

ORGANICALLY MODIFIED SILICATES BY THE SOL-GEL PROCESS

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ABSTRACT

The introduction of organic groups into inorganic networks by the sol-gel process opens the possibility for the preparation of new materials, and typical properties resulting from inorganic as well as from organic components may be combined. Some general aspects and different examples of material developments are reviewed.

1. INTRODUCTION

Generally solid materials are prepared by the sol-gel process by hydrolysis and condensation of metal-organic network forming and network modifying monomers [1-10]. In order to get pure inorganic polymers it is necessary to remove every organic residue, as hydrolyzing groupings or organic solvents. Therefore generally only starting compounds with totally hydrolyzable organic groups are used. In the case of silicon the orthoesters are used, since the organic residues are $\equiv\text{Si-O-}$ bonded and the $\equiv\text{Si-O-C=}$ bond easily can be hydrolyzed. The use of unhydrolyzable $\equiv\text{Si-C=}$ bonded ligands leads to organic modification of the $\equiv\text{Si-O-Si-}$ network. If $-\text{CH}_3$ or $-\text{C}_6\text{H}_5$ are used as modifying components, silicones are obtained [11-14]. The introduction of organic groups may change the material properties strongly: Substitution of one $\equiv\text{Si-O-}$ bridge (e.g. in fused silica) by one $\equiv\text{Si-CH}_3$ group (monomethylpolysiloxane resin) increases the thermal expansion coefficient from $0.5 \cdot 10^{-6}$ to about $100 \cdot 10^{-6} \cdot \text{K}^{-1}$. The question arises, whether it will be a general possibility to develop new materials by introducing other organofunctional groupings into siliceous or homologous networks. It was shown by Gullede and Andrianov that basically it is possible to obtain solids by cocondensation of organo silicon with other network forming components like Ti, Al, P and others [15, 16]. Organically modified or additional network modified silicates are called heteropolysiloxanes in this paper.

The preparation of multicomponent systems is strongly affected by the reactivity of the starting monomers and reaction conditions, since this may influence the condensation, the way of crosslinking and the material properties [17-20, 1]. The strong influence of the type of catalyst (HCl or NH_3) could be demonstrated in [21].

In connection with questions of application, technical aspects of the synthesis of materials and the manufacturing of products from these have to be taken into account. Thus, sometimes a complete line, starting with the synthesis of special monomers and ending up with the manufacturing procedure has to be built up, if new materials for practical use should be developed. In the following chapters some examples will be given to demonstrate how heteropolysiloxanes may be used to fulfill demands for very special materials.

2. RESULTS

2.1. General aspects of the introduction of organic groups

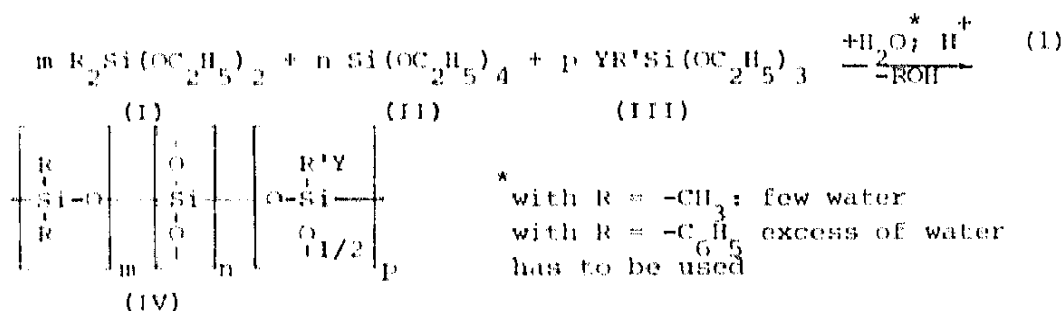
The -Si-C- bond opens the possibility to introduce any organic group Y into an inorganic network by the sol-gel process, if suitable compounds of the type $(\text{YR}')_n \text{Si}(\text{OR})_{4-n}$ ($n = 1-3$; e.g. R = alkyl; R' = alkylene) are available or preparable. If Y is a polymerizable ligand, a second type of crosslinking becomes possible: polymerisation or polyaddition. This opens an almost infinite number of variations, only from the point of view of organic modification.

As known from the preparation of glasses by the sol-gel process, if one wants to receive monolithic materials, shrinking is a serious problem. In principle, these problems should exist with heteropolysiloxanes, too. But the introduction of an organic group as network modifier could help to overcome these problems by generating a more flexible network. How far such effects can be used for suitable material preparation must be subject to investigation. As a function of the degree of condensation brittleness should be able to be varied in a wide range. If in analogy to inorganic gels, with high degrees of condensation porous intermediates appear, they might be used as materials, too [22, 23]. On the other hand, low degrees of polymerization, in connection with organic residues should result in good solubilities in organic solvents and, if the shrinking problem is overcome, useful materials for coatings should be preparable.

2.2. Examples of material development

2.2.1. Special coatings

The covalent coupling of biochemical compounds is of interest from different reasons: Immobilization of enzymes is widely used in the field of bioengineering. The immobilization of antibodies is a powerful tool in medical diagnosis. Immobilized antibodies under certain circumstances are able to bind specifically the antigen against which they are generated. If hormones to be analyzed are used as antigens, they can be separated from other serum proteins by the antibody binding and simultaneously be determined, as described in [24-26]. The important step of covalent antibody immobilization requires proper surfaces. Reactive surfaces could be prepared by cocondensation of $\text{R}_2\text{Si}(\text{OC}_2\text{H}_5)_2$, $\text{Si}(\text{OC}_2\text{H}_5)_4$ and $\text{YR}'\text{Si}(\text{OC}_2\text{H}_5)_3$. Y is an organofunctional group. Therefore $-(\text{CH}_2)_3\text{NH}_2$, $-(\text{CH}_2)_3\text{NHCO}-\langle\text{O}\rangle-\text{NH}_2$, $-(\text{CH}_2)_3\text{S}(\text{CH}_2)_2\text{CHO}$, $-(\text{CH}_2)_3\text{S}(\text{CH}_2)_2\text{CH}_2\text{OH}$ and $-(\text{CH}_2)_3\text{SH}$ were used. R is $-\text{CH}_3$ or $-\text{C}_6\text{H}_5$, R' = alkylene. The reaction was carried out according to eq.(1).



geneous dense layers, (II) in order to get insoluble solids after coating and (III) provides the reactive surface groups. The presence of Y at the surface was proved by surface analysis. In the case of $R = -CH_3$ reactive, non fully condensed prepolymers had to be formed by using understoichiometric addition of water. Excess water led to insoluble materials. After coating hot water treatment accomplished condensation; $-C_6H_5$ groups led to water resistant materials soluble in most organic solvents. Best results for the bonding of T3 (triiodine thyronine) antibodies were achieved by use of $-CHO$ and $-CH_2OH$ group containing coatings.

Since the inorganic sol-gel process requires high curing temperatures for forming dense films, this procedure cannot be applied for building up layers onto organic polymers in order to improve mechanical surface properties. It is an important question, how far low temperature curing coatings with improved properties like scratch resistance may be prepared. In [27] it could be shown that the introduction of titania reduces the shrinkage problem of a $SiO_2/CH_2OHCHOHCH_2O(CH_2)_3SiO_{3/2}$ cocondensate substantially. Understoichiometric (with respect to hydrolysis) addition of water leads to viscous liquids which can be used as coating materials and cured at 90-120°C to clear films showing a good scratch resistance in the Erichson test (the surface is scratched by a Vickers diamond with different loads).

Curing temperature and time are very important with respect to receiving good scratch resistance. Thus, it was possible to develop coatings which did not show any scratches with loadings up to 200 g when applied as thick layers ($>50 \mu m$). The dependence of scratch resistance as a function of curing temperature is shown in figure 1. For example, organic polymers like acryl glasses or polycarbonates are scratched by loadings >15 g. Lowering the content of inorganic compounds leads to softer, less scratch resistant

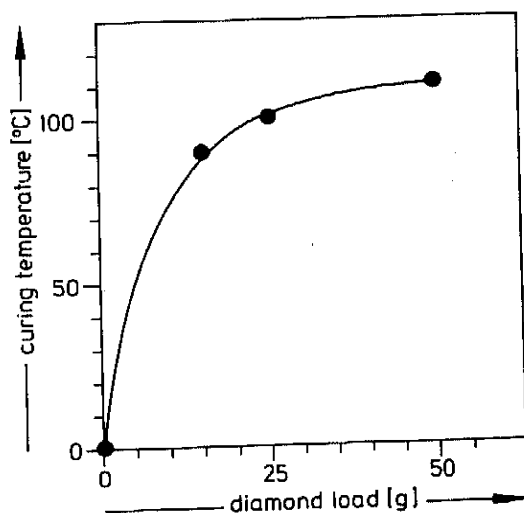


FIG.1. Dependence of scratch resistance on curing temperature (Erichsen scratch test); the curve represents the maximum load without causing scratches; curing time: 30 min; material composition: SiO_2 : 30 mole%; TiO_2 : 20 mole%; $[OCH_2CHCH_2O(CH_2)_3SiO_{3/2}]$: 50 mole%; thickness of the coating: 30 μm ; coating procedure: dip coating; substrate: different organic polymers (e.g. polycarbonate, PMMA, CR 39)

materials. It is not clear how structural factors, especially the incorporation of titania, may be related to mechanical properties. Since the bulk material is flexible (modulus of elasticity about $30 \cdot 10^2 \text{ MN.m}^{-2}$), it seems reasonable that this type of scratch resistance may be a compromise between hardness and flexibility. The best results were obtained with epoxide ligands so far, but the role of the epoxide grouping is not clear, too. If the epoxide is cleaved by addition of water, wettable materials with an antifogging effect are achievable [28]. Measurements show that the contact angle in a simple system decreases to about 20° . However, these systems are not optimized yet.

As pointed out above in connection with the coatings for immobilization of antibodies, the use of diphenylsiloxanes as network formers leads to materials soluble in organic solvents. This is due to the steric hindrance of the phenyl groups lowering the degree of polymerization and leading to reduced chain lengths and, as a consequence, to soluble polymers [14]. Moreover, it could be proved that by use of phenyl groups, =SiOH containing thermoplastic silicates may be developed [29]. This type of thermoplastic polymer forms moisture resistant seals to glass surfaces, if they are sealed onto glass surfaces by a hot melt process. Therefore, aluminum foils are coated with the polymer (thickness about $10 \mu\text{m}$). In order to get proper seals the OH group content of the material has to be adjusted by thermal treatment (see fig.2). The behaviour is interpreted by the formation of =Si-O-Si= bridges with glass surface silanol groups.

Based on these results a technical procedure for sealing glass containers is under development.

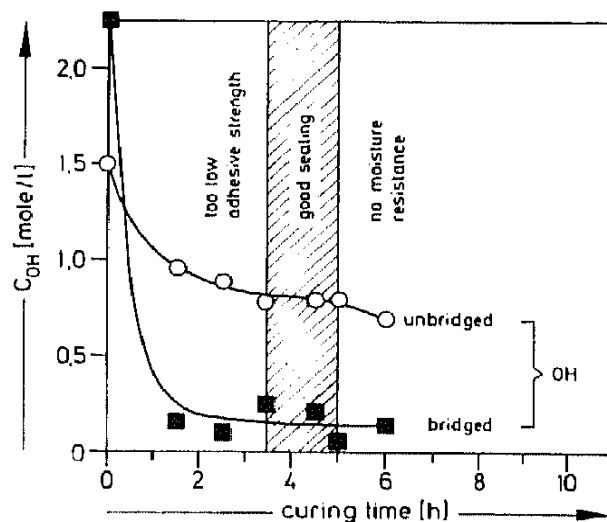


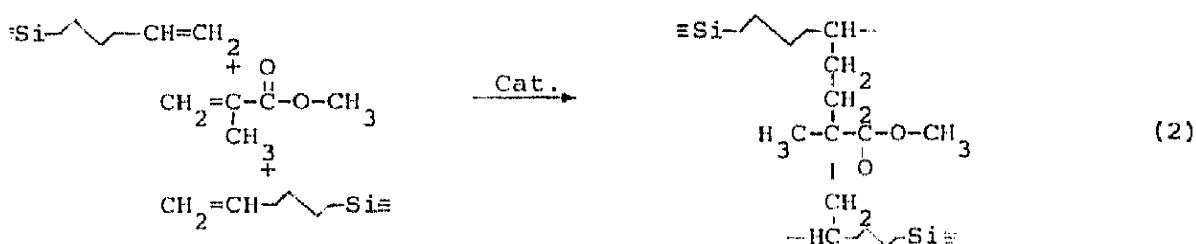
FIG.2. Content of OH groups as a function of tempering time at 150°C . Composition: 65 mole% $(\text{C}_6\text{H}_5)_2\text{SiO}$; 35 mole% $(\text{CH}_3)(\text{CH}_2=\text{CH})\text{SiO}$; OH groups monitored by quantitative IR spectroscopy

For other purposes, e.g. filtration or membrane processes, porous films should be of interest. In order to get porous films a high degree of cross-linking is necessary to prevent collapsing of pores formed during condensation. Therefore the content of organic groups is limited, depending on type of group, reaction condition and type of other components. Low contents of organic groups increase the shrinking problem. Experiments using common membrane preparation techniques like casting showed that it is very difficult to get at least small pieces of thin films without cracks. Better results were obtained by using procedures like interfacial polymerization [30-32]. It is possible to receive membranes by using two immiscible liquids, one containing water and the catalyst and the other containing the silane. These materials are especially resistant against organic solvents and stable against temperatures up to 200°C depending on the organic functions. Another type of reaction was applied for the coating of porous supports, like glass fiber fleeces, with a microporous membrane using the components $(\text{CH}_3)_2\text{SiO}$ and SiO_2 . Therefore the HCl containing fleece was exposed to a $(\text{CH}_3)_2\text{Si}(\text{OC}_2\text{H}_5)_2$ and $\text{Si}(\text{OC}_2\text{H}_5)_4$ containing vapor phase and the membrane reacted directly onto the fleece surface. By this it was possible to improve the filtration behaviour of the filter substantially [32].

2.2. Bulk materials

2.2.1. Dense products

As indicated above, the introduction of organic function into inorganic network may lead to more flexible products and helps to overcome the difficulties of shrinking. Furthermore, this may lead to material properties more related to organic polymers. In the sol-gel process the loss of water during condensation and porous intermediates cause shrinking during the densification process. By this high temperatures and pressures have to be applied to obtain monolithic products. Theoretically low temperature moldable products should be achievable by additional introducing of a second principle of crosslinking which allows curing without any loss of components. Thus, a multicomponent system, where the siliceous crosslinking by condensation does not lead to a brittle solid because of the presence of non-siliceous monomers, is able to be cured e.g. by polymerization according to (2), as shown in [27].



This principle can be realized with other polymerizable substituents, too. Thus, moldable condensates can be cured by using polymerization catalysts (heat or UV initiated). It could be experimentally proved that this method leads to solid products almost without shrinking. In addition to this increased tensile strength in comparison with the unpolymerized sample is observed (table 1).

TABLE 1. Effect of polymerization crosslinking on some material properties

	Composition I* (non-polymerized)	Composition II** (polymerized)
Tensile strength ($\text{MN}\cdot\text{m}^{-2}$) ₂	2.15	5.15
Modulus of elasticity: 10^2 ($\text{MN}\cdot\text{m}^{-2}$)	29	34
Refractive index: n_D^{20}	1.525	1.503
Mohs' hardness	3-4	3

* I: 20 mole% $\text{Ti}(\text{OR})_4$ (a) and 80 mole% $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{OCH}_2\text{CH}(\text{CH}_3)\text{O}^1$ (b);
 ** II: 5 mole% (a); 60 mole% (b); 5 mole% $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{OOC}(\text{CH}_3)-\text{CH}_2$;
 30 mole% $\text{CH}_3\text{OOC}(\text{CH}_3)=\text{CH}_2$

2.2.2. Porous materials

Porous materials play an important role in different fields and are used for very different purposes: As insulating materials, adsorbents, carriers for catalysts and others. There are many ways to generate porosity, e.g. foaming, sintering of powders, precipitation of gels from solution. The gel formation by the sol-gel process in many cases leads to porous intermediates. Porous intermediates may be of interest, if they can be tailored for special applications. Depending on the application special demands have to be fulfilled, if adsorbents are considered: The capacity with respect to the adsorbate has to be high and the interaction strong enough, the adsorption or desorption kinetics should be quick. Organically modified gels

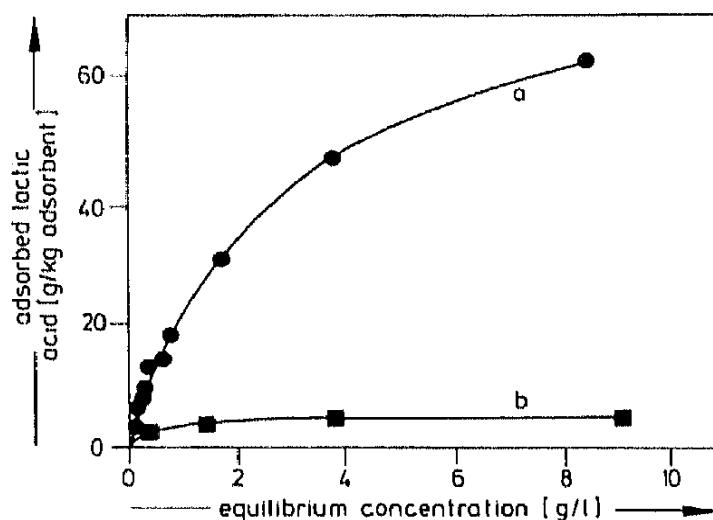


FIG.3. Adsorption isotherms of aqueous solutions of lactic acid. a: adsorbent from $\text{Si}(\text{OC}_2\text{H}_5)_4$ and $(\text{C}_2\text{H}_5\text{O})_3\text{Si}(\text{CH}_2)_3\text{NH}_2$ with $8 \cdot 10^{-5}$ mole $-\text{NH}_2/\text{g}$; BET surface = $350 \text{ m}^2/\text{g}$. b: silica gel; BET surface = $500 \text{ m}^2/\text{g}$.

allow to introduce special adsorbent-adsorbate interaction mechanisms by a simple one step reaction from the monomers to the solids. As described in [30], the content of organic groups must not exceed certain limits. Pore size and specific surface area can be varied by reaction conditions, especially by the choice type and concentration of catalysts, e.g. HCl or NH_3 [33]. Thus, special adsorbents for adsorption of lactic acid show the effect of introducing amino groups in comparison to pure silica gel (fig.3): The results show that it is possible to obtain good adsorption of difficult adsorptives by adapting the system adsorbent/adsorbate to the special problem.

Other investigations showed that by optimizing pore size distribution and number and type of organofunctional groups, carrier for enzymes catalyzed reactions could be optimized. Thus, it could be demonstrated for different enzymes the existence of an optimal surface density of covalent coupling groups.

Microstructure does not only influence the adsorptive behaviour of porous materials, but also the mechanical properties, e.g. abrasion properties. Materials of high porosity generally are not good abrasives in the sense of a long service life. But for special applications, e.g. for grinding the human skin, soft abrasives are necessary. Therefore, especially if a well defined abrasion behaviour is required, it seems reasonable to synthesize such materials from monomers which can generate different properties in the polymer. Thus, $(\text{CH}_3)_2\text{Si}(\text{OC}_2\text{H}_5)_2$ was used as starting material for the "soft" and $\text{Si}(\text{OC}_2\text{H}_5)_4$ for the "hard" component.

By optimizing composition and reaction conditions it was possible to develop an abrasive for an acne preparation which prevents hurting of the skin reliably [21,33,34]. Figure 4 shows the abrasion behaviour as a function of composition, as it was received by a specially developed, skin adapted abrasion test.

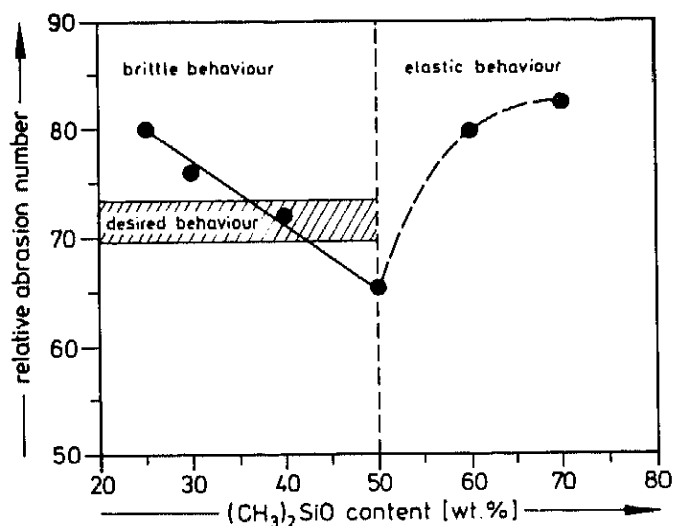


FIG.4. Abrasion test of porous materials of the composition $(\text{CH}_3)_2\text{SiO}:\text{SiO}_2$. Starting grain size: 0.3-0.4 mm.

3. CONCLUSIONS

The introduction of organic functionalities into inorganic networks by the sol-gel method seems to be a useful tool in order to prepare new materials. Examples show that materials with interesting properties for practical application can be prepared. One prerequisite for the preparation of taylor-made materials is the knowledge of the possible influences of composition and reaction conditions on the material properties. A very helpful mean would be the knowledge on structural details of the new polymers. In spite of these limitations the construction principles of these materials open almost unlimited possibilities of synthesizing new materials for new applications.

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5. REFERENCES

- [1] H. Dislich, *Angew. Chem.* **83**, 428-435 (1971).
- [2] R. Roy, *J. Amer. Cer. Soc.* **52**, 344 (1969).
- [3] K. S. Mazdizyasni, R. T. Dolloff, and J. S. Smith, II, *J. Amer. Cer. Soc.* **52**, 523-526 (1969).
- [4] S. P. Mukherjee and J. Zarzycki, *J. Mater. Sci.* **11**, 341-355 (1976).
- [5] B. E. Yoldas, *J. Mater. Sci.* **12**, 1203-1208 (1977).
- [6] K. Kamiya and S. Sakka, *Res. Rep. Fac. Eng. Mie Univ.* **2**, 87-104 (1977).
- [7] M. Nogami and Y. Moriya, *J. Non-Cryst. Solids* **37**, 191-201 (1980).
- [8] G. Carturan, V. Gottardi, and M. Graziani, *J. Non-Cryst. Solids* **29**, 41-48 (1978).
- [9] S. Sakka and K. Kamiya, *J. Non-Cryst. Solids* **43**, 403-421 (1980).
- [10] J. D. Mackenzie, *J. Non-Cryst. Solids* **48**, 1-10 (1981).
- [11] A. Ladenburg, *Ann.* **173**, 143-166 (1874).
- [12] E. G. Rochow in: *An Introduction to the Chemistry of the Silicones*. J. Wiley and Sons, New York 1951.
- [13] K. A. Andrianov in: *Organic Silicon Compounds* (State Scientific Publishing House for Chemical Literature, Moscow 1955).
- [14] W. Noll in: *Chemie und Technologie der Silicone*. 2. Auflage (Verlag Chemie, Weinheim 1968).
- [15] H. C. Gullledge, *US. Pat.* **2,512,058**, 20.6.1950.
- [16] K. A. Andrianov and A. A. Zhdanov, *J. Polym. Sci.* **XXX**, 513-524 (1958).
- [17] E. Åkerman, *Acta Chem. Scand.* **11**, 298-305 (1957).
- [18] R. Aelion, A. Loebel, and F. Eirich, *J. Amer. Chem. Soc.* **72**, 5705-5712 (1950).
- [19] H. Schmidt, H. Scholze, and A. Kaiser, *J. Non-Cryst. Solids* **48**, 65-77 (1981).
- [20] L. H. Sommer, C. F. Frye, M. C. Muslof, G. A. Parker, P. G. Rodewald, K. W. Michael, Y. Okaya, and P. Pepinski, *J. Amer. Chem. Soc.* **83**, 2210-2212 (1961).
- [21] H. Schmidt, H. Scholze, and A. Kaiser, *J. Non-Cryst. Solids* **63**, 1-11 (1984).

- [22] G.Carturan, G.Facchin, V.Gottardi, M.Guglielmi, and G.Navazio, *J.Non-Cryst.Solids* 48, 219-226 (1982).
- [23] G.Carturan, *J.Non-Cryst.Solids* (1984) in press.
- [24] H.Schmidt and O.v.Stetten, DP 27 58 507, 28.12.1977.
- [25] H.Schmidt and H.Scholze, Ger.Offen. 2,758,414, 12.7.1979.
- [26] H.Schmidt, O.v.Stetten, G.Kellermann, H.Patzelt, and W.Naegele, *Proc. Radioimmunoassay and Related Procedures in Medicine 1982*, 111-121, Vienna 1982.
- [27] H.Schmidt and G.Philipp, *J.Non-Cryst.Solids* 63, 283-292 (1984).
- [28] H.Schmidt, G.Philipp, and C.F.Kreiner, Dt.Offen. 31 43 820, 11.5.1983.
- [29] H.Schmidt, G.Tünker, and H.Scholze, DP 30 11 761, 20.3.1980.
- [30] H.Schmidt and H.Scholze, DP 27 58 415, 12.7.1979.
- [31] H.Scholze, H.Schmidt, and H.Böttner, Ger.Offen. 29 25 969, 29.1.1981.
- [32] A.Kaiser and H.Schmidt, *J.Non-Cryst.Solids* 63, 261-271 (1984).
- [33] H.Schmidt, A.Kaiser, H.Patzelt, and H.Scholze, *J.Physique* 43, 275-278 (1982).
- [34] H.E.Kompa, H.Franz, K.D.Wiedey, H.Schmidt, A.Kaiser, and H.Patzelt, *Ärztliche Kosmetologie* 13, 193-200 (1983).