Crosslinking of Alkylpolysiloxane Films on Various Types of Glass Surfaces Including Fused Silica Using γ-Radiation of a 60Co-Source. Comparison to Crosslinking by Thermal Peroxid Treatment

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Summary
Crosslinking of alkylpolysiloxane stationary phases, especially in thick film capillary columns, is useful for the homogenous coating of fused silica and pretreated alkali glass surfaces. The films of the stationary liquid are immobilized against solvent rinsing using CH₂Cl₂, pentane, and acetone, and maintain homogeneity even at high temperature. Various doses of γ-radiation from a 60Co-source were used for the crosslinking instead of the thermal peroxid treatment recently described by other authors. The effect of the γ-radiation crosslinking procedure was investigated in comparison to the peroxid method in regard of: decrease of stationary phase content by solvent rinsing, separation efficiency, tailing behaviour, and bleeding of the columns obtained. Similar results as with the cumylperoxid treatment were achieved using the γ-radiation method. By γ-radiation no polar functional groups or molecules are introduced into the stationary phase, however, as with the peroxid method. Less than 20% of the various stationary liquids are usually removed from the columns by solvent rinsing after crosslinking using both methods depending on the doses of radiation and the cumylperoxid concentration applied respectively.

Introduction
To produce capillary columns, various types of glass surfaces have been coated with different stationary liquids in the past 10 years. Alkali and borosilicate glass were the preferred materials for capillaries of the desired length, the internal diameter and wall-thickness because of low production costs, simple technology of drawing, easy chemical surface treatment, such as leaching or dealkalization, and especially for the reason of easy deactivation and coating with many stationary liquids that are usually applied in the practice of capillary GC. The fused silica material, recently introduced to GC-column technology by R. Dandeneau [1], consists of SiO₂ of very high purity. The capillaries produced with this material are not fragile like the common glass capillaries. Because of thin walls, the general properties of the material and because of a high temperature stable polyimid-coating of the outer surface, such capillaries are flexible. For proper mounting of the column to the instrument, the column ends need not to be straightened in a flame when the common connection techniques are being used.

Undeactivated and deactivated fused silica surfaces can be easily coated with alkylpolysiloxanes if they do not contain strongly polar groups. Generally, polar stationary liquids cannot be easily fixed onto those surfaces, with the exception of polyethyleneglycols, such as Carbowax 20 M. Difficulties also arise with non or weakly stationary liquids, such as Squalane, Apiezons, etc. The alkylpolysiloxane columns with fused silica or classical glass sorts being the support material have become of great importance and appreciation. The high separation efficiency which can principally be achieved even with relatively short columns and the excellent surface deactivations that are attainable with fused silica (but also with well pre-treated alkali glass capillaries) led to the preferred application of non or weakly polar stationary phases, e.g., alkylpolysiloxanes.

However, practical difficulties arise in the use of alkylpolysiloxanes with samples containing for example volatile highly polar solutes, that have a poor solubility in such non-polar stationary phases and exhibit a strong adsorption on surfaces that are poorly deactivated or covered by the stationary phase. Thick films of the stationary phase and lower column temperatures are also necessary to achieve sufficiently high k' and good selectivities. Thick film columns which may, according to the theory, exhibit a large contribution of the C₅ term to HETP and therefore may show lower separation efficiencies, however, suffer from other restrictions as well. Except for silicon gums, thick films (> 0.5 μm) cannot be fixed homogeneously to the surface and may be dehomogenized (droplet formation) at elevated temperature and by displacement caused by
solvents or the other sample constituents. Moreover, thick films mean high retentions for less volatile components and require high column temperatures for reasonable analysis times which may be too high for thermal chemical stability of the molecules of the stationary liquid. The film stability, attainable with the usual alkylpolysiloxanes, increases with their molecular weight and viscosity ("gum"-phases) and decreases with the introduction of polar groups into the molecule. Alkylpolysiloxanes of the "gum"-phase-type (OV 1, SE 30, SE 52, SE 54, OV 1701) can therefore be easily fixed to the various common types of glass surfaces, even without anchoring the polymeric molecules to the surface by chemical bonding. Chemical bonding in the first instance by -Si-O-Si-bonds was claimed to be important for film fixation by various authors. Compare Madani et al. [2], Blomberg et al. [3].

The presence and the effect of chemical bonding is difficult to prove by physical (preferably spectroscopic) methods of surface investigation and even more from chromatographic measurements. In our opinion, which is based on chromatographic experiences only, the widely applied deactivation methods "persilylation" [4], "d4" [5], and PSD [6] (polysiloxane degradation) lead already to chemical bonding to the usual surfaces. It can also be presumed that, through reaction between stationary liquid and support surface, silanol groups are removed from the surface and are no longer effective in regard to adsorption and tailing. The alkyl-groups R of siloxane structures are bonded to the surface via -Si-O-Si-bonds of

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\begin{align*}
\text{CH}_3 & \quad | \\
-\text{Si-O-Si-R} & \quad | \\
\text{CH}_3
\end{align*}
\]

arrangements, thereby. The increase of the viscosity of alkylpolysiloxanes improves already the film fixation, as can be concluded from the experiences with the coating by so-called "gum"-phases. The increase of the viscosity may be due to higher molecular weight and also by "crosslinking" via -Si-O-Si-bonds achieved through the usual polymerization procedure. According to this, several authors made recently use of the well known procedure of alkylpolysiloxane "crosslinking" by C-C-bonds between the alkyl-groups using peroxids to increase the viscosity and to decrease the solubility of the stationary liquid in solvents that are commonly used in gas chromatography, see Grob [8, 10-12], Sandra et al. [9], Lee et al. [13]. As far as we are informed, only the thermal peroxid treatment has been applied for "crosslinking", up to now. In our laboratories, similar experiments were carried out in parallel to the work of the authors mentioned before. However, we have also used "crosslinking" by γ-radiation originating from a 60Co-source and we intend to report our results with both applications of the "cross-linking" methods for reasons of comparison, systematically regarding film stability, bleeding, deactivation effects, and extractability of stationary liquid by solvents. The latter may also be important for the removal of non-volatile contaminations by solvent rinsing, which may have accumulated during practical work, to restore the performance of the column in regard to tailing behaviour and separation efficiency.

**Experimental**

"Crosslinking" by Peroxid Decomposition

Undeactivated and dealkalized PSD-deactivated alkali glass as much as undeactivated and PSD-deactivated fused silica (origin HP) were coated with various alkylpolysiloxanes containing varied concentrations of peroxids (0.5 %), such as dibenzoyperoxid2 and dicumylperoxid2. With dicumylperoxid "crosslinking" was simply effected by the increase of temperature up to 280 °C. The "crosslinked" coatings obtained were tested chromatographically by measurements with polarity mixtures of the Grob type or with the so called "Ring"-test. This "Ring"-test contains: phenol, aniline, 1-octanol, decylamine, C10- and C13-n-alkanes.

"Crosslinking" by γ-Radiation

Undeactivated and dealkalized alkali glass as well as fused silica capillaries were coated as usual with the dynamic or static method, but preferably by the latter method. The coated capillaries were exposed to the γ-radiation of a Co-source, available at the Max-Planck-Institut for Strahlenchemie, in Mühlheim-Ruhr, for 2 to 3 hours. 3 Mrad of γ-radiation proved to be sufficient for these experiments. At the beginning of our experiments various solvents of different polarity (n-pentane, methylenechloride, acetone) were used in the given sequence for rinsing of the columns after the "crosslinking" procedure. The aim of solvent rinsing was to prove the success of the "crosslinking", i.e., the immobilization of the stationary liquid, but also to remove polar decomposition products of the peroxids applied for the "crosslinking" and other polar contaminations contained in peroxids of low purity which could deteriorate the tailing behaviour of the columns obtained. The decomposition products of the peroxids cannot be removed by rinsing, not even with polar solvents, as can be seen from the gas chromatograms shown below. For the immobilization test with the non or weakly polar alkylpolysiloxanes that do not contain polar functional groups such as CN, only the rinsing with n-pentane proved to be sufficient, however, whereas for more polar siloxanes polar solvents should be applied for the testing. By measuring the k'-value of a standard compound (n-nonane) at a defined column temperature (80 °C), relative data on the stationary phase contents of the various columns, before and after the rinsing procedure were obtained.

After the procedure of "crosslinking" and solvent rinsing, the chromatographic performance of the columns obtained, was tested for:

Tailing behaviour : Separation of Grob and "Ring"-test, using temperature programs.

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2 Origin: ElfA, Oxychemie, Zürich, Switzerland.
3 This test had originally been developed for a round robin test, about capillary columns and sampling performance, organized at the 4th Hindelang Symposium, 1981.