The Infrared Spectra of Methoxy-, Methylmethoxy- and Methoxy Endblocked Dimethyl-polysiloxanes

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The group frequency assignments have already been given for the infrared spectra of organoalkoxypolysiloxanes, such as alkylalkoxysilanes[1] and ethoxy- and methylethoxy-polysiloxanes[2]. In this paper the infrared spectra of three types of polysiloxanes represented by A, B and C, which contain methoxy and methyl groups in various proportions, will be described.

A_n : $CH_3O[(CH_3O)_2SiO]_nCH_3$ $n=1\sim3$
B_n : $CH_3O[CH_3OSi(CH_3)O]_nCH_3$ $n=1\sim5$
C_n : $CH_3O[Si(CH_3)_2O]_nCH_3$ $n=1\sim6$

These polysiloxanes have simple structural units, and the infrared spectra seem to be explained fairly well. The vibrational spectrum of C_1 (dimethyldimethoxysilane) has been reported[3] and most of the assignments have agreed with the results which would be described in this paper. Referring to the results of this experiment and the infrared spectra of

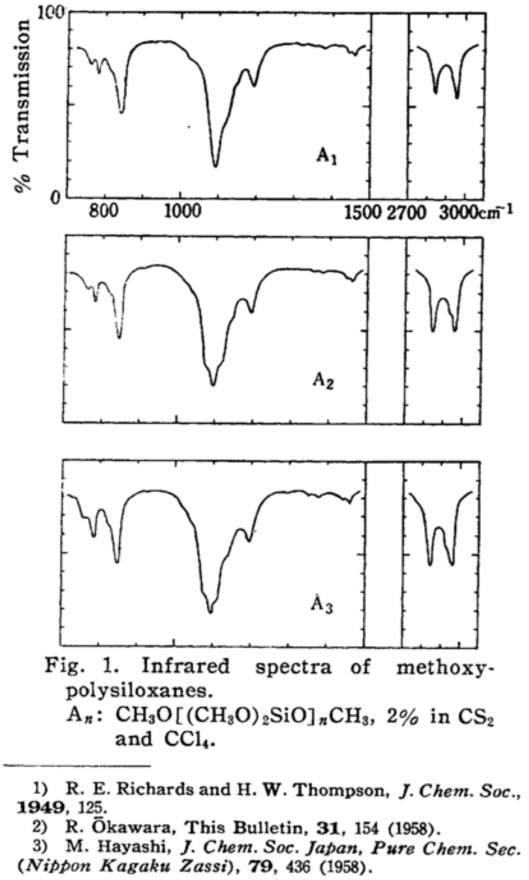

Fig. 1. Infrared spectra of methoxy-polysiloxanes.
A_n: $CH_3O[(CH_3O)_2SiO]_nCH_3$, 2% in CS_2 and CCl_4.

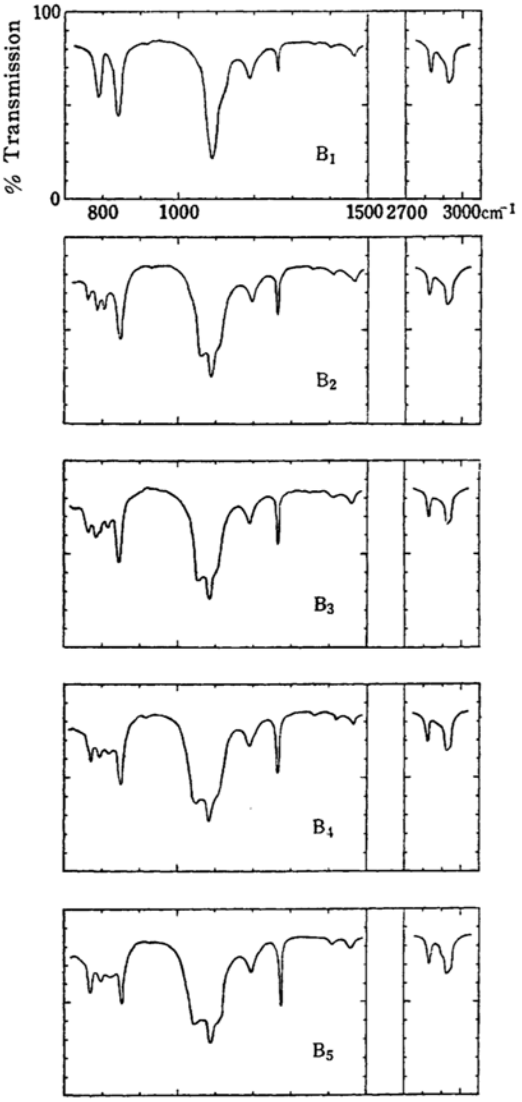

Fig. 2. Infrared spectra of methylmethoxy-polysiloxanes.
B_n: $CH_3O[CH_3OSi(CH_3)O]_nCH_3$, 3% in CS_2 and CCl_4.

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[1] R. E. Richards and H. W. Thompson, *J. Chem. Soc.*, **1949**, 125.

[2] R. Ōkawara, This Bulletin, **31**, 154 (1958).

[3] M. Hayashi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **79**, 436 (1958).

dimethylpolysiloxanes[4] (represented by D), one would make the explanation of the infrared spectra of the more complicated organoalkoxypolysiloxanes.

D_n : $CH_3[Si(CH_3)_2O]_nSi(CH_3)_3$ $n=1\sim7$

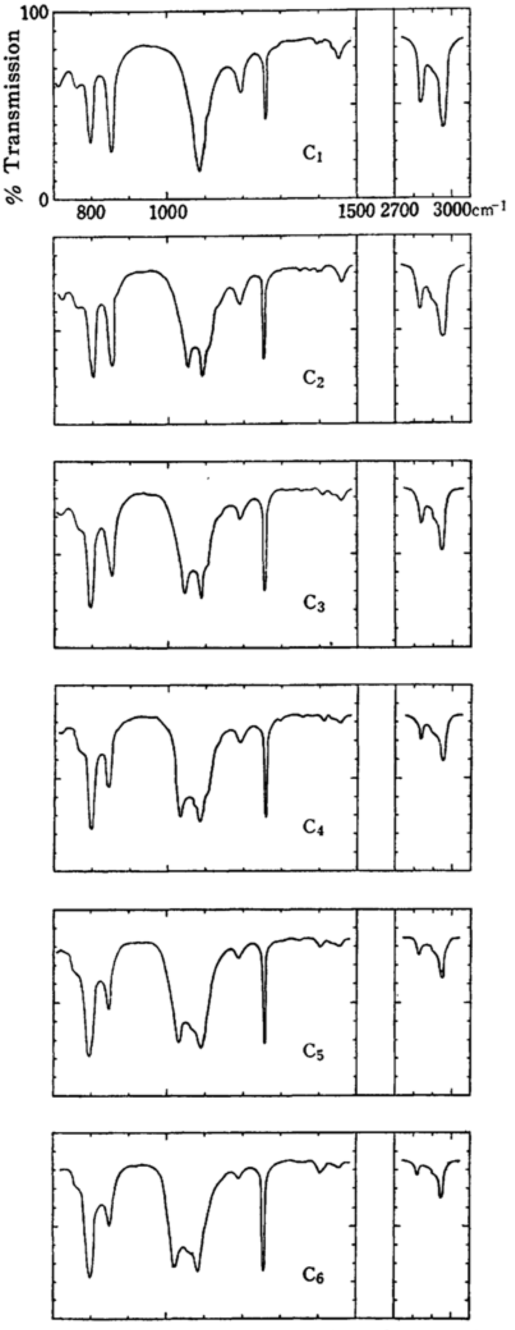

Fig. 3. Infrared spectra of methoxy endblocked dimethylpolysiloxanes.
C_n: $CH_3O[Si(CH_3)_2O]_nCH_3$, 5% in CS_2 and CCl_4.

Experimental

Materials.—The preparations and the properties of the members of A[5], B[6] and C[7] used in this experiment were already reported.

Measurements.—The spectra were obtained by the use of Hilger H-800 infrared spectrophotometer with a rock salt prism. Samples

TABLE I

INFRARED SPECTRA OF METHOXYPOLYSILOXANES: POSITIONS OF BANDS (in cm⁻¹)

A_n		
$n=1$	$n=2$	$n=3$
760 w	762 sh	761 sh
784 m	785 m	784 m
840 s	842 s	842 s
1038 sh	1044 sh	1046 sh
—	1078 sh	1080 sh
1094 vs	1095 vs	1095 vs
1112 sh	1112 sh	1112 sh
—	1143 sh	1144 sh
1195 m	1195 m	1196 m
1352 vw	1350 vw	1351 vw
1381 w	1381 w	1381 w
1444 w	1443 w	1443 w
1458 w	1459 w	1459 w
2350 br	2332 br	2321 w
—	—	2361 w
2847 m	2848 m	2848 s
—	2943 sh	2941 sh
2965 m	2968 m	2967 s

TABLE II

INFRARED SPECTRA OF METHYLMETHOXYPOLYSILOXANES: POSITIONS OF BANDS (in cm⁻¹)

B_n				
$n=1$	$n=2$	$n=3$	$n=4$	$n=5$
—	767 m	767 m	769 m	769 m
790 m	790 m	790 m	791 w	792 w
—	808 m	818 m	821 w	822 w
845 m	847 m	848 m	850 m	850 m
—	1066 m	1051 m	1045 m	1041 m
1089 s	1088 s	1087 s	1085 s	1086 s
1110 sh	1108 sh	1109 sh	1110 sh	1112 sh
1192 m	1192 m	1193 m	1192 m	1194 m
1267 m	1266 m	1267 m	1267 m	1268 m
1402 vw	1404 vw	1403 vw	1402 vw	1405 vw
1459 w	1458 w	1457 w	1457 w	1458 w
2333 br	2342 br	2343 br	2344 br	2338 br
2825 m	2824 m	2823 m	2823 m	2825 m
2931 m	2930 m	2931 m	2930 m	2932 m
2953 sh	2951 sh	2953 sh	2953 sh	2953 sh

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

[5] T. Tanaka and T. Watase, This Bulletin, **28**, 258 (1955).

[6] T. Tanaka, A. Tasaka and R. Ōkawara, *Technol. Repts. Osaka Univ.*, **7**, 193 (1957).

[7] T. Tanaka and R. Ōkawara, This Bulletin, **28**, 364 (1955).

TABLE III

INFRARED SPECTRA OF METHOXY ENDBLOCKED DIMETHYLPOLYSILOXANES: POSITIONS OF BANDS (in cm^{-1})

	C_n					
$n=1$*	$n=1$	$n=2$	$n=3$	$n=4$	$n=5$	$n=6$
730 s	713 w	720 w	716 vw	715 vw	—	—
	761 w	761 w	762 sh	761 sh	762 sh	761 sh
797 s	797 s	798 s	799 s	798 s	799 s	798 s
849 vs	855 s	853 s	851 s	847 s	849 m	850 m
998 vw	—	—	—	—	—	—
—	—	1055 s	1045 s	1036 s	1028 s	1021 s
1089 vs	1083 s	1091 s	1092 s	1092 s	1091 s	1092 s
—	—	1112 sh	1113 sh	1115 sh	—	—
1160 sh	—	—	—	—	—	—
1188 m	1190 m	1189 m	1191 w	1190 w	1190 w	1189 w
1258 m	1258 m	1261 s	1263 s	1263 s	1262 s	1262 s
1295 sh	—	1296 vw	1298 sh	1298 vw	—	—
1340 w	1343 vw	1343 vw	1342 vw	—	—	—
1399 sh	1399 w	1403 w	1403 w	1405 w	1405 w	1406 w
—	—	—	—	1435 sh	1439 sh	1443 sh
1456 s	1460 m	1458 m	1459 w	1458 w	1457 vw	1460 vw
—	—	2342 br	2342 br	2333 br	2316 w	2323 w
					2358 sh	2355 w
—	2830 m	2829 m	2827 m	2825 w	2826 w	2821 w
—	—	2906 sh	2906 sh	2907 sh	2906 sh	2908 sh
—	2947 s	2960 s	2956 s	2955 m	2953 m	2953 m

* M. Hayashi, *loc. cit.*[8]

were observed in this experiment both as a solution in carbon disulfide for the range 700 to 1500 cm^{-1} and in carbon tetrachloride from 1250 to 3500 cm^{-1}, and as pure liquid. The concentration of each solution was 2, 3 and 5% for A, B and C, respectively. The celles were 0.03 mm. thick in the case of the solution and less than 0.01 mm. in the case of pure liquids. No appreciable difference was observed between the two cases.

In order to compare the relative intensity approximately, the absorption of the compounds belonging to the same series have been recorded on the same chart, keeping the conditions as similar as possible. The spectra and the positions of the absorption bands obtained are presented in Figs. 1—3 and Tables I—III, respectively.

Discussion of the Results

All the compounds of A, B and C show two absorption peaks in the region $2800\sim3000\ cm^{-1}$. The members of A have a kind of methyl group attached to oxygen atom, so the two bands near 2847 and 2965 cm^{-1} are assigned to the symmetric and non-symmetric stretching vibration of (O—)CH_3 group*, respectively. These bands are also observed in B and C; the intensities decrease with the decreasing concentration of methoxy group as the polymer sizes increase, and this behavior is distinct in C. Considering this behavior and fairly weak intensity of C—H stretching band in (Si—)CH_3 group* the bands near 2825 and 2930 cm^{-1} in B and near 2825 and 2955 cm^{-1} in C are attributed to the symmetric and the non-symmetric C—H stretching vibration arising mainly from (O—)CH_3 group, respectively**. Thus the band associated with (O—)CH_3 group appears on the low frequency side of the CH absorption in (C—)CH_3 group, and this fact has been observed by Henbest et al.[8] The shoulders near 2953 cm^{-1} in B and near 2906 cm^{-1} in C would be due to the non-symmetric and symmetric C—H stretching modes of (Si—)CH_3 group in each series, respectively.

In B and C, the band near 1460 cm^{-1} decreases in strength with increasing polymer size, and that near 1400 cm^{-1} has the reverse tendency. Accordingly, the

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* Represent the methyl group attached to oxygen atom.

[8] H. B. Henbest, G. D. Meakins, B. Nicholls and A. A. Wagland, *J. Chem. Soc.*, **1957**, 1462.

* It has been reported[4] that the intensity of the C-H stretching band in (Si-)CH_3 was the order of one-third to one-fourth that in (C-)CH_3.

** As the concentration of O-CH_3 group is considerably small compared with that of Si-CH_3 group in the comparative higher members of C, the bands near 2925 and 2955 cm^{-1} would not always be due to the C-H stretching mode in (O-)CH_3 group.

former band is attributed to the methyl deformation vibration in O—CH_3 group referring to the wave number of that found in dimethylether (1466 cm^{-1})[9], and the latter to the methyl deformation vibration in Si—CH_3 group as already assigned[3,10].

The sharp intense band near 1260 cm^{-1} in B and C has been known to be the characteristic absorption of Si—CH_3 group. Some different assignments have been made to this band, that is, the rocking vibration[4], symmetrical deformation vibration[11] and γ-(CH) vibration[12] of (Si—)CH_3 group. In this investigation, it could not be decided what kinds of mode give this band, but considering the question from the relation between the position of methyl symmetrical deformation frequency and the electronegativity of atom, to which methyl group attaches*, the band near 1260 cm^{-1} would arise from (Si—)CH_3 symmetrical deformation mode.

The band near 1190 cm^{-1} is observed in all the members of A, B and C, and in the latter its intensity decreases with increasing polymer size. Diethyldimethoxysilane and ethyltrimethoxysilane show this band at 1189 and 1192 cm^{-1}, respectively[1], but no band is found near this wave number in D[4], and alkylalkoxy-silanes[1,3] and -polysiloxanes[2] not having methoxy group**. Therefore, the 1190 cm^{-1} band is clearly associated with O—CH_3 group, and referring to the wave number of methyl rocking vibration in dimethylether (1180 cm^{-1})[9], this band is considered to be the rocking vibration of (O—)CH_3 group. The wave number of the band associated with $Si(OCH_3)_n$ group is an approximately constant one and is larger than that of C—OCH_3 group, and the band in the region of 1189~1196 cm^{-1} is considered to be the characteristic frequency of Si—OCH_3 group.

In A, B and C, a common strong band appears near 1090 cm^{-1} which may be connected with the Si—O—C linkage*. Referring to the infrared spectra of dimethylether**, this band would be associated with $\overset{\rightarrow}{\text{Si}}\text{—}\overset{\leftarrow}{\text{O}}\text{—}\overset{\rightarrow}{\text{C}}$ stretching vibration†. The common band is also observed as a shoulder in the high-frequency side of the band near 1090 cm^{-1}, except C_1, C_5 and C_6. This band will probably correspond to the band near 1110 cm^{-1} observed in ethoxy- and methylethoxy-polysiloxanes[2].

Except in the case of the first members in each series, other bands having fairly strong intensity are observed at 1080 cm^{-1} in A, 1066~1041 cm^{-1} in B and 1055~1021 cm^{-1} in C. These bands in B and C decrease in wave number with increasing polymer size. This tendency has been observed in D[4] and in methylethoxypolysiloxanes[2], and these bands are clearly connected with Si—O stretching vibration in Si—O—Si linkage. The corresponding band at 1080 cm^{-1} in A would be observed as a shoulder on account of the extremely strong band at 1090 cm^{-1}. Thus, in the compounds except in the case of the first

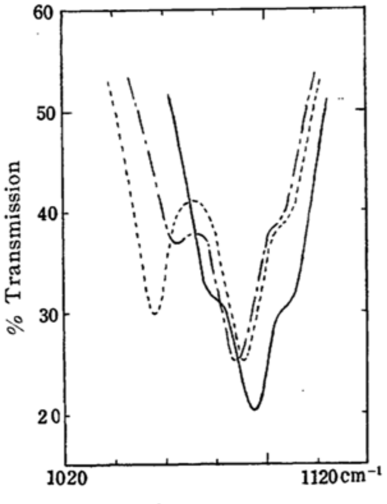

Fig. 4. Spectral sequence corresponding to the structural unit sequence of SiO_4, SiO_3C and SiO_2C_2.
—— $CH_3O[(CH_3O)_2SiO]_2CH_3$
— — — $CH_3O[CH_3OSi(CH_3)O]_2CH_3$
------ $CH_3O[Si(CH_3)_2O]_2CH_3$

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[9] G. Herzberg, "Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules", D. Van Nostrand Company, New York (1949) p. 353.

[10] M. Sakiyama, This Bulletin, **31**, 67 (1958).

[11] C. Y. Young, J. S. Koehler and D. S. McKinney, *J. Am. Chem. Soc.*, **69**, 1910 (1947).

[12] D. H. Rank, B. D. Saksena and E. R. Shull, *Discuss. Farad. Soc.*, **9**, 187 (1950).

* For example, F-CH_3 1475, O-CH_3 1466 (in dimethylether), N-CH_3 1418 (in methylamine), Cl-CH_3 1355, S-CH_3 1323 and P-CH_3 1280 cm^{-1}; L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen & Co. London (1954) p. 24.

** For example, in ethoxypolysiloxanes the corresponding band appears near 1160 cm^{-1}, and has been considered to be the characteristic frequency of Si-OC_2H_5 group[2].

* The band near 1090 cm^{-1} would be also connected with Si-O-Si linkage as later described.

** The band due to the non-symmetric stretching vibration of C-O-C linkage appears at 1110 cm^{-1} [9].

† $\overset{\rightarrow}{\text{Si}}\text{-}\overset{\leftarrow}{\text{O}}\text{-}\overset{\rightarrow}{\text{C}}$ stretching band may be expected to appear in the vicinity of $\overset{\rightarrow}{\text{C}}\text{-}\overset{\leftarrow}{\text{O}}\text{-}\overset{\rightarrow}{\text{C}}$ stretching band, on account of the great force constant of Si-O bond, in spite of the large mass of silicon atom.

members in each series, a spectral sequence corresponding to the structural unit sequence of SiO_4, SiO_3C and SiO_2C_2 is found for the Si—O stretching frequency as shown in Fig. 4.

In D except D_2, the further band connected with Si—O—Si linkage has been found in the region of 1070~1093 cm^{-1} [4]. The corresponding band is expected to appear in A, B and C, but it will probably be comprised in the band due to $\overrightarrow{\mathrm{Si}}$—$\overleftarrow{\mathrm{O}}$—$\overrightarrow{\mathrm{C}}$ stretching. This presumption is considered from the following fact; in C, as the polymer size increases the concentration of Si—O—C linkage decreases rapidly, but the rapid decreasing in strength of 1090 cm^{-1} band is not less noticeable observed.

Some strong bands appear in the region 750~900 cm^{-1}. One of them is observed at approximately constant wave number near 850 cm^{-1} in A, B and C, but is not in D. The intensity of this band decreases with increasing polymer size in B and C, especially in the latter. So there is no doubt that the band is associated with the grouping $Si(OCH_3)_n$ ($n=1\sim4$), and is not considered to be due to the rocking vibration of (Si—)CH_3 group which has been reported by Hayashi[3]. Similar behavior to the above has been observed in the 840 cm^{-1} band of ethoxy endblocked dimethylpolysiloxanes[2]. Referring to the spectra of dimethylether*, this band will probably be associated with the $\overleftarrow{\mathrm{Si}}$—O—$\overrightarrow{\mathrm{C}}$ vibration.

It has been known that the bands near 790 cm^{-1} in B and near 800 cm^{-1} in C have been associated with $SiCH_3$ and $Si(CH_3)_2$ groups, respectively[1,4]. In B except B_1, the absorption bands appear in the frequency on both sides of the 790 cm^{-1} band; the one at the lower wave number increases in strength as well as shifting to the side of less wave number, and the other becomes broader, as the polymer size increases. The band at 795 cm^{-1} in A would be considered to be a harmonics of the deformation vibration band involving Si—O linkage, which has been supported to fall in 770~830 cm^{-1} region by Wright and Hunter[4].

Summary

1) The infrared spectra of the lower members of methoxy-, methylmethoxy- and methoxy endblocked dimethyl-polysiloxanes have been discussed by comparing them with that of dimethylether, dimethylpolysiloxanes, and so on.

2) The characteristic absorption band of Si—OCH_3 group has appeared near 1190 cm^{-1}.

3) Except in the case of the first members of these alkoxysiloxanes, a spectral sequence corresponding to the structural unit sequence of SiO_4, SiO_3C and SiO_2C_2 has been observed in the region of 1000~1100 cm^{-1}.

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* The band due to the symmetric stretching vibration of C-O-C linkage is observed at 940 cm^{-1} [9].