viscous material and then by the addition of wa-
ter the epoxide ring will be opened to the glycol grouping. After
this, the viscous material can be cured at temperatures of 100-
130°C to a solid material. But as a function of the high cross-
linking, brittle material were produced and during the drying
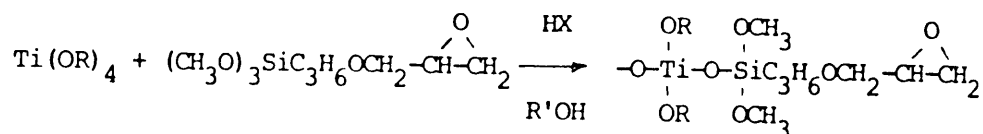procedure the desaggregation to a granulate occurred.

$$2 \equiv SiOR + HX \longrightarrow \equiv Si-O-Si\equiv + ROH + RX \tag{7}$$

$R = alkyl; \; X = halogen$

$$2 \; R'OH + 2 \; HX \longrightarrow 2 \; R'X + 2 \; H_2O$$

$$2 \; H_2O + 2 \equiv SiOR \longrightarrow 2 \equiv SiOH + ROH \tag{8}$$

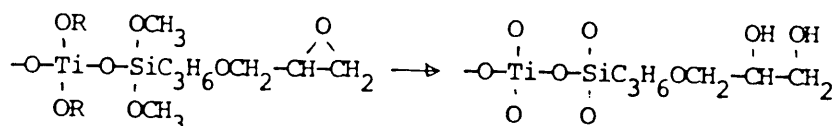$$2 \equiv SiOH \longrightarrow \equiv Si-O-Si\equiv + H_2O$$

$R, \; R' = alkyl; \; X = halogen$

In order to run the condensation reaction to a higher condensed material and to decrease the shrinkage problem, in addition to $Si(OR)_4$ $Ti(OR)_4$ was used. This is easily possible because the water-free precondensation process avoids the precipitation of TiO_2 and leads to a homogeneous Ti-containing precondensate. The use of water in the presence of $Ti(OR)_4$ very often leads to the precipitation of TiO_2, since the hydrolysis and condensation rates are far higher than that of $Si(OR)_4$ containing identical organic substituents. The overall reaction demonstrates equation (9). By addition of water to the precondensate, the epoxyring is opened and the glycol grouping is formed. The viscous is cured to compact rods from which contact lenses can be shaped by a mechanical processing. The materials have an oxygen permeability of $(13+1).10^{-11}$ ml $O_2.cm^2.ml^{-1}.s^{-1}.mm$ Hg^{-1}, a contact angle with water in the hydrated state of $(25+5)°$, a tensile strength of 2.1-3.6 $MN.m^{-2}$ and a modulus of elasticity of $(29-34).10^2$ $MN.m^{-2}$. The handling of contact lenses from these materials is very difficult, since their mechanical strength is not sufficient.

$$Ti(OR)_4 + (CH_3O)_3SiC_3H_6OCH_2\text{-CH-CH}_2 \xrightarrow[\text{R'OH}]{\text{HX}} \text{-O-Ti-O-SiC}_3H_6OCH_2\text{-CH-CH}_2$$

$$\text{-O-Ti-O-SiC}_3H_6OCH_2\text{-CH-CH}_2 \longrightarrow \text{-O-Ti-O-SiC}_3H_6OCH_2\text{-CH-CH}_2$$

(9)

R = alkyl

In order to reduce brittleness, the incorporation of linear polymerizing components should be helpful. Therefore the polymethacrylate system was chosen by reason of their mechanical properties and their very low tendency of deposition of components of the lachrymal fluid.

The realization of the incorporation of PMMA chains should be possible according to equation (10) by the use of methacryloxysilane $(RO)_3SiC_3H_6OOCC(CH_3)=CH_2$ and methylmethacrylate (MMA). Again the water-free precondensation seems to be useful as well as the use of titanium. The precondensation process (equations 7 and 8) is performed by the epoxysilane (III) methacryloxysilane

$$R = \text{glycol group containing organic radical}$$
$$R' = CH_3, C_2H_4OH$$
$$\sim = -C_3H_6OOC-$$

(10)
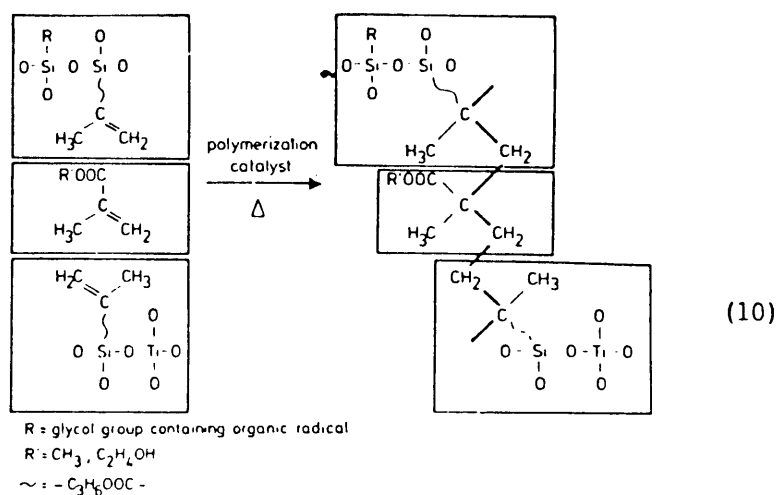
and Ti(OR)$_4$ until a viscous liquid is received. Then this viscous liquid is mixed with MMA or hydroxymethylmethacrylate (HEMA) and a polymerization catalyst and cured at temperatures of 100-130°C. This curing reaction leads to compact rods which easily can be cut into blanks which are processed to contact lenses. The properties of these materials are given in table 2. These materials unify in one and the same product all necessary mechanical, optical and surface properties for a contact lens material since the deposition test with a lachrymal simulation fluid shows that the tendency of deposition of components lachrymal fluid is very low.

Table 2. Main properties of copolymers[a] containing 20-30 mol.%
methacrylates[b], cured at 130°C

Tensile strength[c] (MN m^{-2})	4,85	- 5,15
Modulus of elasticity x 10^{-2} (MN m^{-2})	33	- 34
Mohs'hardness	3	
Shore D hardness	67	- 73
Refractive index n_D^{20} [d]	1,499	- 1,503
Contact angle with water[e] (°)	25	5
O$_2$-permeability coefficient P = 10×10^{-11} ml.O$_2$.cm^2.ml^{-1}.s^{-1}.mm Hg^{-1})	11.5	- 13.3

a) Silicate composition: 60-70 mol% epoxysilane III, 5 mol.% Ti(OR)$_4$ and 5 mol.% methacryloxysilane.

b) Methacrylates R'OOCC(CH$_3$) = CH$_2$ with R' = CH$_3$, C$_2$H$_4$OH.

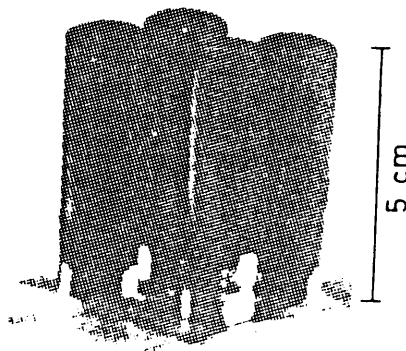Figure 5 shows a photograph of rods processed by the procedure described above.

Fig.5. Examples of monolithic condensates

4 CONLUSIONS

The investigations, carried out in order to combine inorganic and organic networks, show that it is possible to prepare a molecular scale composite material which unifies properties of non-metallic inorganic components (e.g. preparation by sol-gel processing, structure) with that of organic polymers (oxygen permeability elasticity). This leads to the conclusion that this way of material development can be successfully used for the preparation of very special materials.

5 ACKNOWLEDGEMENT

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