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SYNTHESIS AND STRUCTURAL CONSIDERATIONS OF OLIGOETHYLENE OXIDE-CONTAINING POLYSILOXANE STATIONARY PHASES IN CAPILLARY GAS AND SUPERCRITICAL-FLUID CHROMATOGRAPHY

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SUMMARY

A series of oligoethylene oxide-containing polysiloxanes were prepared by hydrosilylating the appropriate oligoethylene oxide-containing alkene onto a well-defined polymethylhydrosiloxane polymer. The most convenient oligoethylene oxide-containing alkenes were prepared from eugenol and the tosylate of di- or triethylene glycol monomethyl ether. The polysiloxane phase prepared from 1-(4-allyl-2-methoxyphenoxy)-5-methoxy-3-oxapentane was found to possess desirable chromatographic properties when used in capillary supercritical-fluid chromatography and is suggested as a substitute for Carbowax 20M. The phase was usable at temperatures from 20°C to 300°C. The synthetic rationale and the effects of structural changes in the polymers on chromatographic performance are discussed in this paper. This paper also contains a systematic study of the influence of chemical structure on chromatographic properties of the resulting polysiloxane phases.

INTRODUCTION

Nearly all of the presently used stationary phases for capillary gas chromatography (GC) are based on the polysiloxane backbone. Thermal stability as well as good diffusion of solutes in the stationary phase are necessary requirements for preferred stationary phases. Polysiloxanes have the best diffusion properties of the polymeric materials known today[1] and they are also very stable. Substitution on the polysiloxane backbone has been diverse, depending on the chromatographic need. Stationary phases range from polar cyanophenyl-substituted[2], to non-polar alkyl-substituted polysiloxanes[3].

The polyethylene glycol (PEG) phases, such as Carbowax, are popular because of their moderate polarities which lead to selective separations of polar and polarizable solutes without exhibiting strong retention of these compounds. A number of studies have been made to modify Carbowax for use at both higher and lower oper-

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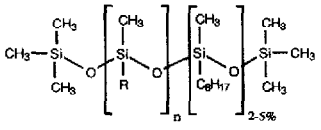
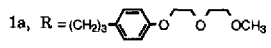
ating temperatures[4]. In a previous paper[5], a comparison was made between a PEG phase (Carbowax 20M) and a phenyl-containing oligo(ethylene oxide)-substituted polysiloxane (phase **1a**, Fig. 1). The new phase was found to have a selectivity similar to Carbowax 20M. In addition, the phase could be crosslinked and was usable at temperatures from 20°C to 300°C in GC. These desirable chromatographic properties of polymer **1a** led us to prepare a series of similar phases shown in Fig. 1, and to study the effects of different structural features on gas and supercritical-fluid chromatographic (SFC) selectivity and stability. Our objective was to prepare a medium polar phase that could be used in SFC as well as in the typical full temperature range of GC.

EXPERIMENTAL

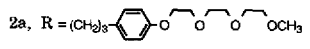
Synthetic procedure for the preparation of oligoethylene oxide-containing polysiloxane phases (Scheme 1)

The new phenyl- and non-phenyl-containing oligoethylene oxide-substituted polysiloxanes were prepared by hydrosilylating the appropriate oligoethylene oxide-containing alkene onto a previously prepared polymethylhydrosiloxane of known composition (Scheme 1). The hydrosilation reaction used to prepare these polymers and the synthesis of the polymethylhydrosiloxanes have been reported previously[5,6]. The number of Si–H units in the polymethylhydrosiloxane determined the extent of substitution on the polymer. For example, a polymer with 50% Si–H (every silicon atom had a methyl group and a hydrogen atom) would produce a final polymer

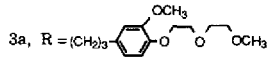




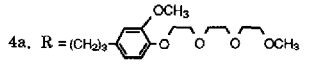
1a, R = $(CH_2)_3$–C$_6$H$_3$(O–O–OCH$_3$)



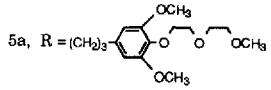
2a, R = $(CH_2)_3$–C$_6$H$_3$(O–O–O–OCH$_3$)



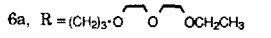
3a, R = $(CH_2)_3$–C$_6$H$_2$(OCH$_3$)(O–O–OCH$_3$)



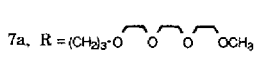
4a, R = $(CH_2)_3$–C$_6$H$_2$(OCH$_3$)(O–O–O–OCH$_3$)



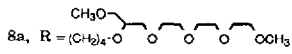
5a, R = $(CH_2)_3$–C$_6$H$_2$(OCH$_3$)$_2$(O–O–OCH$_3$)



6a, R = $(CH_2)_3$–O–O–O–OCH_2CH_3

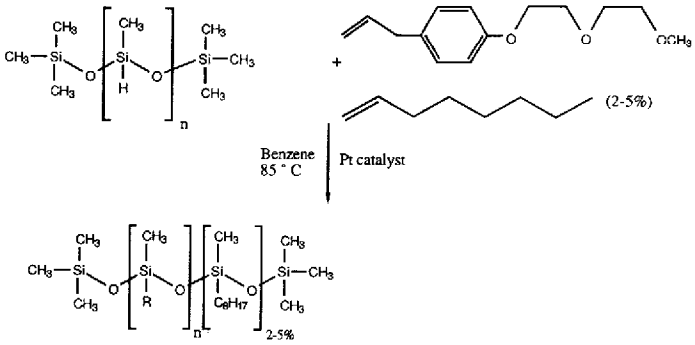


7a, R = $(CH_2)_3$–O–O–O–O–OCH_3



8a, R = $(CH_2)_4$–O–CH_3O–O–O–O–O–OCH_3

Fig. 1. Oligoethylene oxide-containing polysiloxane gum phases.



Scheme 1. Hydrosilylation of a polar substituent onto a preformed polysiloxane. Where R = the above oligoethylene oxide-containing alkene.

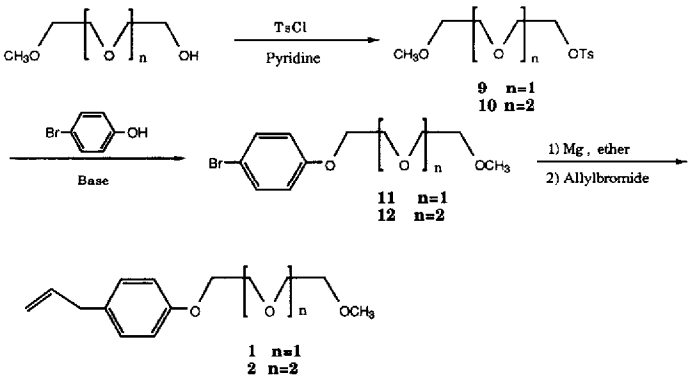
containing approximately 50% substitution. The polymers in this study contained about 47% of the oligoethylene oxide substituent and about 3% octyl substituent. The oligoethylene oxide-containing alkenes were prepared by several different methods as presented below.

Preparation of oligoethylene oxide-containing alkenes (Schemes 2–4)

*1-(4-Bromophenoxy)-5-methoxy-3-oxapentane (**11**) (Scheme 2).* Compound **11** was prepared as reported[5]. In an alternative method, 4-bromophenol was dissolved in 75 ml of dry dimethyl sulphoxide (DMSO), and a slight excess of sodium hydride was added. The tosylate **9** was added over a period of about 20 min and the mixture was allowed to react overnight while keeping the temperature around 40°C. Product **11** was then isolated as reported[5] in a 79% yield.

*1-(4-Allylphenoxy)-5-methoxy-3-oxapentane (**1**) (Scheme 2).* Compound **1** was prepared from **11** as reported[5].

*1-(4-Bromophenoxy)-8-methoxy-3,6-dioxaoctane (**12**) (Scheme 2).* This material was prepared as above for compound **11**[5] except that tosylate **10** (prepared from the monomethyl ether of triethylene glycol and tosyl chloride) was added to the



Scheme 2. Synthesis of alkenes using *p*-bromophenol.

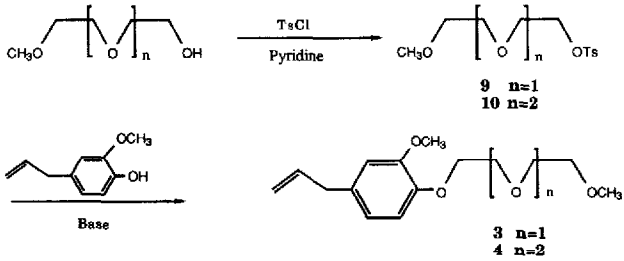
phenoxide. The product was purified by distillation to give 55% of **12**; b.p. 120–125°C/0.07 mm; NMR (δ): 3.4 (3H, s), 3.72 (10H, bm), 4.1 (2H, m), 6.8 (2H, d), 7.36 (2H, d).

*1-(4-Allylphenoxy)-8-methoxy-3,6-dioxaoctane (**2**) (Scheme 2).* Compound **2** was prepared as above for **8** using 1.31 g (0.054 mol) of magnesium turnings, 15 g (0.047 mol) of **12** and 70 ml of anhydrous tetrahydrofuran (THF). After the magnesium was consumed, 5.3 ml of 3-bromopropene in 15 ml of anhydrous THF were added and the mixture was refluxed overnight. The product was purified by distillation to give 0.79 g (6%) of **2**; b.p. 123–125°C/0.04 mm; NMR (δ): 3.40 (3H, s), 3.72 (10H, bm), 4.1 (2H, m), 5.0 (2H, m), 5.95 (1H, m), 6.86 (2H, d), 7.12 (2H, d).

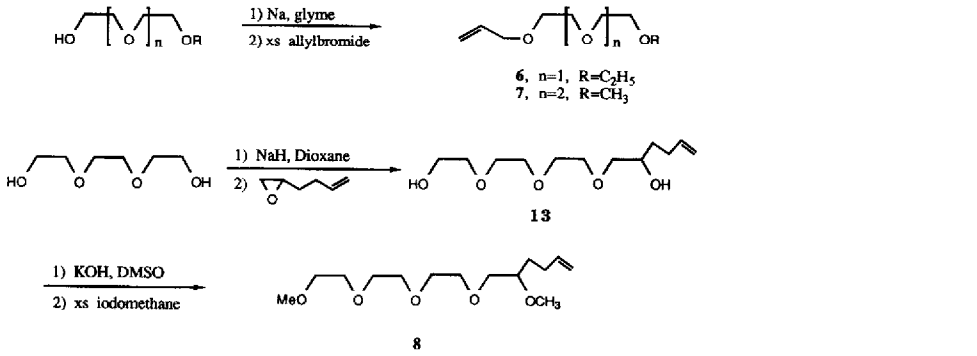
*1-(4-Allyl-2-methoxyphenoxy)-5-methoxy-3-oxapentane (**3**) (Scheme 3).* The potassium alkoxide of eugenol was first prepared by treating 16.91 g (0.103 mol) of eugenol with 5.78 g (0.103 mol) of potassium hydroxide (in as little water as possible) and evaporating the salt to dryness on a rotary evaporator. The salt was then dissolved in DMSO and heated to 40°C while 27.43 g (1.10 mol) of tosylate **9** was slowly added. The mixture was stirred overnight at 40°C and extracted with ether. The ether layer was washed with 5% sodium bicarbonate, dried over anhydrous magnesium sulfate and evaporated. The resulting oil was distilled to give 19.44 g (73%) of **3**; b.p. 127–131°C/0.06 mm; NMR (δ): 3.30 (2H, d), 3.38 (3H, s), 3.5 (2H m) 3.70 (4H, m), 3.85 (3H, s), 4.15 (2H, t), 5.15 (2H, m), 5.95 (1H, m), 6.7 (2H, s) 6.85 (1H, d). Analysis for $C_{15}H_{22}O_4$; calculated: C, 67.66; H, 8.33; found: C, 67.54; H, 8.42.

*1-(4-Allyl-2-methoxyphenoxy)-8-methoxy-3,6-dioxaoctane (**4**) (Scheme 3).* This material was prepared in the same manner as **3** above from 7.36 g (0.045 mol) of eugenol and 10.93 g (0.034 mol) of tosylate **10**. The product was distilled to give 7.32 g (54%) of **4**; b.p. 154–157°C/1.2 mm; NMR (δ): 3.31 (2H, d), 3.38 (3H, s), 3.54 (2H, m), 3.7 (6H, m), 3.81 (3H, s), 3.38 (2H, t), 4.15 (2H, t). 5.06 (2H, dd), 5.92 (1H, m), 6.7 (2H, bs), 6.85 (1H, d). Analysis for $C_{17}H_{26}O_5$; calculated: C 65.79; H, 8.44; found: C, 65.65; H, 8.54.

*1-(4-Allyl-2,6-dimethoxyphenoxy)-5-methoxy-3-oxapentane (**5**).* Compound **5** was prepared as above for **3** from 1.92 g (0.01 mol) of 2,6-dimethoxy-4-allylphenol and 1.37 g (0.01 mol) of 1-chloro-5-methoxy-3-oxapentane (**9** with a chlorine substituted for the tosylate group) using N,N-dimethylformamide (DMF) rather than DMSO as the solvent. The mixture was then heated to 120–135°C overnight. After the reaction mixture had been extracted, product **5** was isolated by distillation to give 1 g (34%) of **5**; b.p. 110–120°C/0.75 mm; NMR (δ): 3.3 (2H, d), 3.4 (3H, s), 3.8 (10H,



Scheme 3. Synthesis of alkenes starting from eugenol.



Scheme 4. Synthesis of oligoethylene oxide alkenes without phenyl rings (xs = in excess).

m), 4.57 (2H, t), 4.15 (2H, t), 5.1 (2H, dd), 6.0 (1H, m), 6.4 (2H, bs). Analysis for $C_{16}H_{24}O_5$; calculated: C, 64.86; H, 8.33; found: C, 64.54; H, 8.42.

*3,6,9-Trioxa-11-dodecene (**6**) (Scheme 4).* Freshly distilled diethylene glycol monoethyl ether (15 g, 0.112 mol) and 2.57 g of sodium were stirred and refluxed overnight in 50 ml of glyme. Allyl bromide (12.6 ml, 0.146 mol) was then added and the mixture was heated at reflux overnight. The resulting mixture was cooled and extracted with 200 ml of ether. The ether layer was washed with 100-ml portions of brine until the aqueous layer was neutral. The ether layer was dried over anhydrous magnesium sulfate and the solvent was removed under vacuum to give 13.5 g of an oil. The oil was distilled to give 8.5 g (43%) of **6**; b.p. 44°C/0.225 mm; NMR (δ): 1.05 (3H, t), 3.4 (10H, bm), 3.85 (2H, d), 5.05 (2H, m), 5.75 (1H, m). Analysis for $C_9H_{18}O_3$; calculated: C, 62.04; H, 10.41; found: C, 61.94; H, 10.47.

*2,5,8,11-Tetraoxa-13-tetradecene (**7**) (Scheme 4).* Compound **7** was prepared as **6** above using 10 g (0.061 mol) of triethylene glycol monomethyl ether (Fluka) and 1.4 g of sodium. The solution was refluxed about 3 h, and 6.9 ml (0.079 mol) of allyl bromide was added. This crude product (5.5 g) was distilled to give 4.1 g (33%) of **7**; b.p. 57°C/0.05 mm; NMR (δ): 3.1 (3H, s), 3.35 (12H, bm), 3.74 (2H, d), 5.05 (2H, m), 5.65 (1H, m). Analysis for $C_{10}H_{20}O_4$; calculated: C, 58.80; H, 9.87; found: C, 58.61; H, 9.64.

*1-(3-Butenyl)-3,6,9-trioxaundecan-1,11-diol (**13**) (Scheme 4).* Dry dioxane (250 ml) and 1.54 g of sodium hydride (60% dispersion) were placed in a large three-necked round bottom flask with 140 ml of triethylene glycol (1.1 mol). The solution was allowed to stir at room temperature until the sodium hydride was dissolved, and then the solution was heated to reflux. 1,2-Epoxy-5-hexene (28.7 ml, 0.26 mol) was added over a 1.5-h period. The mixture was stirred for two days at reflux temperature, after which it was cooled and made slightly acidic with dilute hydrochloric acid, and then neutral with saturated sodium bicarbonate solution. The mixture was then filtered and the solvent was removed to give an oil which was distilled to give 16.65 g (26%) of 1-(3-butenyl)-3,6,9-trioxaundecan-1,11-diol; b.p. 144°C/0.20 mm.

*3-(3-Butenyl)-2,5,8,11,14-pentaoxapentadecane (**8**) (Scheme 4).* DMSO (stored over molecular sieves) (80 ml) and 18 g of powdered potassium hydroxide were placed in a round bottom flask and stirred for 20 min. Compound **13** (10 g, 0.04

mol) was added along with 10 ml (0.080 mol) of methyl iodide. The solution was stirred overnight, poured into 300 ml of water, and extracted with three 200-ml portions of dichloromethane. The combined extracts were washed with four 200-ml portions of dichloromethane and four 200-ml portions of water. The solution was dried over anhydrous magnesium sulfate and the solvent was removed to yield 10.7 g (96%) of an oil. NMR: 1.58 (2H, m), 2.10 (2H, m), 3.30 (3H, s), 3.40 (3H, s), 3.6 (14H, bm), 5.05 (2H, bm), 5.3 (1H, s), 5.8 (1H, bm). Analysis for $C_{14}H_{28}O_5$; calculated: C, 60.84; H 10.21; found: C, 60.67; H, 10.33.

Column preparation and evaluation

Capillary columns for GC and SFC were prepared according to the method described by Jones *et al.*[7]. The fused-silica columns were deactivated with cyanopropylhydrosiloxane deactivation reagent[8], and the oligoethylene oxide stationary phases were immobilized using azo-*tert.*-butane or dicumyl peroxide free radical initiator. GC column evaluations were performed with a Carlo Erba 5160 Mega Series GC using hydrogen gas at 50 cm s^{-1} starting linear velocity and a flame ionization detector. SFC column evalutations were performed using a Lee Scientific 501 supercritical-fluid chromatograph with a flame ionization detector using CO_2 as carrier fluid at 2 cm s^{-1} starting linear velocity and using a frit restrictor (Lee Scientific, Salt Lake City, UT, U.S.A.). The injected sample amounts and the detector attenuation settings were adjusted to give 1–10 ng full-scale response.

RESULTS AND DISCUSSION

The search for a stationary phase which possesses many of the desirable properties of a PEG such as Carbowax, led to the investigation of a series of oligoethylene oxide-containing polysiloxane stationary phases (see Fig. 1). The objectives in preparing the oligoethylene oxide-substituted polysiloxanes were: first, to lower the glass transition temperature (t_g), making the phase useful at lower temperatures; second, to extend the upper temperature limit, increasing the utility of the phase in GC; third, to produce a phase that was inherently crosslinkable, allowing the phases to be highly reproducible from batch to batch and allowing the crosslinked phase to be physically stable for both high temperature GC and SFC use; and finally to find the optimum structure to give the best selectivity for chosen test solutes.

The first two objectives were achieved by grafting the alkenes onto preformed polysiloxanes containing Si–H sites (see Scheme 1). This provided a route to many structurally similar compounds which all possessed the advantages of the polysiloxane backbone, *i.e.* thermal stability and high flexibility, which tends to lower the glass transition temperature. The chromatographic testing of phase **1a** indicated that in fact, these new materials possessed superior physical properties over PEGs. The temperature range for this material was found to be 20–300°C.[5] The low bleeding of this stationary phase is demonstrated in Fig. 2 in which a paraffin wax extract was eluted during a temperature program up to 300°C, resulting in a baseline rise of only 1 pA.

The third objective, to have a crosslinked phase, was achieved by including a measured amount of 1-octene in the hydrosilylation reaction along with the oligoethylene oxide-containing alkene (see Scheme 1). This results in a polymer which contains from 2–5% octyl substitution and greatly enhances the crosslinkability of

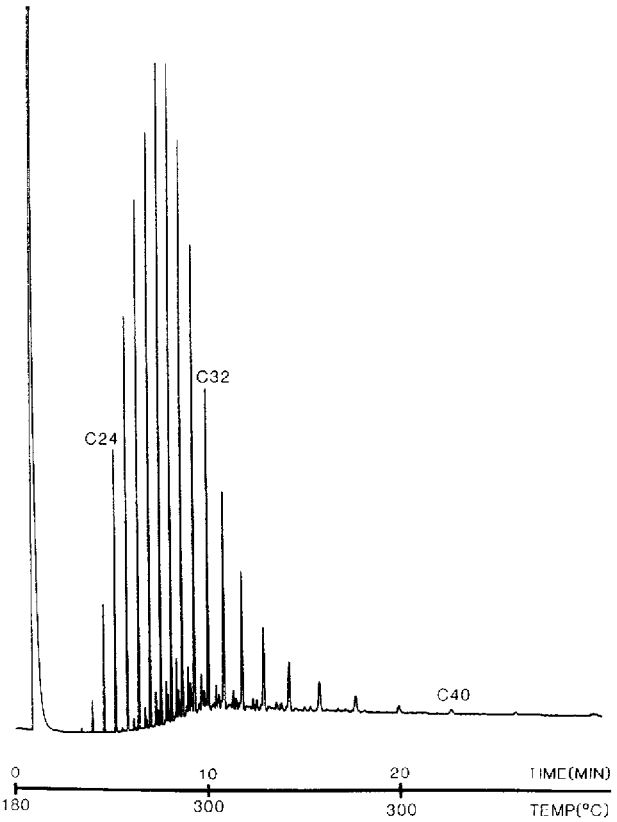


Fig. 2. Gas chromatogram of a paraffin wax oil extract on oligoethylene oxide stationary phase **1a**. Conditions: 10 m × 200 μm I.D. column with a 0.25-μm film thickness.

the phase[6], therefore providing much needed long term physical stability when the phase is used in both GC and SFC. The octane side chain had another beneficial effect. When the polymer was prepared by hydrolysation without octene, the polymer precipitated from the hot reaction mixture[5]. Even lower molecular weight polymers, when hydrosilylated without some octene present, behaved in a similar manner. One of the gelled polymers was pressure filtered through a 2-μm filter, leaving no residue, and the solution gelled again upon standing at room temperature for several hours. Even though the solution could be filtered, it could not be coated. This polymer property could be due to the strong interactions between individual substituents on the polysiloxane backbone, resulting in a thixotropic gel. The addition of octane substituents made the polymers dissolve nicely and retain a homogeneous consistency. The inclusion of the octene in slightly different amounts from batch to batch was found to have no measurable effect on the chromatographic properties of the phases[7].

The major differences in the chemical structures that were studied included: (1) presence or absence of a phenyl group between the hydrocarbon spacer and the oligoethylene oxide chain, (2) presence or absence of a methoxy group on the above

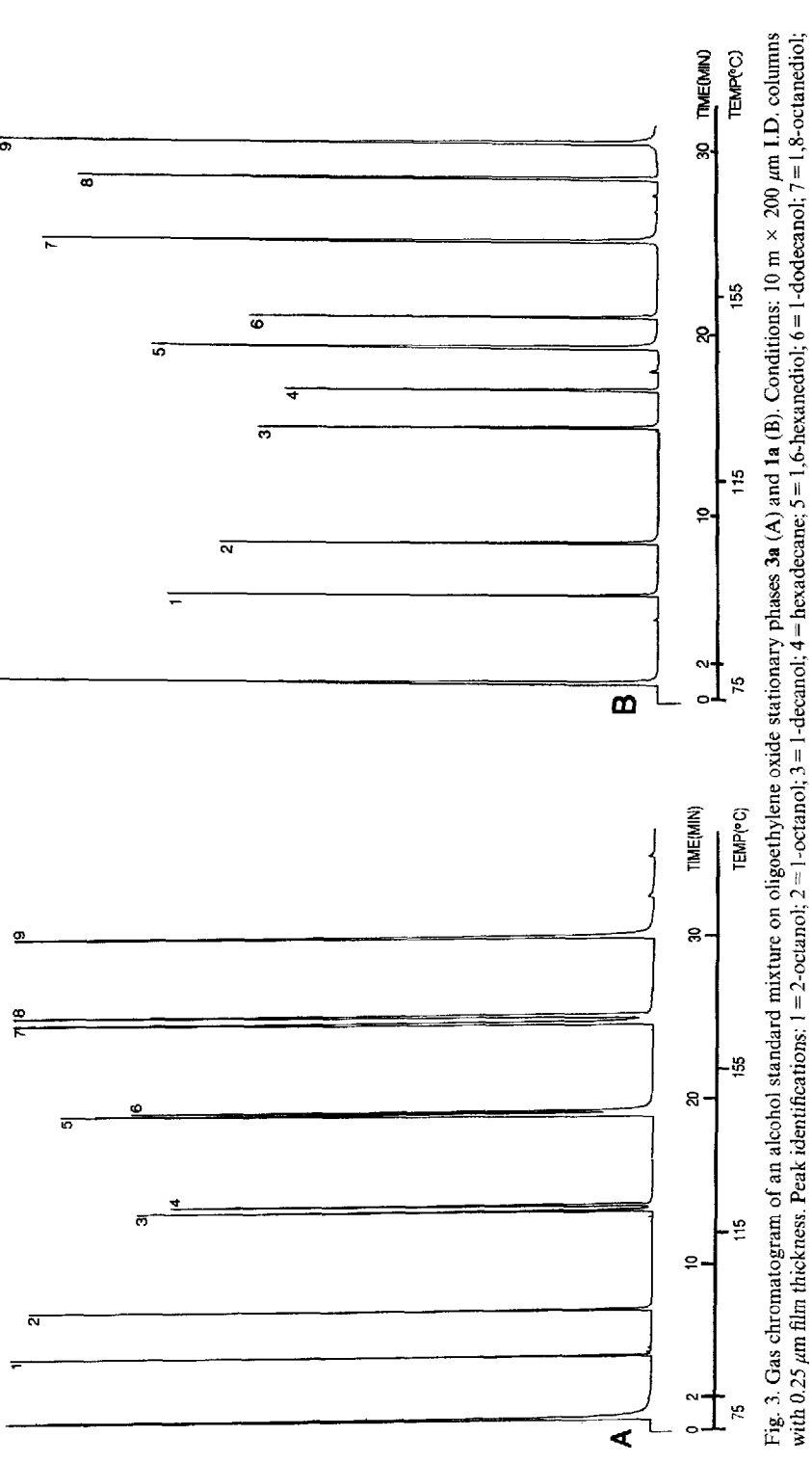


Fig. 3. Gas chromatogram of an alcohol standard mixture on oligoethylene oxide stationary phases **3a** (A) and **1a** (B). Conditions: 10 m × 200 μm I.D. columns with 0.25 μm film thickness. Peak identifications: 1 = 2-octanol; 2 = 1-octanol; 3 = 1-decanol; 4 = hexadecane; 5 = 1,6-hexanediol; 6 = 1-dodecanol; 7 = 1,8-octanediol; 8 = eicosane; and 9 = 1,10-decanediol.

mentioned phenyl group, (3) number of oxygens in the oligoethylene oxide chain, and (4) methyl or ethyl end groups on the oligoethylene oxide chain. The preferred oligoethylene oxide-containing polysiloxanes have a phenyl unit in the side chain (**1a**–**5a**). These materials were found to have higher thermal stability than those that did not have a phenyl unit in the chain (*e.g.* phases **6a**–**8a**). These latter phases showed serious degradation above 240°C. The higher stability is due to many factors, however it is possible that the phenyl groups afford some steric protection to the polysiloxane backbone.

The alkenes needed to prepare the different polysiloxane phases shown in Fig. 1 were prepared as shown in Schemes 2–4. The best method to join the oligoethylene oxide group to the benzene ring employed sodium or potassium hydroxide in DMSO to remove the proton from 4-bromophenol, and then slow addition of the tosylate (Scheme 2). It was possible to run the complete set of reactions in one pot with mechanical stirring as follows: the tosylate of the monomethyl ether was formed using hydroxide and DMSO, the phenoxide was prepared in a separate container also in DMSO and slowly added to the tosylate. The resulting solution was allowed to react at 45–65°C for 3–5 h. The allyl group was then attached by forming a Grignard reagent in THF and trapping the Grignard with allyl bromide.

The procedure shown in Scheme 2 to prepare the alkene containing both a benzene ring and the oligoethylene oxide unit is not synthetically convenient because of the need to use a Grignard reaction to attach the allyl group. A more convenient method is to prepare the oligoethylene oxide-containing alkenes from eugenol (4-allyl-2-methoxyphenol) as shown in Scheme 3. Oxide materials **3** and **4** are similar to **1** and **2**, respectively, except for the added methoxy substituent on the benzene ring. Excellent yields of both **3** and **4** were realized. Care must be taken to exclude all acid before the final distillation step in the purification of **3** and **4**. Acid causes the allyl group to isomerize to form a methylvinyl substituent.

Polysiloxane phase **3a**, which was prepared using the more convenient synthetic pathway, was found to provide somewhat different performance than phase **1a**. The only structural difference between **1a** and **3a** is the methoxy substituent on the benzene ring of **3a**. Phase **3a** was tested in detail and compared to phase **1a**.

Fig. 3 shows chromatograms of an alcohol standard mixture separated on phases **3a** (A) and **1a** (B), respectively. Both phases demonstrate comparable retention of polar solutes. This is shown by the retention times of the diols of peak numbers 5, 7 and 9. The alkenes (peaks 4 and 8) on the other hand, are less retained on methoxy-substituted phase **3a**. High-molecular-weight alcohols are also less retained on phase **3a** as their alkane chains get longer. Phase **3a** would indicate higher polarity than phase **1a** if the phases were compared using a retention index scale.

Phase **3a** was found to have low thermostability before it was crosslinked. At 210°C the bleed from the uncrosslinked phase was 2 pA using a flame ionization detector and a 10 m × 200 μm I.D. column having a 0.15-μm polymer film thickness. A dynamic free radical initiated crosslinking procedure using dicumyl peroxide improved the thermal stability of phase **3a** to 260–270°C. The solute retention properties of crosslinked **3a** was changed unless mild crosslinking conditions were used. Phase **3a** is not as thermally stable as **1a** and, therefore, has no advantage over **1a** except for its ease of preparation. No further tests of phase **3a** for use in GC were carried out.

Phase **5a**, with two methoxy groups on the benzene ring, exhibited poor GC

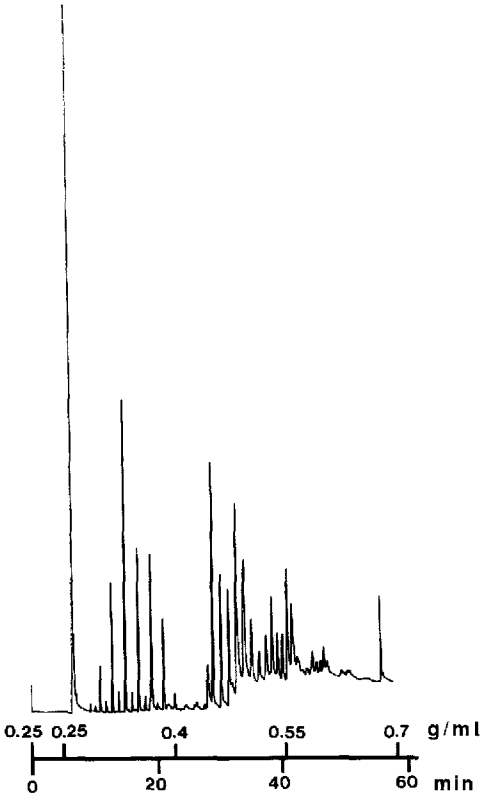


Fig. 4. Supercritical-fluid chromatogram of a beeswax extract on oligoethylene oxide stationary phase **3a**. Conditions: CO_2 at 120°C, 9 m × 50 μm I.D. capillary column with 0.25 μm film thickness.

performance in all aspects of efficiency, selectivity and thermostability and was not tested further. It is obvious, from the above results, that having methoxy groups on the benzene ring in phases **3a** and **5a** significantly affects the selectivity and thermal stability of the phase.

Fig. 4 shows a capillary supercritical-fluid chromatogram of a beeswax extract using phase **3a**. After crosslinking, this phase remained stable under stringent SFC conditions for several weeks. Also, the limited thermostability of the phase as mentioned above is not a problem for use in SFC. The non-polar hydrocarbon series, in the early part of the chromatogram, and the medium polar long chain ester series starting to elute after 25 min in the chromatogram, are both well resolved.

Removal of the benzene ring from these phases greatly lowers their stability as shown by the fact that phases **6a–8a** could not be used above 240°C and showed severe bleeding from around 180°C. Also, the addition of another ethylene oxide unit at the end of the arm as in phases **2a** and **4a** resulted in decreased thermostability without any measurable gain in selectivity.

The importance of having a benzene ring in a medium polar oligoethylene oxide-substituted polysiloxane phase has been demonstrated in this systematic study of the structural influence on the chromatographic performance of these oligoethylene

oxide phases. New phases containing different substituents at the end of the oligoethylene oxide chain are presently under study to see if stable phases with unique selectivities can be prepared based on the phenyl-containing oligoethylene oxide polysiloxane structure.

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