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CHARACTERIZATION AND EVALUATION OF CYANOPROPYL POLYSILOXANE STATIONARY PHASES FOR GAS CHROMATOGRAPHY

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SUMMARY

The compositions of commercial cyano-containing polysiloxane stationary phases were determined using infrared, nuclear magnetic resonance, and proton-induced X-ray emission spectroscopies. Varying amounts of the polar carboxamide group were found in most polymers. This group, which is inadvertently formed during the hydrolysis step in the synthesis of the polymers, affects the polarity and selectivity of the phase. The chloride ion (believed to be present as HCl as a result of the synthesis from dichlorosilane monomers) was also detected. A specially synthesized 88% cyanopropyl polysiloxane from dimethoxysilane monomers, containing no detectable carboxamide groups or adsorbed HCl, possessed different properties than the comparable commercially available phases.

INTRODUCTION

Stationary phases containing the cyano functional group are popular for use in gas chromatography (GC) because of the selectivity of these phases for various important classes of compounds such as the fatty acid methyl esters, pharmaceuticals, sugars, and other compounds that are polar or polarizable. Cyano-containing polysiloxane stationary phases normally contain 2-cyanoethyl or 3-cyanopropyl functional groups; attempts to couple the cyano moiety closer to the silicon atom have resulted in polymers with less thermal stability^{1,2}.

In addition to the selectivity offered by the cyano-containing polysiloxanes, they possess reasonable thermal stability compared with other polar stationary phases. The most thermally stable and widely used phases are the non-polar methyl and phenyl polysiloxanes, the latter of which can withstand temperatures as high as 400°C³. Unfortunately, more polar phases including those containing the cyano group are usually much less thermally stable. Recent efforts to produce cross-linkable cyano polysiloxanes⁴⁻⁹ have resulted in more thermally stable phases, principally by controlling the reduction in viscosity with temperature¹⁰ which is characteristic of the non-cross-linked polymers.

The cyanoethyl and cyanopropyl polysiloxanes possess both polar and polarizable characteristics¹¹. They rank near the top of the list of useful stationary phases

with respect to polarity. More polar functional groups are often less thermally stable and, therefore, not useful for GC. There are, however, various problems associated with the use of the cyano polysiloxanes as stationary phases for GC. These include the following: (a) It is difficult to obtain batch-to-batch reproducibility during synthesis of the polymers. Slight differences in time, temperature, catalyst, and purity of reagents can significantly affect the results, more so than observed for other polymer types. Lipsky and McMurray⁹ recently observed significant differences in polarity and activity between the various commercially available and specially synthesized cyano-containing polysiloxanes. (b) The resultant polymers possess shorter chains (lower molecular weight) than corresponding methyl and phenyl polysiloxane phases. This is a result of the higher polarity of the cyano group, and lower solubility in solvents used for coating. Higher levels of free-radical initiators are subsequently needed in order to produce sufficient crosslinking in the column. (c) The cyano polymers are susceptible to oxidation in the presence of air, certain free-radical initiators, and oxidizing solutes, especially at higher temperatures⁷. Care must be exercised in order to protect the column from oxidative degradation during use and storage.

In this study, various commercially available and specially synthesized cyano-containing polysiloxane stationary phases were characterized by infrared (IR), nuclear magnetic resonance (NMR), and proton-induced X-ray emission (PIXE) spectroscopies. The effect of the polymer synthetic route and final polymer composition is discussed with respect to the resultant polymer polarity and selectivity.

EXPERIMENTAL

Cyano-containing polysiloxanes

Samples of SP-2300, SP-2310, SP-2330, and SP-2340 (Supelco), Silar-5C and Silar-10C (Applied Science), and OV-275 (Ohio Valley) were obtained commercially for evaluation. An 88% cyanopropyl polysiloxane was synthesized from the following silanes: bis(3-cyanopropyl)dimethoxysilane, di-*p*-tolyl dimethoxysilane, 1,4-dimethyl-1,1,4,4-tetramethoxydisilethylene, vinyl dimethylchlorosilane, and 1,1,3,3-tetramethyl-1,3-divinyl disilazane. All methoxysilanes were prepared as previously reported⁸ from the chlorosilanes which were purchased commercially (Petrarch) or synthesized in this laboratory.

The polymers were prepared by combining the methoxysilanes in PTFE vials to give the desired composition to the final polymer (89.5% bis(3-cyanopropyl)dimethoxysilane, 9.5% di-*p*-tolyl dimethoxysilane and 1% 1,4-dimethyl-1,1,4,4-tetramethoxydisilethylene). An equal volume of acetonitrile was added and the silanes dissolved. A one-half volume portion of deionized water was added, and the solution was stirred for 1 h. Volatile byproducts were removed by purging with nitrogen gas at 130°C for 1 h. NMR analysis verified that hydrolysis was complete.

To 3 g of this prepolymer were added 15 μ l of tetramethylammonium hydroxide solution in methanol (10%, w/v) and 1 ml of methanol. The solution was mixed until homogeneous and then heated under nitrogen at 120°C for 4 h. The temperature was raised to 130°C for one additional hour, whereupon the vial was removed from the oven and 10 ml of methylene chloride were added. When solution was complete, 20 μ l of vinyl dimethylchlorosilane and 200 μ l of 1,1,3,3-tetramethyl-1,3-divinyl disil-

lazane were added to effect endcapping. The mixture was then allowed to stand at room temperature overnight.

The solvent and excess endcapping reagents were removed by purging with nitrogen gas at 80°C. The polymer was fractionated three times, each by dissolution in 3 ml of methylformate and precipitation with 15 ml of methanol. The product was then washed three times, each with 15 ml of methanol. Vacuum drying at 80°C left a clear, colorless gum.

IR and NMR spectroscopy

The synthesized cyanopropyl polysiloxane and commercially available stationary phases were analyzed using a Beckman Acculab 2 IR spectrometer and a JEOL FX-90Q NMR spectrometer. The carboxamide content was determined by inspection of the IR spectra (NH₂ stretch at 3360 and 3470 cm⁻¹ and C=O stretch at 1680 cm⁻¹), verification from the ¹³C NMR spectra [δ 38.4 (CH₂CONH₂) and 175.1 (CONH₂)], and integration of the ¹H NMR spectra (CONH₂ at δ 5.4–6.0). The polymer compositions were quantified by integration of the ¹H NMR spectra.

PIXE

Analysis for chlorine content in two of the stationary phases (SP-2340 and the newly synthesized polymer) was accomplished using PIXE. Polymer samples were dissolved in acetonitrile (60 mg ml⁻¹). Targets were prepared by depositing a 5.0- μ l aliquot onto a thin Mylar backing. A High Voltage Engineering Van de Graaff accelerator was the source of the 2.0 MeV proton beam with cross-sectional area of 0.38 cm². The sample targets were placed in the proton beam and irradiated with 50 μ coulombs of protons at a current of 130 nA. The emitted X-rays were collected with a Nuclear Semiconductor Si(Li) solid state detector. Pulses from the detector were analyzed and stored in a Canberra multichannel analyzer under the control of a PDP-11 minicomputer. Final data analysis was performed using a VAX 11/780 main-frame computer.

Gas chromatography

Capillary columns were prepared by statically coating untreated fused-silica capillary tubing (10 m \times 0.32 mm I.D., Hewlett-Packard, Avondale, PA, U.S.A.). Coating solutions of the polymers were prepared by dissolving 3.20 mg ml⁻¹ (film thickness = 0.25 μ m) in purified methylene chloride. Azo-*tert*.-butane and azo-*tert*.-dodecane were used for cross-linking the newly synthesized polymer as previously described¹². The extent of cross-linking was evaluated by slowly purging the column with *ca.* 10 ml of methylene chloride for a 10-h period. Chromatographic retention measurements (*k'* values) before and after rinsing provided the information for calculating the percent washout¹³.

Column evaluations were accomplished using a Hewlett-Packard 5880A gas chromatograph equipped with a split-splitless injector and a flame ionization detector. Hydrogen was used as carrier gas at a linear velocity of 60 cm sec⁻¹. The sensitivity was set to give a full-scale peak height for 1 ng of *n*-dodecane.

RESULTS AND DISCUSSION

Recent studies⁴⁻⁹ have emphasized the significant differences in chromatographic performance observed with columns coated with various commercially available and specially synthesized cyano-containing polysiloxanes. These differences are obviously related to the polymer composition and structure. All of the polymers in this study contained cyanopropyl as the major cyano-containing functional group. One polymer (OV-275) contained a significant concentration of cyanoethyl. The cyanoethyl group gives a higher nitrile to hydrocarbon ratio than does the cyanopropyl group, and hence should lead to higher polarity. Most of the commercial phases contained substantial phenyl substitution. Increased polymer stability is obtained when a phenyl group is bonded to the same silicon atom as a cyanopropyl¹⁴. However, the phenyl group is polarizable and will be polarized by the cyanopropyl groups in the polymer or by polar solutes, leading to different selectivity. The synthesized polymer in this study contained cyanopropyl and *p*-tolyl functional groups. The *p*-tolyl groups were used to facilitate cross-linking⁵⁻⁸.

In addition to planned variations in cyano polymer composition, other variations were observed from IR and NMR spectroscopy. Most significant is the carboxamide content of most of the commercially available polymers. Table I lists the polymers characterized and quantified by ¹H NMR spectroscopy. The carboxamide content was as high as 5% in OV-275. Fig. 1A shows the IR spectrum of OV-275. Immediately apparent are the large signals at 3360 and 3470 cm⁻¹ due to the NH₂ stretch, and at 1680 cm⁻¹ due to the amide carbonyl stretch. Fig. 1B is the IR spectrum for the newly synthesized cyanopropyl polysiloxane which shows the absence of the carboxamide functional group. Fig. 2 shows a ¹³C NMR spectrum of SP-2310, verifying unequivocally the presence of carboxamide (δ 38.4 and 175.1), and Fig. 3 shows the ¹H NMR spectrum of SP-2330, illustrating the integration of the amide protons (δ 5.5-6.0) for quantification. Heckers *et al.*¹⁵ observed a carbonyl vibration in the

TABLE I

AMIDE CONTENT OF VARIOUS CYANO POLYSILOXANE STATIONARY PHASES*

Phase	% Amide	% Cyanopropyl	% Cyanoethyl	% Phenyl
SP-2330	2	88	—	10
SP-2340	3	97	—	—
SP-2310	3	71	—	26
OV-275**	5	57	38	—
SP-2300	—	50	—	50
Silar-10C	trace	100	—	—
Silar-5C	—	51	—	49
Synthesized				
88% cyanopropyl***	—	88	—	10 [§]

* Quantitative results were calculated from the ¹H NMR spectra. Quantitative accuracy is within $\pm 1\%$.

** Some vinyl protons were also observed.

*** Remaining 2% is due to the added tetramethoxydisilylethylene for cross-linking during synthesis.

§ *p*-Tolyl substituent.

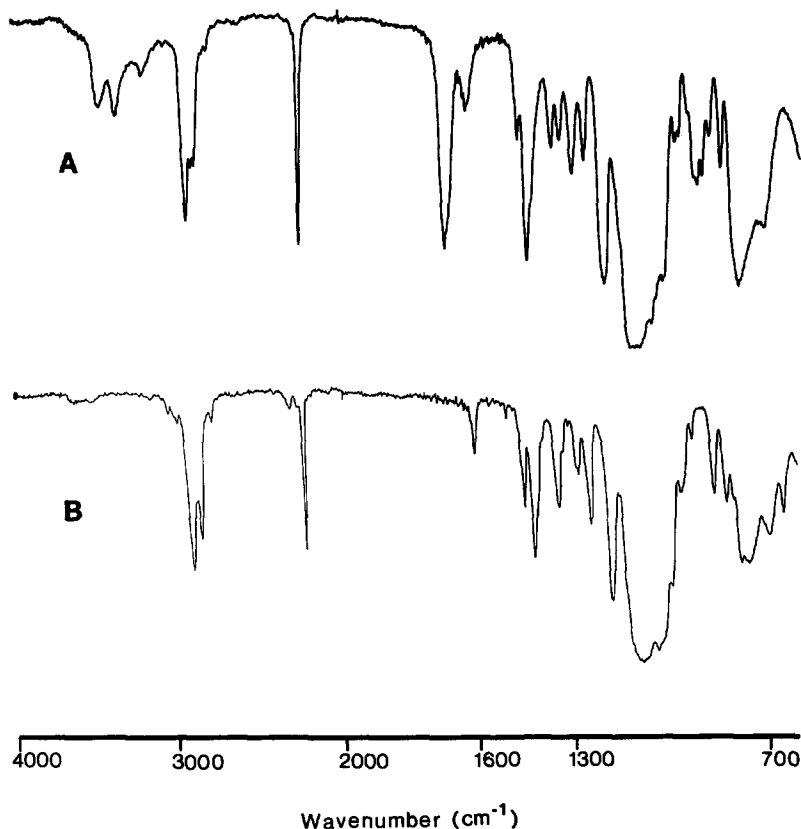


Fig. 1. IR spectra of (A) OV-275 showing carboxamide bands at 3360 and 3470 cm^{-1} ($-\text{NH}_2$) and 1680 cm^{-1} ($\text{C}=\text{O}$), and (B) specially synthesized 88% cyanopropyl polysiloxane.

IR spectra of OV-275 and SP-2340, but incorrectly attributed it to acetyl end-groups. It is interesting to note that the Silar phases, which were prepared by a procedure¹⁶ similar to the one described here, contained very little, if any, carboxamide.

The formation of the carboxamide groups was an unsuspected result of the conditions of hydrolysis during the synthesis of the polymers. Possible causes include catalysis by residual Lewis acids present or by large amounts of HCl produced during hydrolysis. The carboxamide group is expected to produce different selectivity for certain separations than the cyanopropyl group. While the dipole moments for acetamide and acetonitrile are very similar (3.44 and 3.92, respectively), their dielectric constants (59 for acetamide and 37.5 for acetonitrile)¹⁷ show that amide functional groups are quite different. Hydrogen bonding is expected to be particularly more prevalent for separations obtained on phases containing the carboxamide group.

PIXE analysis for chlorine yielded no detectable quantity for the newly synthesized polymer, but gave an average amount of 5.9 ppm for SP-2340 near the minimum detection limit of *ca.* 4 ppm. It appears that during hydrolysis of the dichlorosilane monomers in the synthesis of the polymers, HCl produced is adsorbed

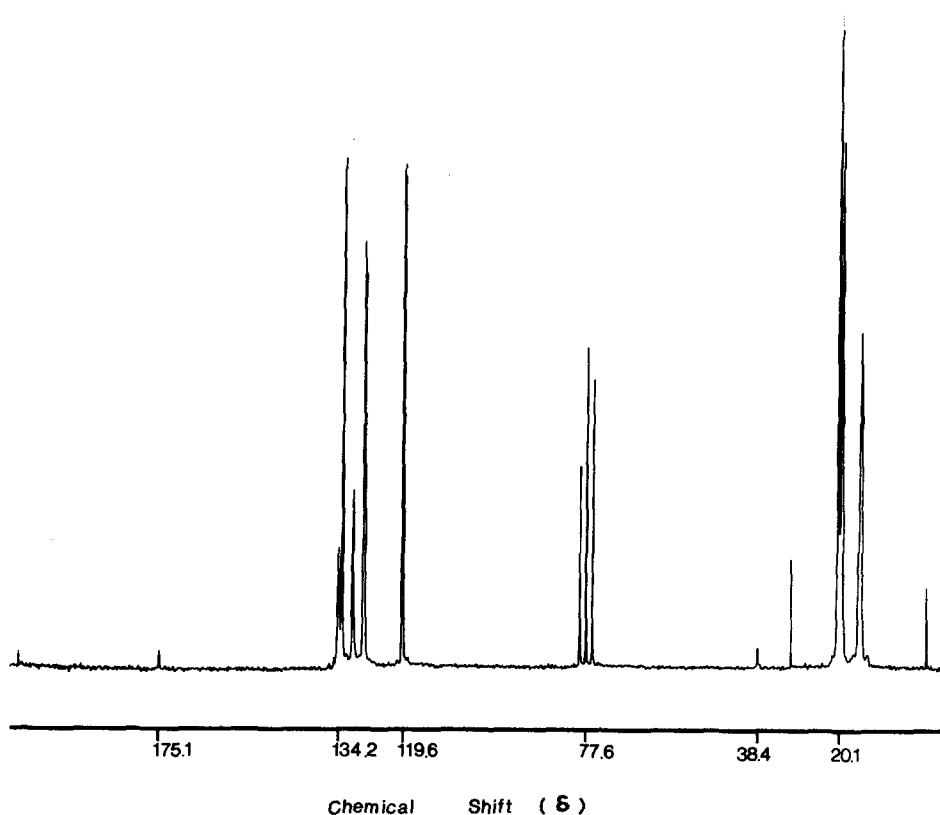


Fig. 2. ¹³C NMR spectrum of SP-2310 showing carboxamide peaks at δ 38.4 (CH_2CONH_2) and at δ 175.1 (CONH_2).

rather strongly by the cyanopropyl groups and cannot be completely removed, even by extensive washing. It is expected that adsorbed HCl could significantly affect the polarity of the stationary phase. Conversion of the dichlorosilanes into dimethoxysilanes before hydrolysis is one way to eliminate this problem.

It has generally been observed that cyanopropyl polysiloxanes are difficult to crosslink. As the cyanopropyl content increases, the difficulty of cross-linking increases. It was found in this laboratory that the addition of vinyl groups to facilitate cross-linking was largely ineffective⁷. The addition of 10% *p*-tolyl groups to a *ca.* 90% cyanopropyl polysiloxane greatly improved cross-linking. After cross-linking with *azo-tert.*-butane and rinsing with methylene chloride for *ca.* 1 h, less than 10% washout was observed. Rinsing for 10 h in this study yielded an average of 37% washout. When 10% *azo-tert.*-dodecane was used for free-radical initiation, an average of 15% washout was observed. While shorter rinse periods are adequate for the evaluation of methyl and phenyl polysiloxanes, longer periods are necessary for the proper evaluation of the less soluble cyanopropyl phases.

The resultant selectivity demonstrated by a specific stationary phase is a combination of the contribution of the various functional groups and polar impurities.

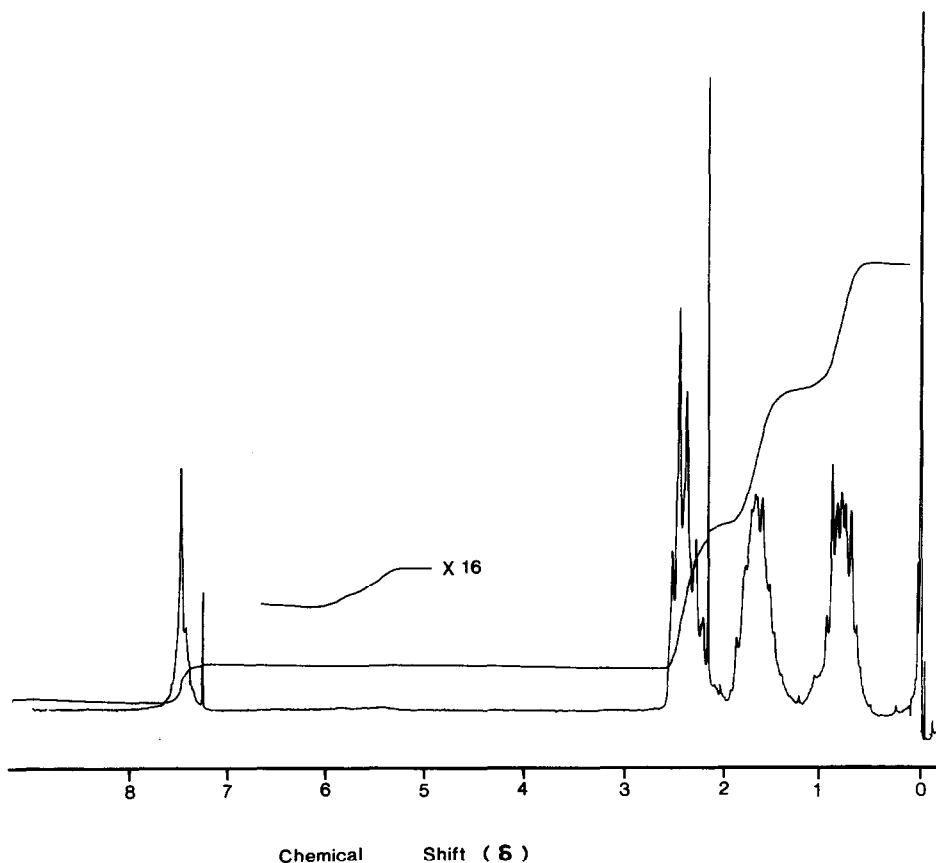


Fig. 3. ^1H NMR spectrum of SP-2330 showing the integration of NH_2 protons of the carboxamide group at δ 5.4-6.0.

In addition to cyanopropyl groups, cyanoethyl, carboxamide, and phenyl groups, as well as adsorbed HCl will affect polarity. Previous polarity tests⁹ have indicated that our 88% cyanopropyl polymer was less polar than comparable commercially available phases. The difference in retention of polar solutes could certainly be attributed to the variability in phase compositions. Testing conditions are also important and should be standardized for proper comparisons. Fig. 4 shows a gas chromatogram of fatty acid methyl esters obtained on a column coated with the synthesized 88% cyanopropyl polysiloxane. In this example, the 18:3 methyl ester eluted before the 20:0. Under isothermal conditions at 125°C on a thicker phase film (*ca.* 1 μm), the reverse in elution order was obtained, similar to results observed on the commercially available SP-2340 phase.

The results from this study emphasize that the polarities and selectivities of the various cyano-containing polysiloxane stationary phases are a result of the specific compositions of the polymers. It is extremely difficult to control the purity of the polymer during synthesis. Indeed, it is very difficult to prepare the exact same phase from one batch to another. These cyano phases are somewhat susceptible to oxida-

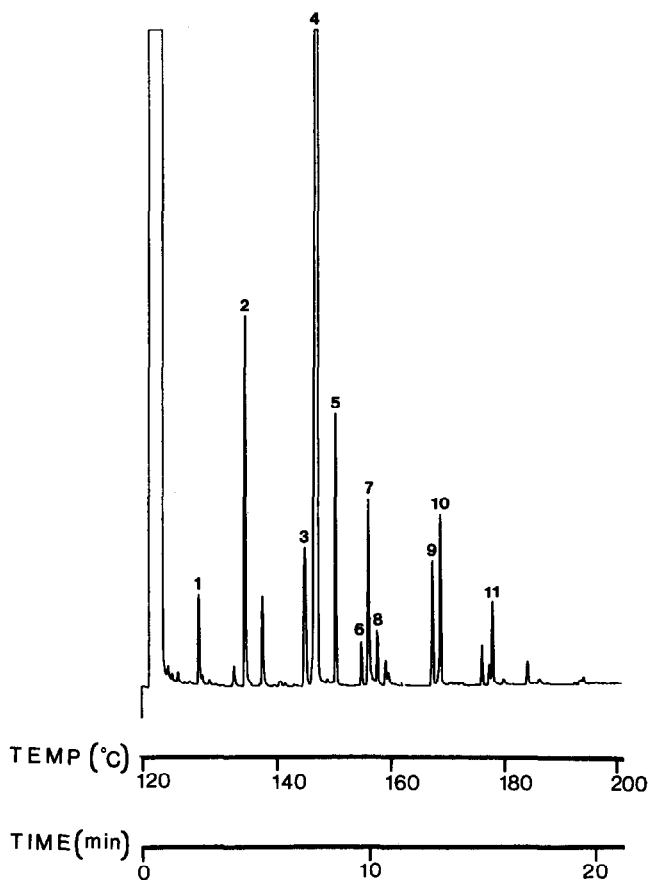


Fig. 4. Gas chromatogram of a mixture of fatty acid methyl esters. Conditions: 10 m \times 0.31 mm I.D. fused-silica column coated with a specially synthesized 88% cyanopropyl polysiloxane (0.25- μ m film thickness); temperature program, 120 to 200°C at 4°C min⁻¹; hydrogen carrier gas at 60 cm sec⁻¹. Peak identifications: 1 = 14:0, 2 = 16:0, 3 = 18:0, 4 = 18:1, 5 = 18:2, 6 = 18:3, 7 = 20:0, 8 = 20:1, 9 = 22:0, 10 = 22:1, 11 = 24:0.

tion, and they are more difficult to cross-link than other phases. These results suggest that additional polar stationary phases with more acceptable properties and reproducibility are clearly needed.

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