The Infrared Spectra of Ethoxy- and Methylethoxy-polysiloxanes

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In this report, the studies of infrared spectra of three types of methylethoxy-polysiloxanes represented by A, B and C, and linear and cyclic ethoxypolysiloxanes D and E will be described, of which the spectra of A_1[1], B_1[1] and D_1[2] have already been reported briefly.

A_n $C_2H_5O((CH_3)_2SiO)_nC_2H_5$ $n=1, 2, 3, 4$
B_n $C_2H_5O((CH_3)Si(OC_2H_5)O)_nC_2H_5$ $n=1, 2, 3, 4, 5$
C_n $((CH_3)Si(OC_2H_5)O)_n$ $n=3, 4$
D_n $C_2H_5O(Si(OC_2H_5)_2O)_nC_2H_5$ $n=1, 2, 3$
E_n $(Si(OC_2H_5)_2O)_n$ $n=4, 5$

One of the objects of this study is to find characteristic absorption bands associated with the group $(Si)OC_2H_5$*. The spectra of methylpolysiloxanes F and G, which were discussed by Wright[3] and Richards[1], are used to explain the spectra obtained in this study.

F $CH_3((CH_3)_2SiO)_nSi(CH_3)_3$
G $((CH_3)_2SiO)_n$

Experimental

Materials.—The preparation and the properties of the members of B, C and E used in this experiment have already been reported[4,5]. Authentic samples were used for the measurement of the spectra of A and D.

Measurements.—Spectra were obtained with a Hilger H-800 infrared spectrophotometer with a rock salt prism. Samples were used both as pure liquid and as solutions, 2—5% in carbon disulfide for 700 to 1500 cm^{-1}, and 5—10% in carbon tetrachloride for 1250 to 3500 cm^{-1}. No appreciable difference was observed between the two cases. The cells were 0.03 mm. thick for the solution and less than 0.01 mm. for pure liquid. In order to compare relative intensity, the absorption of the compounds belonging to the same series was recorded on the same chart, keeping the conditions as much alike as possible.

TABLE I
INFRARED SPECTRA OF METHYLETHOXYPOLYSILOXANES : POSITIONS OF BANDS (in cm^{-1})

A_n					B_n						C_n	
$n=1$*	$n=1$	$n=2$	$n=3$	$n=4$	$n=1$*	$n=1$	$n=2$	$n=3$	$n=4$	$n=5$	$n=3$	$n=4$
798	785	797	798	803	732		759	760	760	762	755	761
841	835	841	838	844	780	775	779	785	784		791	
846					806		794	799		791	809	801
953	949	955	953	952	820	818						
		1059	1043	1034	831	824	820	821	820	827	843	
1078	1075	1080	1080	1078	960	956	959	958	960	959	960	957
1105	1102	1111	1109	1111			1060	1056	1060	1056	1023	1068
1166	1160	1162	1156	1162	1078	1074	1073	1071	1071	1070	1078	1087
1260	1254	1256	1256	1256	1100	1098	1099	1096	1096	1096		
					1120		1116	1114	1117	1114	1111	1117
					1166	1164	1163	1162	1162	1158	1160	1159
					1266	1259	1260	1260	1259	1262	1260	1262

* R. E. Richards and H. W. Thompson, *loc. cit.*[1]

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[1] R. E. Richards and H. W. Thompson, *J. Chem. Soc.*, **1949**, 124.

[2] I. Šimon and H. O. McMahon, *J. Chem. Phys.*, **20**, 905 (1952).

[3] N. Wright and M. J. Hunter, *J. Am. Chem. Soc.*, **69**, 803 (1947).

* $(Si)OC_2H_5$ indicates an ethoxy group attached to silicon atom.

[4] R. Ōkawara, S. Hotta and T. Shimura, This Bulletin, **28**, 541 (1955).

[5] R. Ōkawara, G. Minami and Z. Oku, ibid., **31**, (1958).

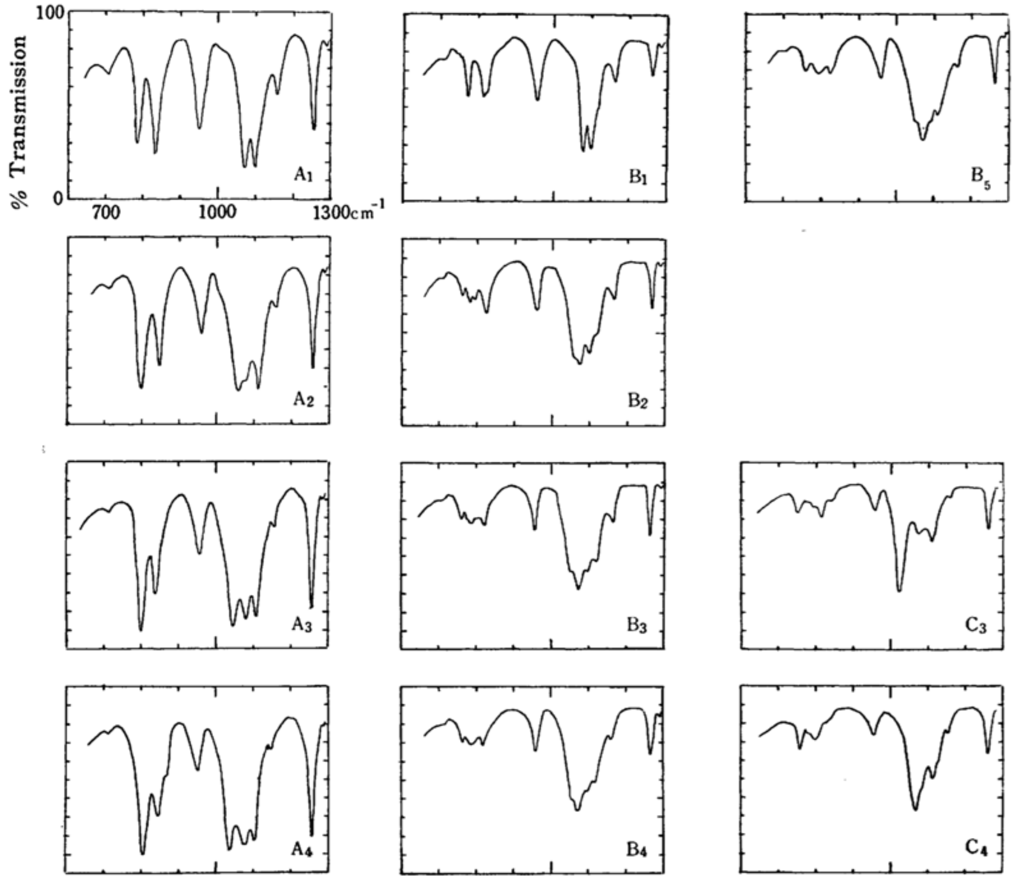

Fig. 1. Infrared spectra of methylethoxypolysiloxanes.

A_n: $C_2H_5O((CH_3)_2SiO)_nC_2H_5$, 5% in CS_2
B_n: $C_2H_5O((CH_3)Si(OC_2H_5)O)_nC_2H_5$, 3% in CS_2
C_n: $((CH_3)Si(OC_2H_5)O)_n$, 2% in CS_2

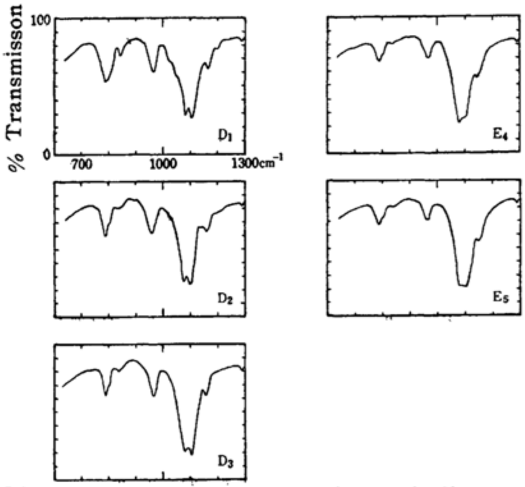

Fig. 2. Infrared spectra of ethoxypolysiloxanes.
D_n: $C_2H_5O(Si(OC_2H_5)_2O)_nC_2H_5$, 2% in CS_2
E_n: $(Si(OC_2H_5)_2O)_n$, 2% in CS_2

TABLE II
INFRARED SPECTRA OF ETHOXYPOLYSILOXANES: POSITIONS OF BANDS (in cm^{-1})

D_n			E_n	
$n=1$	$n=2$	$n=3$	$n=4$	$n=5$
790	790	788	791	790
846	847	848		
962	966	968	968	968
1081	1079	1080	1078	1079
1104	1102	1102	1101	1099
1163	1162	1160	1163	1163

The spectra of A, B and C, and those of D and E are shown in Fig. 1 and Fig. 2, respectively. The positions of the bands up to 1300 cm^{-1} are given in Table I and II.

Discussion of the Results

In the region 750—1000 cm^{-1}, there are some strong bands. Among them the one near 960 cm^{-1} has an approximately constant wave number and no neighboring absorption band in any of the compounds investigated. Since this band does not appear in F and G, it seems certain that the band is associated with the grouping (Si)OC_3H_5. This presumption is further supported by comparing the relative intensity of the band of each member belonging to the same series. For example in A and B, the intensity of this band decreases as n increases. A similar band appears at 960 cm^{-1} in the compounds having (Si)CH_2CH_3 grouping[6]; accordingly it is probably possible to attribute those to the vibration in ethyl group, probably to that of the stretching of C—C bond.

In A, there are two common bands near 800 cm^{-1} and 840 cm^{-1}. The intensity of the former becomes stronger and that of the latter becomes weaker, as n increases. It may be concluded that the former corresponds to 800 cm^{-1} band characteristic of $(CH_3)_2SiO$[1,3] unit in F and G, and the latter is connected with the OC_2H_5 group in $(CH_3)_2Si(OC_2H_5)O_{1/2}$ unit. In B and C, there are overlap bands near 800 cm^{-1}, and their shape is so complex that they may be considered to consist of many bands. In D and E, a band is observed near 790 cm^{-1}, which may be thought to be a characteristic band of ethoxypolysiloxanes.

The absorption bands in 1000—1200 cm^{-1} are probably associated with Si—O—Si and Si—O—C linkages. Since the absorption band, though not very strong in intensity, appeared at constant wave number of 1160 cm^{-1} in all the compounds, and the intensity decreases clearly with increasing polymer size in A, it seems certain that this band is associated with (Si)OC_2H_5 grouping. Though quite tentative, this band would be connected with the stretching vibration of C—O bond, because this band is not found in the spectra of the compounds containing (Si)CH_2CH_3 group[6]. In A and B, common strong bands occur at 1080 cm^{-1} and 1110 cm^{-1} which may be connected with the Si—O—C linkage and are attributed probably to the stretching of Si—O bond. In A_n except A_1, another band of comparative intensity is observed near 1050 cm^{-1}, which decreases in wave number as n increases. Since Wright and Hunter have assigned 1050 cm^{-1} band in F and G to the stretching mode of Si—O vibration and have pointed out their shift to a smaller wave number with increasing polymer size, it seems possible to connect this band with Si—O stretching mode of Si—O—Si linkage. B_1 has only two bands at 1070 and 1098 cm^{-1} in this region, while in the higher members of this series another two bands are observed, of which the one found at 1060—1056 cm^{-1} would correspond to the band at 1050 cm^{-1} in A. It has been known[7] that stable cyclotrisiloxanes of the type $(RR'SiO)_3$ (R, R$'$= alkyl or aryl group) have their Si—O(—Si) stretching band in the region 1000—1020 cm^{-1}. As already reported[5], this band appears also in the spectra of unstable C_3 as well as $(C_2H_5Si(OC_2H_5)O)_3$ at 1023 cm^{-1}. With samples of the former reserved in a glass ampule, this band decreased in intensity after 500 days, while the refractive index and the viscosity increased. As in the case of unstable $((C_2H_5)HSiO)_3$[8], this band will be associated with the stretching vibration of Si—O bond of cyclotrisiloxane ring, and the 1068 cm^{-1} band of C_4 will be attributed to the same vibration of cyclotetrasiloxane ring.

A fairly successful explanation of the spectra of this region from the similarity of the structure to dimethylpolysiloxanes may be made only in the case of A, and it becomes difficult in the case of D and E. All the members of series D and E appear to have only two bands. It is likely that the bands associated with Si—O—Si and Si—O—C linkages cover each other.

To a sharp intense band near 1265 cm^{-1}, some different assignments[9] have been

TABLE III

INFRARED SPECTRA OF POLYSILOXANES IN 1300—1500 CM^{-1} REGION:

POSITIONS OF BANDS (in cm^{-1})

A, B, C	D, E	F*	G**
1295	1295	—	1300
1365	1365	—	—
1390	1390	—	—
1410	—	1410	1405
			1417
1440	1442	1442	1446
1485	1483	—	—

* N. Wright and M. J. Hunter, *loc. cit.*[3]

** R. E. Richards and H. W. Thompson, *loc. cit.*[1]

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[6] M. Sakiyama, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zassi*), **60**, 1385 (1957).

[7] C. W. Young, P. C. Servais, C. C. Currie and M. J. Hunter, *J. Am. Chem. Soc.*, **70**, 3758 (1948).

[8] R. Ōkawara, U. Takahashi and M. Sakiyama, This Bulletin, **30**, 608 (1957).

[9] C. W. Young, J. S. Koheler and D. S. McKinney, *J. Am. Chem. Soc.*, **69**, 1410 (1947); D. H. Rank, B. D. Saksena and E. R. Shull, *Discuss. Farad. Soc.*, **9**, 187 (1950).

made. In this study, it has become clear that this band is related to the (Si)CH_3 group since this band is observed in A, B and C.

In 1300—1500 cm^{-1} region, six weak bands are observed. For comparison the absorption bands in this region are presented in Table III together with those of F and G.

From Table III, 1295, 1365, 1390, 1440 and 1485 cm^{-1} bands are supposed to be associated with (Si)OC_2H_5 group.

Summary

1) The infrared spectra of the lower members of ethoxy-, and methylethoxypolysiloxanes measured in the rock salt region are discussed.

2) Up to 1200 cm^{-1}, the common bands near 960 and 1160 cm^{-1} are certainly to be connected with the grouping (Si)OC_2H_5.

3) Moreover, characteristic bands of (Si)OC_2H_5 group appear near 840 cm^{-1} in ethoxy end-blocked dimethylpolysiloxanes and near 790 cm^{-1} in ethoxypolysiloxanes.

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