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## Note

### Chloromethyl methyl polysiloxane as a stationary phase

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Almost since the inception of gas chromatography a variety of industrially available polysiloxane products with small amounts of chlorosubstitution have been reported as stationary phases. While the compositions have not been definitely indicated the chlorine has normally been associated with a phenyl group. A periodic review<sup>1</sup> of polysiloxanes has shown the products that have been reported in gas chromatography with the materials DC-560, F-60, F-61 and SP-400, all being of similar composition with *ca.* 11% chlorophenyl substitution. The presence of *p*-chlorophenyl and phenyl groups have been suggested but Coleman<sup>2</sup> has reported infrared absorption bands due to dichlorophenyl groups. The product SP-400 marketed by Supelco (Bellefonte, Pa., U.S.A.) is the only chlorinated product specifically offered as a stationary phase. Another product, F-50, is of less definite composition, it having been reported as containing methyl *p*-chlorophenyl groups<sup>3</sup>, methyl (10%) trichlorophenyl groups<sup>4</sup>, methyl, trichlorophenyl, trisilyl ether groups<sup>5</sup> and tetrachlorophenyl groups<sup>2</sup>. The McReynolds constants however are in substantial agreement with dimethyl polysiloxane. A further material<sup>6</sup> which has been suggested as a stationary phase is Dow Corning (Midland, Mich., U.S.A.) Fluid F-4050. This utilises a different chlorophenyl substitution being a short chain dimethyl polysiloxane end terminated with a 3,5-dichlorophenyl group.

Examination of a representative of the first group of phases did not suggest any specific contribution of the halogen<sup>7,8</sup> this being in agreement with a study of phase selectivity using factor analysis by Weiner and Parcher<sup>9</sup>. This performance is not unexpected from the constants shown in Table I where the materials are comparable with a phase containing 5% phenyl substitution. With steroid analyses Horning *et al.*<sup>10</sup> reported a similarity to SE-30.

Any acceptor character  $u'$  of the substituent due to the halogen would appear to be minimised by the effects of the aromatic ring, while with F-50 no influence of the chlorine or the aromatic ring is evident, the material essentially being comparable with dimethyl siloxane. In both cases it is evident that the low degree of substitution retards any specific influence that may be inherent.

Giles and his coworkers<sup>11,12</sup> have reported hydrogen bonding between chloro groups and esters which appear to act as inter- and intra-molecular proton donors, the CH group in the ester residue having enhanced activity due to its proximity to the carbonyl groups.

TABLE I

McREYNOLDS CONSTANTS AND GENERAL POLARITY OF CHLOROPHENYL SUBSTITUTED AND OTHER COMPARABLE POLYSILOXANES

Phase	$\Delta I$ (McReynolds solutes)					
	X	Y	Z	U	S	$\Sigma \Delta I$
DC-560*, F-60*, F-61*, SP-400**	32	72	70	100	68	342
SE-52***	32	72	65	98	67	334
Versilube F-50***	19	57	48	69	47	240
OV-1 <sup>§</sup>	17	57	45	67	43	230
Methyl chloromethyl polysiloxane	141	217	245	309	254	1166
OV-25 <sup>§</sup>	178	294	298	305	280	1175
QF-1*	144	233	355	463	305	1500

\* Dow Corning, Midland, Mich., U.S.A.

\*\* Supelco, Bellefonte, Pa., U.S.A.

\*\*\* General Electric, New York, N.Y., U.S.A.

<sup>§</sup> Ohio Valley Specialty, Marietta, Ohio, U.S.A.

To examine the particular character of a halogenated polysiloxane the material chloromethyl methyl polysiloxane prepared as an intermediate for further synthesis has been studied with regard to any acceptor character such as is evident with the trifluoromethyl siloxane<sup>1</sup>.

#### EXPERIMENTAL

The chloromethyl methyl polysiloxane was prepared by conventional hydrolysis and condensation of chloromethyl(methyl)dichlorosilane. The silane was hydrolysed under controlled conditions of temperature with the reaction conducted in toluene solution to control the substantial exotherm and the molecular weight and was not allowed to increase above 30°. The hydrolysis and polymerisation occur simultaneously and care is necessary to ensure that on separation of the aqueous and organic layers that some of the acidic aqueous layer is retained to ensure that hydrolysis of the alkyl chlorine group does not occur. While maintaining slightly acidic condition the polymer was terminated by the addition of trimethylsilane.

Recovery of the polymer was carried out after removal of water by heating to remove excess of the chain terminator. The viscosity of the polymer was controlled by the reaction temperature and the toluene concentration such that a final product with a viscosity of *ca.* 10,000 cSt was achieved.

The infrared spectrum of the polymer showed bands attributable to the composition desired<sup>13</sup> while microanalyses were in agreement with the calculated results.

To minimise crosslinking which markedly affects the viscosity and the solubility, it is important that the toluene solutions should not be left in prolonged contact with the aqueous hydrochloric acid layer which if in high concentration will split the carbon-silicon bond and induce crosslinking. Throughout the reaction stirring is essential as the hydrolysis takes place at the water-toluol interface.

The polymer was soluble in aromatic solvents and in chloroform which was used in preparing the chromatographic column.

*Gas chromatography*

The analyses were carried out using 10% of the stationary phases on Chromosorb W AW DMCS. Columns of 1/8-in. and 1/4-in. O.D. of aluminium and stainless steel were employed. Determinations were carried out at 120°.

To increase the speed and accuracy of the determination of retention data, a Hewlett-Packard 5750 research gas chromatograph has been interfaced to a 16 K P.D.P. 11/40 digital computer. The chromatograph employed a splitter and individually operated detectors with injection by a Hewlett-Packard 7670A automatic sampler. Calculation of dead time and of retention indices was conducted mathematically within the system.

## RESULTS AND DISCUSSION

The McReynolds constants of the chloromethyl methyl polysiloxane are shown in Table I, together with data of other available polysiloxanes with low degrees of substitution where it is evident that the values of the materials prepared are substantially higher than the earlier materials and indicating that at least the polarity is increased. The table also includes data for OV-25 [polyphenyl (75%) methyl siloxane (25%)] which has the same general polarity as indicated by a summation of the index differences of the five established McReynolds solutes and for QF-1 (poly trifluoropropyl methyl siloxane) a phase with known selectivity towards certain carbonyl functional groups<sup>14</sup>.

VandenHeuvel *et al.*<sup>14</sup> indicated selective behaviour in the order ether, hydroxy, ester and keto groups, the material having subsequently found considerable use with ketone materials.

The McReynolds constants of the chloromethyl methyl polysiloxane indicate a general polarity comparable with OV-25 however the *X* and *Y* values are low and comparable to those of QF-1. While some similarities to QF-1 are evident the position is best examined by comparison with compounds of various functional classes of equivalent boiling point. The retention indices of the compounds considered are shown in Table II.

The retention index of ethyl acetate (b.p. 77.2°) on SE-30 is 592 almost equiva-

TABLE II

RETENTION INDICES OF HOMOLOGOUS ESTERS AND KETONES OF EQUIVALENT BOILING POINT

<i>Compound</i>	<i>B.p.</i>	<i>SE-30</i>	<i>OV-25</i>	<i>Chloromethyl methyl polysiloxane</i>	<i>QF-1</i>
<i>n</i> -Ethyl acetate	77.2	592	738	740	855
<i>n</i> -Propyl acetate	101.6	695	835	846	960
<i>n</i> -Butyl acetate	126.5	794	934	948	1066
<i>n</i> -Pentyl acetate	148.0	891	1029	1044	1161
2-Butanone	79.6	569	751	780	903
2-Pentanone	102.0	673	836	872	994
2-Hexanone	127.0	778	931	974	1100
3-Pentanone	102.7	660	814	862	940
3-Heptanone	147.6	870	1028	1076	1193

lent to that of *n*-hexane (b.p. 68.7°) while the retention of 2-butanone (b.p. 79.6°) is 569. With OV-25 the general polarity and donor character are increased and while the retention value are generally increased the 2-butanone ( $I = 751$ ) retention is now slightly greater than that of the ester ( $I = 738$ ) and thus while the increased polarity has an effect on enhancement of the ketone value it is evident that with QF-1 the retention differences of 2-butanone ( $I = 903$ ) and of the ester ( $I = 855$ ) have increased by a factor of 3, *i.e.*, 13 units to 45 units.

With the chloromethyl methyl polysiloxane retention of 2-butanone ( $I = 780$ ) is greater than for ethyl acetate ( $I = 740$ ) and the retention difference, *i.e.*, 40 units, is similar to that experienced with QF-1.

With higher homologs of comparable boiling points 2-hexanone (b.p. 127°) and *n*-butyl acetate essentially identical retention on OV-25 values are achieved, *i.e.*,  $I = 931$  and 934 respectively, while with the chlorinated phase the corresponding values are  $I = 974$  and 941 showing a slight enhancement of the ketone retention as with the lower boiling homologs. The same pattern follows with QF-1 where these increases are from 1100 and 1066, *i.e.*, *ca.* 40 units. Higher boiling esters, *i.e.*, 3-heptanone (b.p. 147.6°) and *n*-pentyl acetate (b.p. 148°) show the same trends with QF-1. The enhancement of the ketone retention is 32 index units, *i.e.*, from 1161 to 1193 while with the methyl chloromethyl polysiloxane the retention enhancement is 29 units.

It is evident that the retention of benzene is much higher on the OV-25 phase than on the chlorinated phase where the retention is comparable with that observed with QF-1. this observation being in agreement with low donor activity.

While the chlorosilanes and related compounds show considerable reactivity with a wide variety of functional groups and find use as basic reactive intermediates<sup>15,16</sup> examination has shown that the chloromethyl methyl polysiloxane is of low reactivity. With the use of alcohols, attempts to achieve on-column abstraction were made without success. If on-column chemical reaction occurs this is readily apparent as has been demonstrated most recently by the reaction of aminoalkyl polysiloxanes<sup>17</sup> and polyalkylimines<sup>18</sup> with ketones and aldehydes.

## CONCLUSION

Definite acceptor character is exhibited by the chloromethyl methyl polysiloxane with considerable enhancement of ketone retention similar to that observed with QF-1. Similarly both phases show rapid elution of benzene, this being particularly apparent with the phase prepared which has general polarity similar to OV-25, a highly aromatic material that shows greater retention of benzene. With the acceptance of an acceptor character it is likely that further enhancement would be achieved by the presence of increased chlorine substitution.

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