BULLETIN
OF THE KOREAN CHEMICAL SOCIETY

VOLUME 8, NUMBER 3
JUNE 20, 1987

BKCS 8(3) 133-224 (1987)
ISSN 0253-2964

Immobilization of Polysiloxane Liquid Phase on the Gas Chromatographic Solid Supports via *In-Situ* Cross-Linking

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Polysiloxane SE-54 liquid phase was immobilized on the support surface as coated in thin film via in-situ cross-linking. The cross-linking between liquid molecules was initiated by dicumylperoxide. Among the supports investigated, only Chromosorb W provided the cross-linkable surface. The optimal in-situ cross-linking was achieved when Chromosorb W was coated with 5% (w/w) SE-54 and cross-linked with 1% (w/w) dicumylperoxide. The cross-linked support was useful for the trace analysis as well as for the trace enrichment.

Introduction

Conventional gas chromatographic columns, either packed or capillary, have been prepared by depositing stationary liquid phases on the support surfaces as homogeneous thin films. The liquid films are only held mechanically on the supports and their integrity is thus easily damaged upon heating and by solvents or polar compounds contained in samples.

If the liquid film is chemically immobilized on its support, it will become thermally stable and insoluble in common solvents. Thus, it will withstand various strains. The column efficiency will also be relatively unchanged since there is less risk of phase-rearrangement by heat, and phase-stripping by solvents. The column performance will be easily rejuvenated by rinsing out non-volatile contaminants from an used column with appropriate solvents.

During the last two decades, much work has been undertaken in the method development of preparing immobilized phase columns for improving the stability of liquid films. This efforts culminated with the advent of immobilized phase columns of different polarity. Gas chromatographic capability is thus greatly expanded for the analysis of polar, thermally labile, and high molecular weight compounds.

At present liquid films are immobilized mainly by two methods: chemical bonding and in-situ cross-linking. Chemical bonding is based on the condensation reaction of the stationary liquid phases with silanol groups on the surfaces of silicic supports such as silica gel, diatomaceous earth or glass bead, forming either Si-O-C or Si-O-Si bonds.

The silicate ester (Si-O-C) bonded phase packings (BPPs) have been prepared by bonding alcohols.[1,2] They have, however, been reported to possess low thermal and hydrolytic stability.

Thermally more stable siloxane (Si-O-Si) BPPs were prepared by bonding silicone monomers to the support surfaces, followed by the in-situ polymerization of the bonded monomers.[3-6] Cyclic silicone polymers were reported to be good candidates for the synthesis of siloxane BPPs.[7] Various siloxane BPPs are now used for the trace analysis of environmental samples.

Siloxane BPPs, though thermally stable, are chemically labile toward acids and bases. Moreover, the preparation procedures involve relatively complicated and laborious steps. In-situ cross-linking was thus introduced as the simpler approach to the immobilization of liquid films on the capillary columns.[8-20] This has turned out to be a fruitful approach in capillary gas chromatography.

In-situ cross-linking is based on the free radical initiated chemical bonding between vinyl or methyl groups of polysiloxane chains of silicone gums as coated film on the support surface, forming Si-C-C-Si bonds into three-dimensional polymer which is no longer soluble in solvents.

Si-C-C-Si bonds are chemically more stable than Si-O-Si bonds and thus more suitable for polar samples such as drugs, polycyclic aromatics and pesticides.[17-20]

Free radical formed from organic peroxides[8-13] and azocompounds[16], or free radicals induced by γ-radiation,[14] accelerated electron[15]or ozone[17] were reported to be effective for the in-situ free radical cross-linking. Among the peroxides, dicumylperoxide (DCUP) has been extensively used as the radical generator because of its mild reactivity.

Recently, the free radical initiated cross-linking using DCUP has been applied to the immobilization of nonpolar phase SE-54 on the surface of Chromosorb W.[21] This packing material was found to be stable up to 280°C when used as an analytical packed column.

In this report, the optimization of in-situ free radical cross-linking with DCUP for the preparation of the immobilized SE-54 packing material with good chromatographic performance is described. Its applications to the trace analysis as well as to the trace enrichment are presented. It was desired also to block active sites of molecular sieve by this simple reaction without resorting to the sophisticated procedures of surface deactivation, and to fix the liquid film on the glass bead having inherently poor coatable surface.

Experimental

Materials and Reagents. Chromosorb W, 100/120 mesh; molecular sieve 13X, 60/80 mesh; and glass bead, 100/200 mesh (Alltech Associates Inc., Deerfield, Illinois, USA) were examined for this study. SE-54 (Alltech Associates Inc., Deerfield, Illinois, USA) was the liquid phase for cross-linking. Dicumylperoxide (Pfaltz & Bauer Inc., Stamford, Conneticut, USA) was the cross-linking initiator. All solvents were of analytical grade (J.T. Baker, Phillipsburg, N.J., USA). Toluene and n-pentane were dried over anhydrous magnesium sulfate.

Pretreatment of Solid Supports. Solid supports were sequentially cleaned with methanol, acetone, dichloromethane and n-hexane, followed by drying at 200°C under vacuum for 5 h before use.

Coating. A measured amount of solid support was placed into a round bottom flask and sufficient amount of n-pentane was added to wet the whole support. The calculated volume of SE-54 coating solution (4% w/v in n-pentane) was added to make 1,4,5, or 10% loading of SE-54 relative to the support by weight. DCUP solution (30% w/v in toluene) was then added to make 1 or 10% loading of DCUP relative to the weight of SE-54. Utmost care was taken to minimize the contact with moisture during the whole procedure. A vacuum stop-cock was attached to the flask before connecting to a rotatory evaporator. The flask was rotated to mix its content (30 min, room temperature and no vacuum). Vacuum (water pump) was then applied to remove the solvent (room temperature, 10 h).

Cross-linking. After closing the vacuum stop-cock, the flask was heated at 150-200°C for 1-2 h to perform cross-linking statically. The reacted vapors formed during reaction were then removed under vacuum after opening the stop-cock. The speed of rotation was kept at the lowest to minimize the crushing of the solid particles.

Conditioning and Solvent Washing. The cross-linked packing materials were packed into stainless steel (S.S.) columns (0.9-1.8 m × 2 mm ID). The packed columns were conditioned in a slow stream of nitrogen up to 190°C overnight. Unreacted phase or decomposition products were washed by passing methanol, dichloromethane and n-pentane (20 ml twice each), followed by conditioning up to 350°C at 5°C/min for 7h.

Gas chromatographic Analysis. A Perkin Elmer Model 3920 gas chromatograph was equipped with a flame ionization detector. The carrier gas was helium at a flow rate of 30 ml/min. The injector temperature was held at 250°C for hot on-column injection or below 60°C for cold on-column injection. The detector temperature was set to 330°C. A S.S. capillary column (100 m × 0.5 mm ID) coated with Witconal was used for testing the trace enriching performance of the packed column. Helium flow rate was 5 ml/min.

Test for the Solvent Washing Effect. The column performances of the packed columns before and after solvent washing was tested with isooctane solution containing n-C_{14} through n-C_{16}. 1 μl introduced in hot on-column injection mode was run isothermally at 140 or 160°C. Capacity factor (k'), separation factor (α), resolution (R), and separation number (SN) were calculated for the n-C_{15} and n-C_{16} peaks, and unit total plate number (N) for n-C_{16}.

Test for the in situ Cross-linking Conditions. n-Hexane solution spiked with n-C_{12} through n-C_{30} at 20 ppm each was used for evaluating the effects of cross-linking conditions one the column efficiency. After 1 μl in cold on-column injection mode was injected, the column was held at 60°C until the elution of hexane peak and raised to 120°C, followed by temperature programming at 10°C/min to 300°C. The values of α, R, SN and N were calculated for the n-C_{28} and n-C_{30} peaks.

Test for the Trace Analysis. 100 μl of hexane containing n-C_{12} through n-C_{30} at 0.2 ppm each was injected in cold on-column injection mode into the packed column prepared under the optimal cross-linking conditions. The column temperature was maintained at 60°C until the solvent peak eluted and then programmed at 10°C/min to 300°C.

Test for the Trace Enrichment of Hexane Impurities. According to the heart-cutting cold trapping method: 100 μl of hexan was injected into the packed column which was held at 60°C until the elution of solvent peak. After connecting a S.S. capillary column to the end of the packed column, the column temperature was programmed at 20°C/min to 160°C while the capillary column was kept at liquid nitrogen temperature. The impurities eluted from the packed column during this period was cold trapped as a plug in the first part of the capillary column for 15 min. The capillary column was heated at 2°C/min to 160°C to start the chromatographic analysis of the enriched trace compounds.

Test for the Trace Enrichment of Volatile Metabolites in Serum. A glass column (5 cm × 2 mm ID) packed with the immobilized Chromosorb W was served as a concentration column. Volatile metabolites in 100 μl of serum were eluted through Porasil with 600 μl of 2-chloropropane into the concentration column according to the reported method.[22] The enriched metabolites were desorbed from the concentration column at 250°C and analyzed in the same manner as for the hexane impurities.

Results and Discussion

Among the solid supports examined, Chromosorb W was

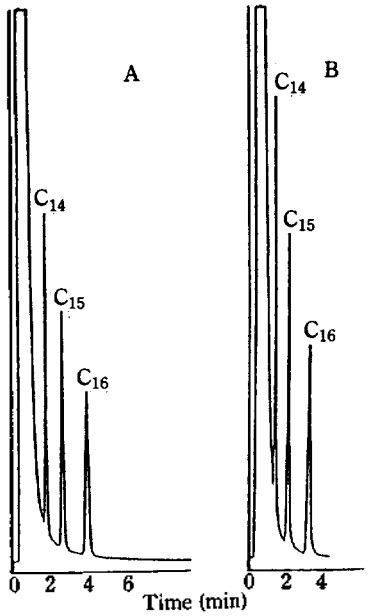

Figure 1. Gas chromatogram of n-hydrocarbons on a Chromosorb W packed column (0.9 m × 2 mm ID) 4% SE-54 cross-linked with 1% dicumylperoxide. 1 μl hot on-column injected; 30 ml/min of helium; column temperature, (A) 160°C before solvent washing, (B) 140°C after solvent washing.

Table 1. Effect of Solvent Washing on the Column Performance of the Cross-Linked Chromosorb W

Chromatographic data[c]	Cross-Linking of 4% SE-54[a]	
	Before washing	After washing
k'_{C15}	6.6	3.1
k'_{C16}	10.5	4.6
α	1.58	1.46
R	4.85	4.37
$SN_{C15\text{-}C16}$	3.12	2.71
N_{C16}[b]	2900	3800

[a]S.S. column (0.9 m × 2 mm ID). [b]Total plate number/meter. [c]"1 μl of n-C_{14} n-C_{16} in isooctane injected on hot on-column mode (at 250°C), was run isothermally at 140° or 160°C".

the only support to provide cross-linkable surface to the SE-54 film as seen in Figure 1. By comparing the K′ values obtained before and after solvent washing, we could estimate that about 45% of the phase was cross-linked (see Table 1). 31% increase in N value indicates that there was a considerable improvement in the column efficiency after washing.

The active surface of molecular sieve 13X could not be blocked by the simple in-situ cross-linking. Trace amount of moisture seemed to have remained on the surface of the active support, consuming the DCUP before its initiation of cross-linking. The inert but poor wettable surface of glass bead could not be improved by this reaction either. No further experiments were performed on these supports.

In order to find the optimal percent loadings of SE-54 and DCUP, SE-54 loading was varied from 1 to 10% for the 10% DCUP. Cross-linking was carried out at 170°C for 2 h in all cases. Two extreme cases of 1 and 10% phase loadings are compared in Figure 2. No complete separation of n-C_5, n-C_6 and n-C_7 was achieved on 1% SE-54 cross-linked column even at room temperature. The tailing of n-C_8 and n-C_9 peaks

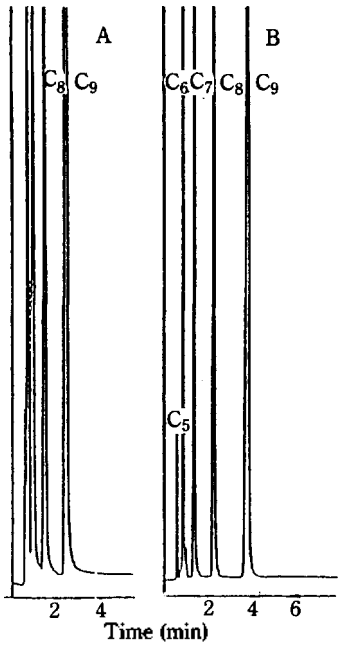

Figure 2. Gas chromatograms of n-hydrocarbons on a Chromosorb W packed columns (1.8 m × 2 mm ID), (A) 1% SE-54 and (B) 10% SE-54 each cross-linked with 10% dicumylperoxide. 1 μl hot on-column injected; 30 ml/min of helium; column temperature, (A) room temperature and (B) programmed from 80°C at 2°C/min.

Table 2. Effect of Stationary Phase Loading on the Column Performance of the Cross-Linked Chromosorb W

Chromatographic data[c]	Cross-Linking with 10% DCUP[a]	
	10% SE-54	5% SE-54
α	1.13	1.08
R	7.67	7.84
SN	5.52	5.67
N_{C30}[b]	29000	69000

[a]S.S. column (1.8 m × 2 mm ID). [b]Total plate number/meter measured in the temperature programmed run mode. [c]"1 μl of n-C_{12} n-C_{30} in n-hexane injected on cold on-column mode (at 60°C), was run by temperature programmed mode (120°C, 300°C, at 10°C/min.)".

indicates that the surface of Chromosorb W was not completely covered with the immobilized phase layer.

As the phase loading increases, the coated film gets thicker and the film homogenity throughout the whole support surface tends to be poor. When 5% phase loading was compared to the 10% loading, the column efficiency was increased by a factor greater than two (see Table 2). The N values were measured in temperature programmed run mode. It appears that the film evenness of the large phase loading was not corrected during cross-linking. 5% was chosen as the optimal phase loading.

Likewise, DCUP loading varied between 1 and 10% for the phase loading. Effect of the DCUP amount is summarized in Table 3. The column length of 1% DCUP was half of that of 10%. R and SN values were thus dropped. N value was, however, increased by a factor greater than two. This high column efficiency is demonstrated in Figure 3. 1% was selected as the optimal DCUP loading.

The resolving power of this non-extractable packed col-

Table 3. Effect of DCUP Loading on the Column Performance of the Cross-Linked Chromosorb W

Chromatographic data[d]	Cross-Linking of 5% SE-54	
	10% DCUP[a]	1% DCUP[b]
α	1.08	1.07
R	7.84	6.33
SN	5.7	4.4
N_{C30}[c]	69000	1570000

[a]s.s. column (1.8 m × 2 mm ID). [b]s.s. column (0.9 m × 2 mm ID). [c]Total plate number/meter measured in the temperature programmed run mode. [d]"1 μl of n-C_{12} n-C_{30} in n-hexane injected on cold on-column mode (at 60°C), was run by temperature programmed mode (120°C 300°C, at 10°C/min.)".

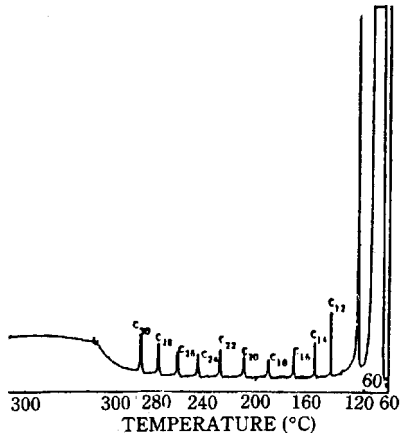

Figure 3. Gas chromatogram of n-hydrocarbons on a Chromosorb W packed column (0.9 m × 2 mm ID) 5% SE-54 cross-linked with 1% dicumylperoxide. 1 μl cold on-column injected; column temperature, 60°C until hexane peak, then raised to 120°C and programmed to 300°C at 10°C/min; 30 ml/min of helium.

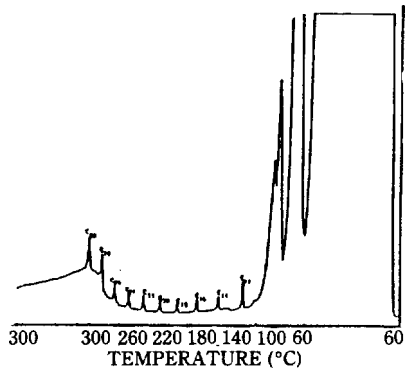

Figure 4. Gas chromatogram of n-hydrocarbons on a Chromosorb W packed column (1.8 m × 2 mm ID) 5% SE-54 cross-linked with 1% dicumylperoxide. 100 μl of hexane spiked with n-hydrocarbons at 0.2 ppm, cold on-column injected; 30 ml/min of helium; column temperature, 60°C until hexane peak, then programmed to 300°C at 10°C/min.

umn was tested with 100 μl of hexane containing n-hydrocarbons at 0.2 ppm concentration. Without a big loss in the column efficiency as compared with Figure 3, trace hydrocarbons could be well resolved as seen in Figure 4. This demonstrates that the present cross-linked column as an analytical column can handle large size of dilute samples for the trace analysis, and thus the preconcentration step can

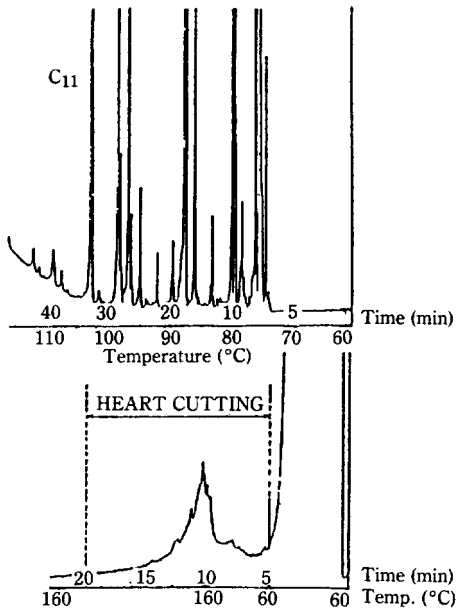

Figure 5. Gas chromatograms of hexane impurities preconcentrated (Bottom) on a cross-linked packed column (0.9 m × 2 mm ID) then analyzed (Top) on a Witconal capillary column (100 m × 0.5 mm ID). Chromatographic conditions in text.

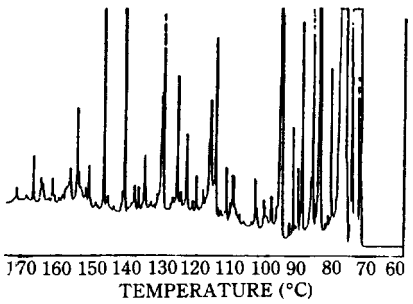

Figure 6. Gas chromatogram of serum volatile metabolites on a witconal capillary column (100 m × 0.5 mm ID) after their trace enrichment on the cross-linked Chromosorb W. Same conditions as in Figure 5.

be eliminated.

The heart-cutting portion in Figure 5-Bottom represents the hexane impurities in the cross-linked column. This impurities were transferred to the capillary column via cold trapping, to be analyzed as shown in Figure 5-Top. In the same manner, the volatile metabolites of serum present in 600 μl of the extracting solvent were preconcentrated and analyzed (Figure 6). Two figures illustrate that the present packing material as a concentrating sorbent is well suited for the trace enrichment of organic compounds from highly diluted samples as well.

Acknowledgement. This work was financially supported by the Korea Science Foundation (1986).

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Preparation and Properties of New Metal-chain Compounds with Commensurate Peierls Structure

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Received December 15, 1986

New platinum chain compounds, $[M(en)_2]_{0.80}[Pt(ox)_2].2H_2O$ where M = Cu or Pt, en = ethylenediamine and ox = oxalate, have been prepared and found to have a commensurate Peierls structure as evidenced by the five-fold Pt chain periodicity and unusually low electrical conductivity ($1.5 \times 10^{-5} \sim 5.7 \times 10^{-3}$ S/cm). Including two other compouds with the Peierls structure, their characteristic features were deduced and explained from the point of view of the band theory.

Introduction

Last decade has witnessed a renewed interest in the novel features of the linear platinum chain complexes. Peierls instability is one of the major characters to be related with the 1-D conductors as predicted by Peierls[1] and evidenced by Comes et al[2] in KCP (Br) using X-ray diffuse scattering technique.

Quasi-1-D compounds are inherently unstable to the lattice distortion with charge density wave $q = 2k_F$, where k_F is the Fermi wave vector. The importance of the lattice distortion is increasing with decreasing temperature and at certain temperature T_p the 1-D conductor goes to a semiconductor which is called as the Peierls transition.

However, when the original lattice periodicity is commensurate with respect to the Peierls distortion $2k_F$, the condensation of this phonon anomaly into a pattern of static displacements occurs. As a consequence a gap appears at the Fermi surface. The resultant structure is referred to the Peierls structure. Most of the partially oxidised platinum chain compounds studied so far have lattices incommensurate with the charge density wave (CDW) $2k_F$. But some of them have the commensurate Peierls structures at room temperature.

α-Rb-OP$[Rb_{1.67}Pt(C_2O_4)_2.1.5H_2O]$ is the first compound found to have the Peierls structure and its 3-dimensional structure has been studied in detail[3]. The second one is $[(CH_3)_3NH]_{1.59}[Pt(C_2O_4)_2]$ (TriAm-OP) which has unusual five-fold Pt-chain structure[4]. In the present work, two new 1-D metal chain compounds with the commensurate Peierls structure, $[M(en)_2]_{0.80}[Pt(C_2O_4)_2].2H_2O$ where en = ethylenediamine and M = Cu or Pt, will be reported[5].

Experimental

Preparation of $[Cu(en)_2][Pt(C_2O_4)_2]$ (Cuen-OP(II)). 1g of $Ag_2[Pt(C_2O_4)_2].2H_2O$ was suspended in 50 ml of water and heated to boiling. 0.47g of $Cu(C_2N_2H_8)_2Cl_2.2H_2O$ dissolved in 10 ml of water was added slowly. The reaction mixture was stirred well until the white ppt of AgCl coagurates. The ppt was removed by a filtration and the blue filtrate was cooled down to room temperature to obtain red-brown glittering