

PREPARATION OF MEMBRANES BASED ON HETEROPOLYSILOXANES*

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(Received October 4, 1983; accepted in revised form March 28, 1984)

Summary

Heteropolysiloxanes are a new type of material and can provide some advantages when used as membranes. The backbone consists of a siliceous network modified by the incorporation of special organofunctional groups. First results of membrane preparation from heteropolysiloxanes are presented. Variation of the composition by a choice of suitable starting materials together with proper adjustment of the reaction conditions allows tailoring of the properties of the material. This wide variability in the system can also be used advantageously for membrane preparation. For this purpose, different membrane preparation techniques can be applied. The best method for the coating of supports is reactive synthesis. This technique makes possible the preparation of membranes from monomers at the surface of a porous or nonporous support. General membrane preparation possibilities and basic properties of membranes obtained by these techniques, as well as possible applications, are described.

1. Introduction

By far the majority of membrane materials is prepared from organic polymers, since for practical use this type of material proves to be the most advantageous [1–5]. However, these materials show limited stability at high temperature, at high pressure and in organic solvents. Pure inorganic materials like glasses or ceramics have doubtless advantages with respect to these properties, but problems may result from techniques for preparation of membranes from these materials, especially with respect to thin films or anisotropic membranes [6–9]. The question arises as to whether it is possible to combine the basic advantages from both organic and inorganic materials. Heteropolysiloxanes, which are built up from inorganic and organic components containing monomers, should in principle be useful for this purpose. In this paper, some first results will be reported concerning how

*Paper presented at the 4th Symposium on Synthetic Membranes in Science and Industry, Tübingen, F.R.G., September 6–9, 1983.

far silicic acid heteropolycondensates are useful as materials for membrane preparation. The first steps in this basic work were to evaluate the general possibilities and principles of preparation, rather than the detailed characterization of the membranes.

2. Definition and synthesis principles of heteropolysiloxanes

Heteropolysiloxanes are defined by Noll [10] as compounds with a —Si—O—Si— backbone, characteristic of siloxanes, and modified either by silicon-bonded organofunctional radicals or by network-forming elements

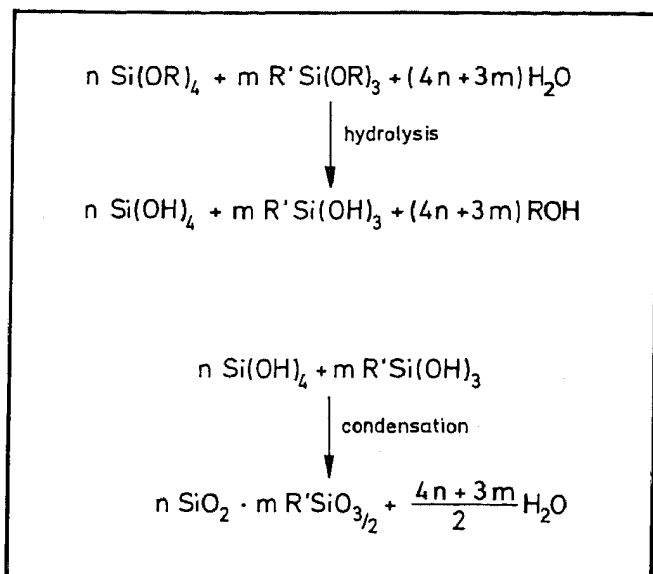


Fig. 1. Reaction scheme of hydrolysis and condensation of silicic acid derivatives.

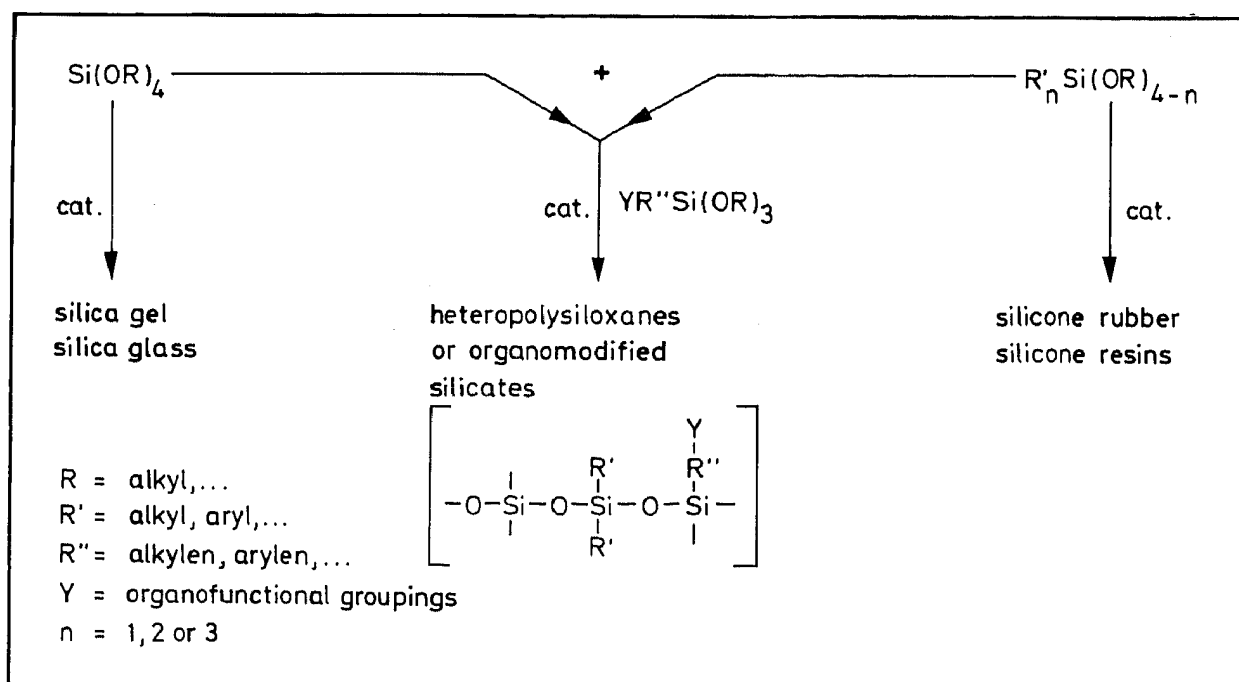


Fig. 2. Chemical deduction of heteropolysiloxanes.

(e.g., Al or Ti). Generally, they are prepared by hydrolysis and condensation of silicic acid derivatives, as shown in Fig. 1. In the simplest case this involves hydrolysis and condensation of a tetraalkoxysilane, leading to pure silica, but if, in addition to this, one or more organofunctional silanes are used as starting materials, products with properties between silicates and silicones are obtained, as outlined in Fig. 2. The hydrolysis rate is affected by hydrolysable as well as by non-hydrolysable groups [11, 12]. While the hydrolysable groups do not appear in the final product, the non-hydrolysable groups do, and influence the material properties strongly.

TABLE 1

Organic groupings as possible ligands of hydrolysable silanes; the definitions of R, R', R'' and Y are those given in Fig. 2

R	R'	R''	Y
- CH ₃	- CH ₃	- CH ₂ -	- NH ₂
- C ₂ H ₅	- C ₂ H ₅	- C ₃ H ₆ -	- COOH
- C ₄ H ₉	- C ₆ H ₅	- C ₆ H ₄ -	- COOR
		- C ₃ H ₆ -O-C ₃ H ₆ -	- C ₆ H ₄ NH ₂
		- C ₃ H ₆ -S-C ₂ H ₄ -	- CH=CH ₂
			- CH-CH ₂ \ / O

Table 1 shows a selection of variations of R, R', R'' and Y. Silanes containing these radicals are commercially available or at least easily preparable from available starting compounds. From this modular system, materials with a wide variation in properties can be built up. The additional incorporation of heteroatoms like Ti, Al or Zr leads to extended variation possibilities. Of course, suitable reaction conditions have to be established which then offer other possibilities for tailoring the material properties, as shown in Table 2. An indispensable prerequisite for any tailoring is the knowledge of how parameters affect properties; generally this has to be worked out experimentally.

3. Methods of preparation

3.1. General aspects

Since membrane materials have to separate one substrate from another, they should be permeable for the one and non-permeable for the other.

TABLE 2

Reaction parameters for heteropolysiloxane synthesis and product properties influenced by variations of these parameters

parameter	influenced properties
composition	mechanical properties
- inorganic : organic	shape
grouping ratio	porosity
	wettability
organofunctional groupings	surface properties
	adsorption
	adhesion
reaction conditions	mechanical properties
- catalyst	shape
- temperature	porosity
- solvent	microstructure

This might be (e.g., for UF purposes) achieved by using a proper pore size. If one starts to consider porous materials, the first task is to find conditions for the synthesis of such materials. Heteropolysiloxanes are able to be synthesized as either dense (silicone-like) or porous (silica-like) [13] materials; whereas the latter type is brittle, the former is very flexible.

Starting from this consideration, experiments were carried out on model systems to develop a basic knowledge about the preparation of any type of material thought to be useful as a membrane. Since in this paper the general aspects of heteropolysiloxanes will be described, no experimental details are given. It was found that there are generally valid dependences of product properties on composition, catalyst type, catalyst concentration, solvent/silane ratio and so on. As an example, a system of a linear, as well as of a three-dimensional cross-linking compound ($\text{SiO}_2/(\text{CH}_3)_2\text{SiO}$) was chosen; the influence on the porosity was determined and, as a simple means, the specific surface area was measured using the method of Brunauer, Emmett and Teller (BET). Using this example, in Figs. 3 and 4 it can be seen how strongly the composition, catalyst type and concentration can influence the specific surface area. Calculation of pore size distribution from N_2 isotherms (evaluation of the Kelvin equation) indicates microporosity if low catalyst concentrations are applied. At high concentrations ($> 1 \text{ mol/l}$), in

addition to micropores, mesopores with increasing diameters are observed, which contribute more and more to the total porosity. These results show that, in principle, it is possible to vary the microstructure in a way that may be useful for separation purposes.

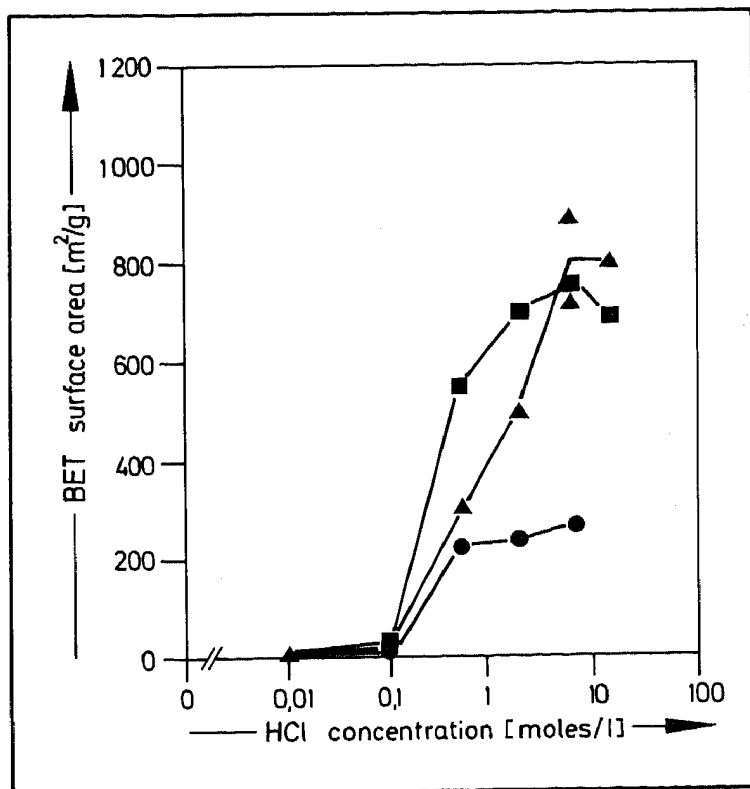


Fig. 3. Influence of composition and catalyst concentration on BET surface area of heteropolysiloxanes ($(\text{CH}_3)_2\text{SiO}/\text{SiO}_2$ weight ratio: 20:80 (▲), 40:60 (■), 60:40 (●)); catalyst HCl.

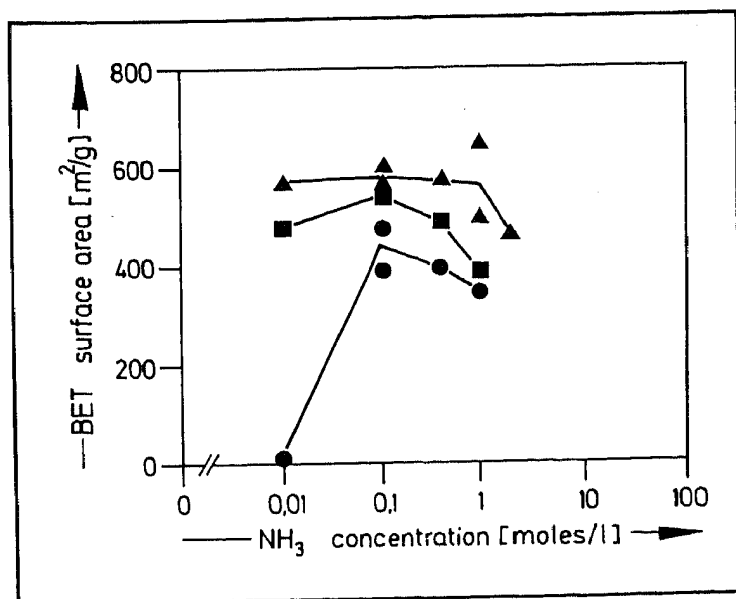


Fig. 4. Influence of composition and catalyst concentration on BET surface area of heteropolysiloxanes ($(\text{CH}_3)_2\text{SiO}/\text{SiO}_2$ weight ratio: 20:80 (▲), 40:60 (■), 60:40 (●)); catalyst NH_3 .

3.2. Bulk condensation

Since heteropolysiloxanes at higher degrees of polymerization are completely insoluble in organic solvents, there is no way that dissolved polymers can be used for membrane preparation techniques. In order to carry out preliminary experiments, it was decided to use bulk materials and cut off thin discs. The process of hydrolysis and condensation at first leads to a gel, from which monolithic pieces have to be prepared by drying. The drying is accompanied by shrinking, and the procedure has to be carried out very carefully to avoid cracks. The membranes then have to be formed by cutting and grinding. As mentioned above, mechanical properties like elasticity and brittleness can be influenced by composition variations; depending on these properties it is possible to obtain membrane discs with a thickness down to about 0.5 mm which may be used to carry out laboratory separation experiments. Figure 5 shows a photograph of some pieces of membranes obtained by this method. Significant differences are evident in the appearance of the samples. Microporous samples appear clear and transparent (sample a); with increasing pore diameter they appear lightly opaque (sample d); other samples (b, c, e) are completely white and non-transparent, representing pore size diameters of about $0.1 \mu\text{m}$ and a microstructure with ball-shaped primary particles.

Generally, it was found that higher contents of linear cross-linking structure elements like $(\text{CH}_3)_2\text{SiO}$ or $(\text{C}_6\text{H}_5)_2\text{SiO}$ lead to a higher elasticity of

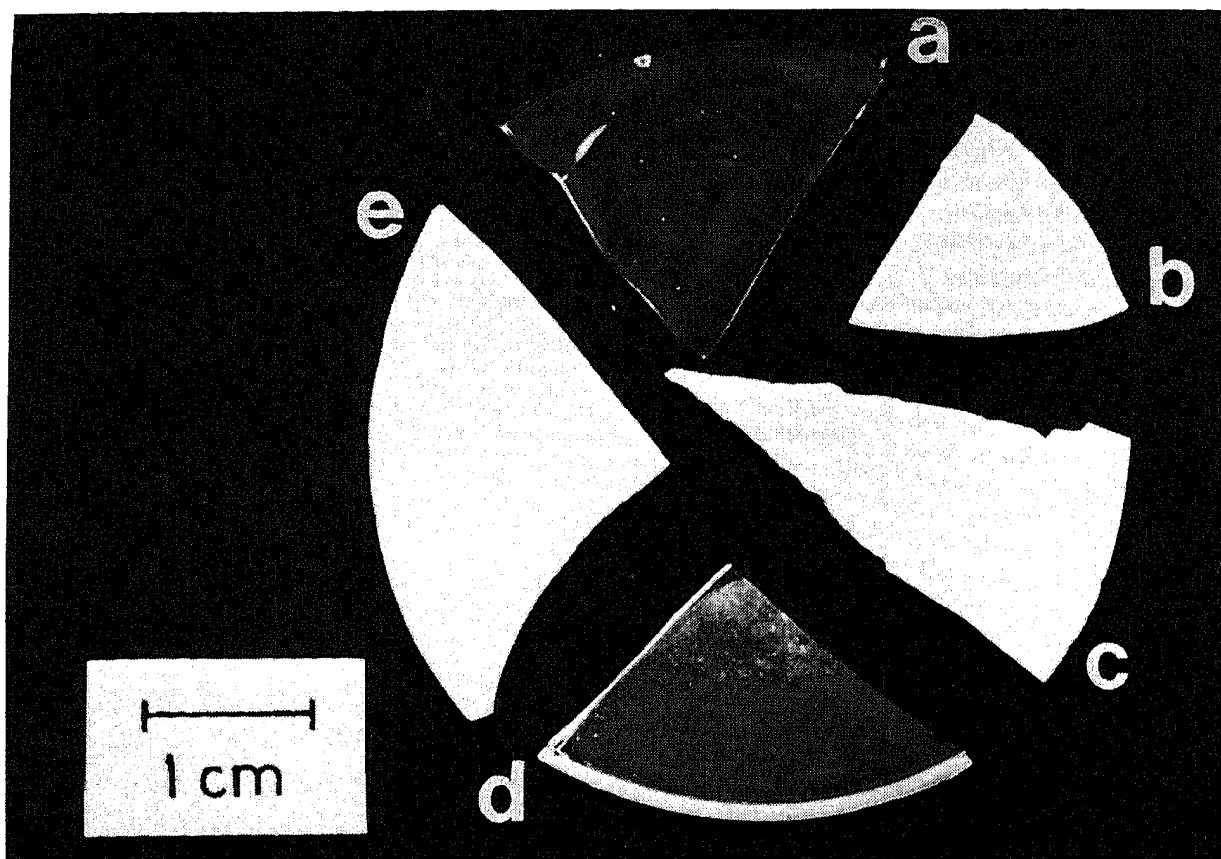


Fig. 5. Photograph of some pieces of membranes obtained via bulk condensation.

the material. Up to certain limits, increasing acid catalyst concentration results in higher bulk porosities and specific surface areas. In the case of base catalysis, the behaviour is somewhat more difficult but similar tendencies are observed. Type and quantity of the solvent and type of hydrolysable (R) and non-hydrolysable (R', R''Y) groups influence hydrolysis and condensation rates. Higher rates lead to larger pore size diameters.

Some preliminary separation measurements with different types of membranes showed significant differences in fluxes and cut-off behaviour. It can be seen that, with a microporous type of membrane of the system $(\text{CH}_3)_2\text{SiO}/\text{SiO}_2$ (Fig. 5d), fluorescein could be retained from methanolic solution almost completely. Polyvinyl alcohol could be passed up to a molecular weight of 72,000 through membranes with larger pore sizes (Fig. 5b). With organic solvents, as well as with water, no significant swelling was observed. The membranes are completely insoluble in organic solvents and resistant against acids and bases up to pH 9. With this method, membranes containing functional groups like $-\text{NH}_2$ and $-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}_2$ were synthesized; other functional groups like $-\text{COOH}$, $-\text{CHO}$, $-\text{C}_6\text{H}_4-\text{NH}_2$ and epoxy are possible.

Since the type of preparation described is not very satisfying for most practical applications, some basic experiments were carried out in order to examine whether other techniques are possible.

3.3. Casting or spraying

Since the fully condensed material (with very few exceptions) is completely insoluble, the only way to apply common techniques is to use non-fully reacted oligomers and to complete the cross-linking reaction during moulding. In these cases, precondensates can be used which are still soluble in organic solvents. In preliminary experiments with such techniques, it was found that the most difficult step was to run the condensation reaction to well-defined, reproducible oligomers. If those can be prepared, they can be dissolved in organic solvents, cast or sprayed, and then allowed to undergo a final cross-linking and membrane-forming process during solvent evaporation. This leads to membranes in the form of thin films (10–500 μm thickness) with suitable porosities. This seems to be a promising method, but it requires more data in order to develop reproducible preparation processes.

3.4. Direct reactive preparation

Analogous to the well-known interfacial polymerization of organic compounds, the hydrolysis and condensation reaction of silanes can be carried out at the interface of two immiscible liquids, one containing the silane, the other containing the catalyst (Fig. 6a). Another possibility is to force the condensation process to take place at the surface of a silane-containing liquid by transmitting the catalyst to the surface via the vapour phase (Fig. 6b). The latter technique also enables a membrane to be formed directly at the surface of a support. In this case, the support is wetted with a liquid

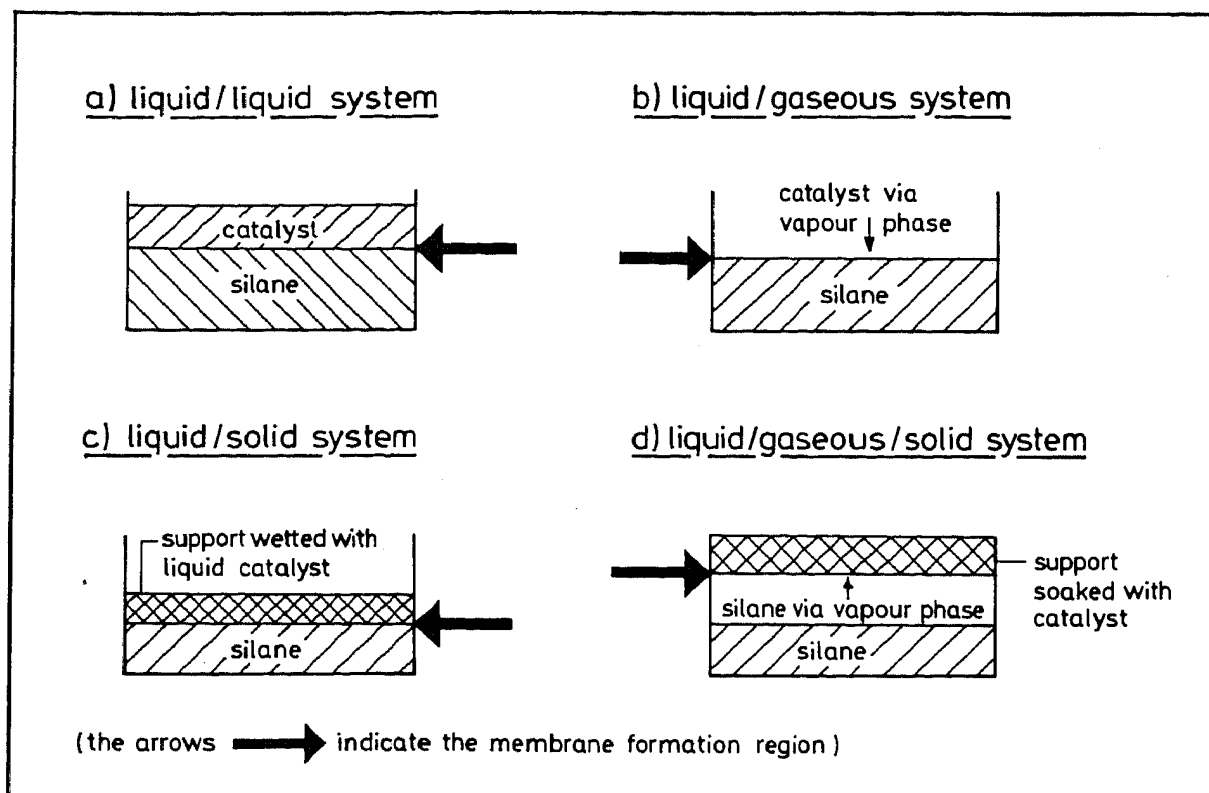


Fig. 6. Possible membrane preparation techniques using direct ("reactive") synthesis.

containing the catalyst and then placed at the surface of a silane phase immiscible with the catalyst phase (Fig. 6c). Another way is to expose the catalyst-filled support to silane vapors (Fig. 6d). Of course, many additional variations of these principles can be realized.

The application of those techniques for reacting porous silica membranes at support surfaces are described in the literature [14]. Those investigations were carried out in order to improve the filtration behaviour of a glass fiber fleece. It was necessary to coat the fleece with a thin membrane layer of high porosity in order to maintain a high gas flux rate. For the purpose of dust filtration, it was not necessary to totally avoid cracks and holes in the coating. The results showed that it is very difficult, because of the irregular surface of the fleece, to obtain a 100% coverage, but in this case the coverage was sufficient for improved filtration. For reasons of comparison, the same support was used to prepare two-component organomodified silicate membranes; however, this reaction is more complicated because the different silanes used as starting materials have different vapor pressures. It is thus necessary to adjust silane ratio and temperature of the silane bath in a proper way, or to use separate silane containers, to take the single components separately into the vapor phase and condense them together at the support surface. Again, as in the SiO_2 -coating experiments, it was possible to restrict the membrane-forming region to a narrow zone at the surface, whereas the volume of the support was free from condensation products. The membranes obtained from these experiments (silane ratio $\text{Si}(\text{OCH}_3)_4:(\text{CH}_3)_2\text{Si}$ -

$(\text{OC}_2\text{H}_5)_2 = 1:1$), directly reacted at the fleece surface, were similar to those obtained in Ref. [14]. A complete surface coverage was not possible but should not be any problem in the future, if a homogeneous support material can be used. The derived coatings were microporous and showed a better flexibility than the SiO_2 coatings.

Depending on the reaction conditions, it is also possible to build up asymmetric membranes. This is demonstrated in Fig. 7, which shows scanning electron micrographs of the two sides of a condensate obtained from the "interfacial polymerization"-like technique. In these experiments anisotropy was emphasized. The holes in the surface caused by bubbles can be avoided by improvement of the technique. The denser surface (Fig. 7a) is the membrane side facing the catalyst containing aqueous phase. The side facing the silane phase shows a more open structure (Fig. 7b).

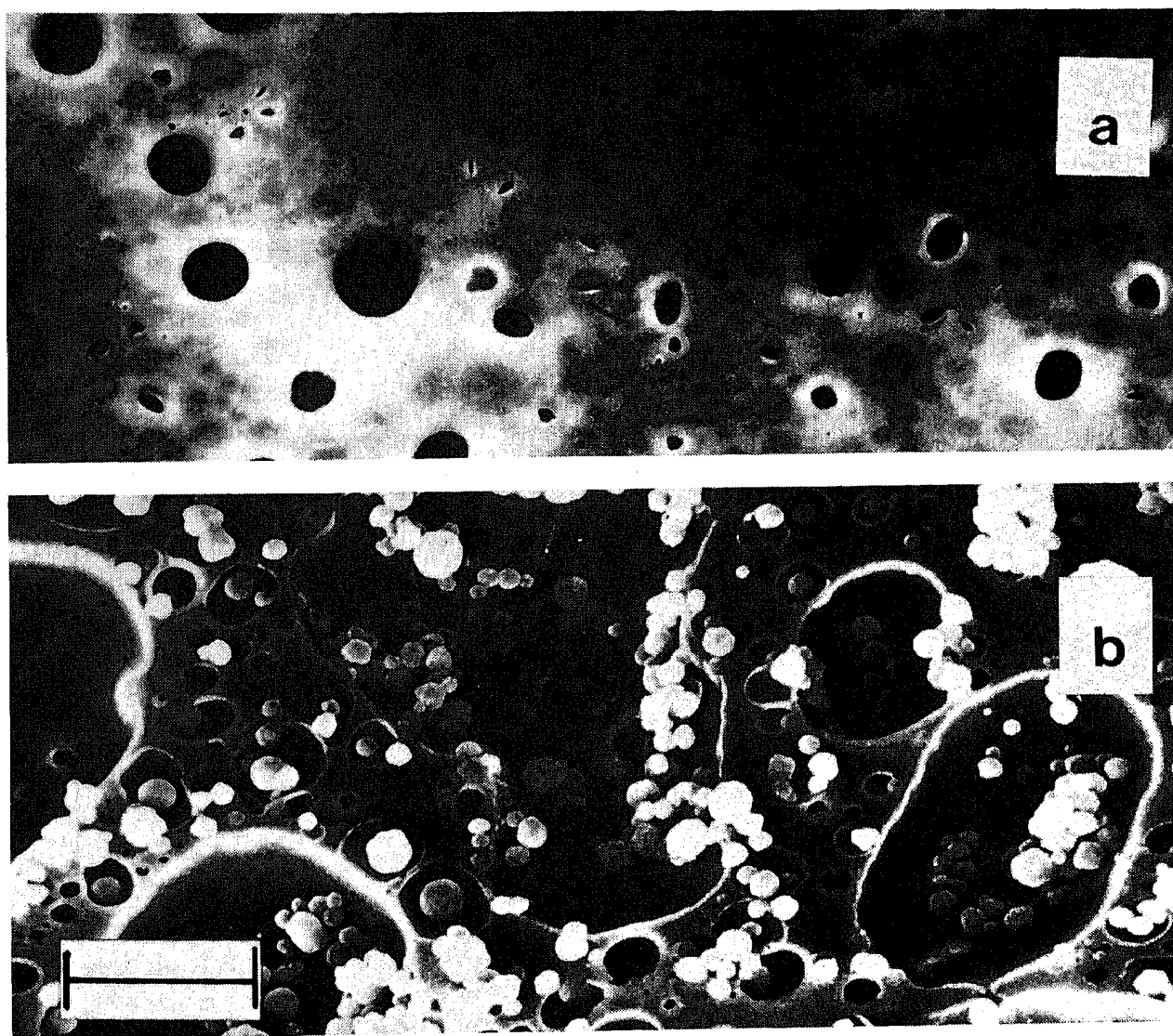


Fig. 7. Scanning electron micrographs of both sides of a membrane obtained according to the method of Fig. 6a: a: catalyst-containing phase faced side; b: silane-containing phase faced side (length of bar: $10\ \mu\text{m}$).

The most important reaction parameters affecting the membrane properties are the kind of catalyst and the concentrations of silane and catalyst. However, other reaction parameters are important, too. Table 3 summarizes, how membrane properties can be influenced by various parameters; it also indicates the magnitude of the individual influences. It can be seen how essential characteristics of the membranes like microstructure, porosity, pore size distribution, etc. can be strongly influenced — especially by variation of kind of catalyst and catalyst concentration — thus providing useful tools for tailoring membrane properties.

TABLE 3

Influence of various reaction parameters on membrane synthesis and membrane properties

membrane characteristic	influenced by	magnitude of influence [♦]
membrane building time	monomeric silanes solvent : silane ratio catalyst (kind) catalyst (concentration) temperature	m w m s n.d.
shape microstructure pore size distribution mechanical properties	composition catalyst (kind and concentration) solvent : silane ratio temperature	m s w m
chemical properties (wettability; resistance against org. solvents, acids; thermal resistance)	composition catalyst (kind and concentration)	s w

♦ w = weak ; m = medium
s = strong; n.d.= not determined

4. Discussion

The experimental results show that it is possible to prepare membranes from heteropolysiloxanes by different methods. One remarkable result is the formation of anisotropic membranes by the interfacial polycondensa-

tion technique. The question arises as to which mechanisms may cause this effect. Since the dense side faces the catalyst-containing phase, one can conclude that in the first reaction step, when high catalyst and silane concentrations occur in the boundary layer, a high reaction rate can be assumed, leading to a dense membrane layer. Although this does not correlate with the bulk condensation results, it does not necessarily have to, since interfacial reactions are not comparable with bulk reactions. Contrary to bulk condensation — where water, catalyst and silane are homogeneously distributed over the whole volume — in the case of interfacial polycondensation, H^+ and H_2O have to diffuse through the dense layer after this has been formed, resulting in a slowing down of the reaction rate, which leads to an open structure network.

It has to be taken into consideration that this method of membrane formation, contrary to most other processes, is based on a polycondensation reaction. Therefore, some significant differences to other membrane systems occur. Firstly, it is more difficult to run that complicated reaction in a way to obtain reproducible products with specific properties. Secondly, shrinking may be a serious problem under certain circumstances, especially when highly porous and, as a consequence, more brittle materials are prepared. Thirdly, the set of parameters which can be varied and which influence the reaction is increased by the use of a multicomponent system. It is therefore necessary to work out the detailed experimental conditions in order to overcome these problems.

On the other hand, these points open a wide range of possibilities for modifying the material properties of the membrane. Knowing the influence of the different parameters, it becomes possible to create membranes with very different performances using one basic principle; e.g., to adjust porosity, pore size and matrix (hydrophilic or hydrophobic), to incorporate organofunctional groups (basic or acid for ion exchange; reactive groups like $-CHO$ for immobilization of enzymes or antibodies), and to direct the formation process.

As a consequence of material properties and tailoring possibilities, application of heteropolysiloxane membranes appears to have some interesting aspects. Advantages can be expected from their insolubility and lack of swelling in organic solvents and from their resistance against high temperatures. For example, a membrane similar to that of Fig. 5e showed no remarkable changes after a heat treatment of 24 hr at $200^\circ C$. That means that heteropolysiloxanes could be used in high-temperature membrane processes or processes employing organic solvents. Further applications would seem to be possible if special organofunctional groups were to be incorporated by a condensation process. Membranes with additional functionalities can be prepared by using this method.

It has to be emphasized that, up to now, only preliminary results have been obtained, and more investigations have to be carried out concerning preparation techniques as well as membrane characterization; however, it

seems certain that these materials have a good chance of being used to advantage as membranes.

5. Conclusions

It was shown in basic investigations that heteropolysiloxanes or organo-modified silicates are materials which can be useful for preparation of membranes. They provide a wide variability in membrane preparation techniques as well as in the possibility of tailoring important membrane properties. Many different applications are possible, but for more general applications further research and development work is necessary.

Acknowledgement

The authors are very grateful to Prof. H. Scholze for many helpful discussions and to the Bundesminister für Forschung und Technologie, Federal Republic of Germany, for financial support.

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