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The Effect of Temperature on the Low-frequency Raman Scattering from Pentadecaethylene Glycol Di-n-hexyl Ether† and Related Materials

BY KYRIAKOS VIRAS

Physical Chemistry Laboratory, University of Athens, 13A Navarinou Street, Athens, Greece

AND TERENCE A. KING* AND COLIN BOOTH

Departments of Physics and Chemistry, University of Manchester, Manchester M13 9PL

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A systematic investigation has been made of the temperature dependence of the Raman spectrum of homogeneous poly(oxyethylene) di-n-alkyl ethers $H(CH_2)_nO(CH_2CH_2O)_m(CH_2)_nH$. Here details are reported for the sample with $n = 6$ and $m = 15$ and with less complete data on samples ($n = 8$, $m = 15$) and ($n = 4$, $m = 9$). Many vibrational features are observed including longitudinal and transverse acoustical modes. Reduction of temperature from 293 to 77 K reveals three components of the LAM-1 mode.

Homogeneous triblock oligomers of the general formula

$$H(CH_2)_nO(CH_2CH_2O)_m(CH_2)_nH$$

have been prepared[1] with $m = 9$ or 15 and $n = 1$-30. They form a range of crystalline structures which includes those in which only the oxyethylene central block crystallises (type I), those in which all blocks crystallise (type II) and those in which only the n-alkyl end blocks crystallise (type III). The structure formed depends mainly upon the chain length (n) of the alkyl end block.[1] Broadly, the oligomers crystallise as follows: I, $n = 3$-6, II, $n = 12$-21 and III, $n = 26$-30. The lowest members of the series ($n = 1$ or 2) crystallise essentially as poly(oxyethylene). Chain-folded structures are found[1] for oligomers with $m = 15$ and $n = 26$-30.

With regard to Raman scattering, the interesting feature of the oligomers is the large difference in elongational modulus (E) between the helical oxyethylene blocks and the planar zig-zag methylene blocks: $E_{me}/E_{oe} \approx 10$. Consequently their longitudinal vibrations are at very different frequencies and are largely uncoupled.

Raman scattering from the longitudinal acoustical modes, both oxyethylene LAM-1 and n-alkyl LAM-1, is readily observed in the completely crystalline type II materials.[1-3] Moreover, the type II structure is unchanged[3] when the temperature is reduced from 293 to 77 K and so it is possible to study the temperature dependence of the LAMs over a wide range[3] and, coincidentally, to study Raman scattering from a transverse acoustical mode (TAM-1) of the crystalline oxyethylene block.[3,4]

In the type I structure at room temperature only the central oxyethylene block is crystalline. The n-alkyl end blocks maintain an approximately parallel alignment[1] but are too widely spaced to crystallise, owing to the large cross-sectional area of the oxyethylene helix compared with the n-alkyl planar zig-zag. The alkyl layers in the structure can be categorised as liquid crystalline. Here we report a systematic

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† Systematic name: α-(n-hexyl)-ω-(n-hexyloxy)pentadeca(oxyethylene).

investigation of the temperature dependence of Raman scattering from the oligomer 6-15-6,† supported by less complete results for oligomer 4-9-4 of structure I and oligomer 8-15-8, which has a structure intermediate between I and II.

EXPERIMENTAL

MATERIALS

The homogeneous oligoethylene glycols and their di-n-alkyl ethers were prepared and purified as described earlier.[1,5] The purity of the samples with respect to block length and composition exceeded 99% (*i.e.* exceeded the limits of detection of impurities).

RAMAN SCATTERING

Raman spectra were recorded as described previously[4] by means of a Cary 82 spectrometer with samples maintained at several temperatures in the range 293-77 K by means of an Oxford Instruments CF104 cryostat. Low-frequency spectra (100-5 cm^{-1}) were recorded with narrow spectral bandwidths (down to 0.5 cm^{-1}) which allowed close approach to the Rayleigh scattering peak. Otherwise the spectral band width was *ca.* 4 cm^{-1} and the lower limit of observation *ca.* 30 cm^{-1}. Samples were crystallised by cooling from a temperature above the melting point to room temperature. Small corrections were made to the scattering frequency, as described earlier,[4] for the background of Rayleigh scattering and for frequency and temperature.

RESULTS

Sample 6-15-6 was investigated at several temperatures within the range 77-293 K, sample 8-15-8 at five temperatures within the range 113-293 K and sample 4-9-4 at 243 K only. The results for sample 6-15-6 are most complete and mainly these are used for illustration. The spectra of the other two samples are less satisfactory, owing to high background scattering, particularly that of sample 4-9-4, which was a liquid at room temperature and which was enclosed in a capillary tube. As in earlier work,[2-4,6] it was necessary to replicate spectra many times in order to define certain features, owing to the low signal-to-noise ratio of some of the spectra.

It is convenient to describe separately the scattering observed in the frequency ranges 1500-150 and 150-10 cm^{-1}. Corrected frequencies are quoted.

FREQUENCY RANGE 1500-150 cm^{-1}

A spectrum of sample 6-15-6 at 293 K is illustrated in fig. 1(*a*). Compared with published[4,7] spectra of oligo(oxyethylene)s, scattering attributable[1,3] to alkyl blocks is observed as a broad shoulder at 1455 cm^{-1}, a shoulder at *ca.* 1300 cm^{-1} and a broad peak centred on 895 cm^{-1}. Reduction of temperature has the effect on the higher-frequency spectrum of causing a sharpening of the peaks and some splitting. For example, the spectrum of sample 6-15-6 at 77 K ([shown in fig. 1(*b*)] allows better definition of a number of minor features, such as the peaks due to the n-alkyl blocks at 1462 and 1296 cm^{-1} and a weak peak at 1102 cm^{-1}, and also indicates splitting of the broad peaks centred on 231 cm^{-1} (as noted earlier[3,4]) and 535 cm^{-1}.

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† Samples are denoted by their alkyl-end-block length in number of carbon atoms (n) and their nominal oxyethylene-central-block length in number of oxyethylene units (m). Thus sample 6-15-6 is pentadecaethylene glycol di-n-hexyl ether. Note that this sample has an overall chain length of 58 chain atoms (C and O).

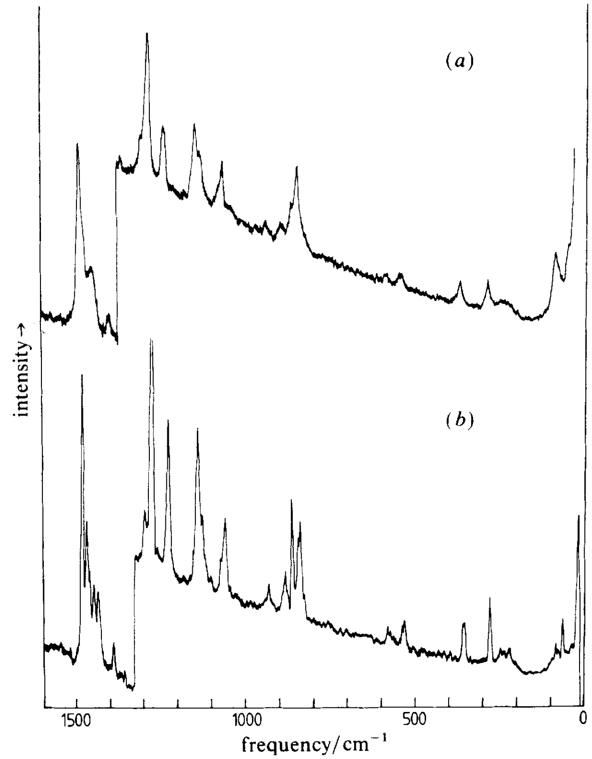

Fig. 1. Raman spectra of sample 6-15-6: (a) $T = 293$ K and (b) $T = 77$ K. The intensity scales are arbitrary. There is a change in sensitivity near 1325 cm^{-1}.

There are also pronounced changes with temperature in the regions 1350-1500 and 820-900 cm^{-1}; *e.g.* the peaks at 862 and 1432 cm^{-1} are very sensitive to temperature, particularly that at 862 cm^{-1} (see fig. 1). There are no significant changes in peak position observed with temperature over the range 293-77 K.

FREQUENCY RANGE 150-10 cm^{-1}

A spectrum of sample 6-15-6 for the range 100-10 cm^{-1} at 293 K is shown in fig. 2. This spectrum is similar to those recorded for oligo(oxyethylene)s at room temperature,[4,6] with prominent peaks assignable to the crystalline oxyethylene block LAM-1 (at *ca.* 17.5 cm^{-1} and narrow), and LAM-3 (at *ca.* 40 cm^{-1} and broad) and to crystalline oxyethylene block CO internal rotation plus lattice vibration (at *ca.* 80 cm^{-1} and broad). The effect of reducing the temperature successively to 77 K is illustrated in fig. 3. A striking feature of the results is the broadening towards high frequencies and eventual splitting of the scattering peak associated with LAM-1 of the oxyethylene block. A spectrum of sample 4-9-4 at 243 K (illustrated elsewhere,[8] frequency range 20-50 cm^{-1}) shows a similar effect, as does the series of low-frequency spectra for the sample 8-15-8 shown in fig. 4 for variation of temperature over the range 293-113 K. There is evidence of broadening and possibly splitting of the LAM-3 peaks of a similar nature.

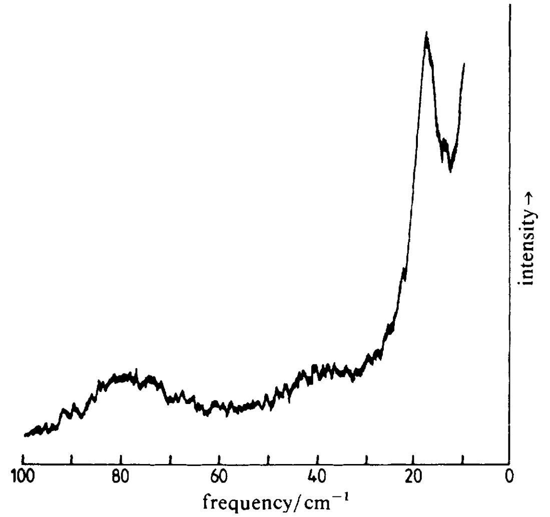

Fig. 2. Low-frequency Raman spectrum of samples 6-15-6 at 293 K.

Corrected peak frequencies for sample 6-15-6 are listed in table 1. The assignments, where possible, are by analogy with previously published results[3,4,6,9] and will be discussed later. For samples 4-9-4 and 8-15-8 the quality of the spectra is too low to permit identification of frequencies for the separate components of LAM-1. The intense peak at 71 cm^{-1} independent of temperature in the spectrum of 6-15-6 (see fig. 3) is also observed in the spectra of 8-15-8. The weak temperature-independent peaks at 60–61 and 103 cm^{-1} are also seen in the spectra of both samples.

Plots of peak frequency against temperature for LAM and TAM peaks are shown in fig. 5 and 6 for samples 6-15-6 and 8-15-8. For the intermediate peak around 80–90 cm^{-1} the temperature dependence is found to be linear. This is shown in fig. 7 for both samples 6-15-6 and 8-15-8.

DISCUSSION

The Raman spectra of these oligo(oxyethylene)di-n-alkyl ethers reveal a wealth of detail and marked effects with reduction of temperature over the range 293–77 K.

In the higher-frequency region the spectra derive mainly from the central crystalline oxyethylene block, and assignment of the bands can be made following Koenig and Angood.[7] The crystalline n-alkyl blocks contribute features at 1296 and 1462 cm^{-1}. For sample 6-15-6 the prominent peaks at 862 and 1432 cm^{-1} assigned to oxyethylene and apparent in the low-temperature spectrum are more sensitive to temperature, particularly that at 862 cm^{-1}, than found in samples studied earlier, *e.g.* the oligo(oxyethylenes) 2-15-2 and 2000H and the type II di-n-alkyl ether 18-15-18.

The temperature-dependent band observed in the region of 80–90 cm^{-1} is assigned[4] to a lattice mode of the crystalline oxyethylene block. The temperature dependences of the lattice mode in samples 6-15-6 and 8-15-8 are similar to those observed[4] for the oligo(oxyethylenes). They fit linear equations of the form

$$\nu/\text{cm}^{-1} = 96.1 - 0.057T \text{ for 6-15-6}$$

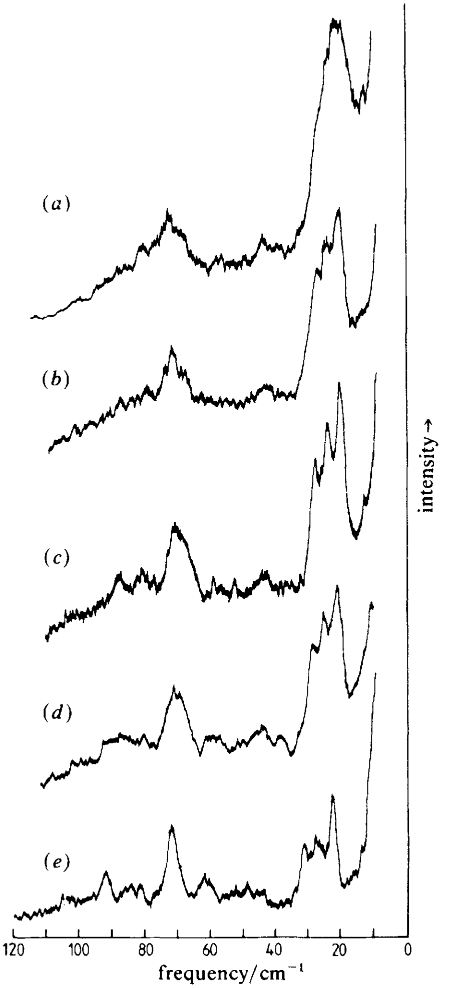

Fig. 3. Temperature variation of the low-frequency Raman spectrum of sample 6-15-6: (*a*) 243, (*b*) 203, (*c*) 173, (*d*) 143 and (*e*) 77 K.

and

$$\nu/\text{cm}^{-1} = 96.0\text{–}0.060T \text{ for 8-15-8.}$$

The temperature-independent bands at *ca.* 103, 80 and 61 cm^{-1} have been assigned,[4] by reference to earlier work,[9] to internal deformations of the oxyethylene helix. The peak at *ca.* 71 cm^{-1}, which is very prominent in the spectra of sample 6-15-6 (see fig. 3) has no counterparts in the spectra of the oligo(oxyethylene)s[4] and their type II di-n-alkyl ethers.[3] The frequency of this peak does not change with temperature, which characterises it as an internal deformation of the molecule.

In the very-low-frequency range the prominent peak in the spectra of the samples at room temperature (*e.g.* at 17.5 cm^{-1} for sample 6-15-6: see fig. 2) can be assigned to LAM-1. This assignment has been discussed earlier[2,3] and is based on a comparative study of the spectra of the series of di-n-alkyl ethers *n*-15-*n*[2,3] and also upon

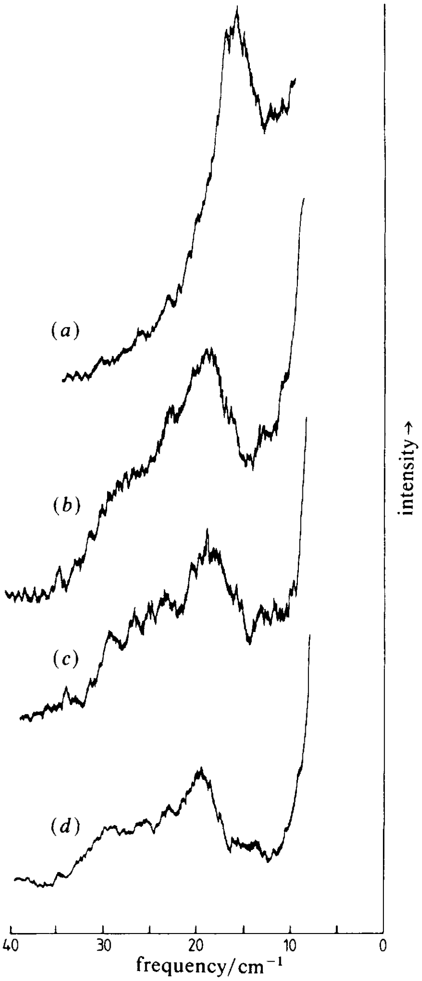

Fig. 4. Temperature variation of the low-frequency Raman spectrum of sample 8-15-8: (*a*) 293, (*b*) 203, (*c*) 173 and (*d*) 113 K.

the temperature dependence of the peak frequency.[3,4] Similar considerations serve to identify LAM-3 and TAM-1. The remarkable feature of the present results is the temperature dependence of LAM-1 (and possibly LAM-3), which is observed to broaden and then split on reduction of temperature (see fig. 3 and 4). Three components of the LAM-1 can be identified in the spectra of sample 6-15-6 at low temperatures, and all have the same temperature dependence in the range 203-77 K (see table 1 and fig. 3). This temperature dependence is very similar to that found earlier[3,4] for the oligo(oxyethylene) 2-15-2 and the di-n-octadeyl ether 18-15-18, as illustrated in fig. 5.

Broadening and splitting of the LAM-1 peak when the sample is cooled have been detected in all the samples investigated in this work (*i.e.* 6-15-6, 8-15-8 and 4-9-4) but have not been observed in earlier work[3,4] on oligo(oxyethylene)s and di-n-alkyl ethers of structure II (*e.g.* 2-15-2 and 18-15-18). The obvious structural

Table 1. Corrected peak frequencies of Raman bands for sample 6-15-6, assigned by reference to earlier work[3,4,6,9]

$T = 293$ K	$T = 173$ K	$T = 77$ K	assignment[a]
[b]	13.0	13.1	OE
12.7	14.5	16.0	TAM-1
17.5	20.8	22.4	
—	24.4	27.3	LAM-1
—	28.1	31.0	
42	44	49	LAM-3
61	60	61	OE
[b]	71	71.5	?
79	81	83	OE
79	87	91.5	lattice
—	103	103	OE

[a] OE, internal mode of the oxyethylene chain: otherwise longitudinal acoustical mode (LAM), transverse acoustical mode (TAM) or lattice mode (as indicated).
[b] Peak unresolved.

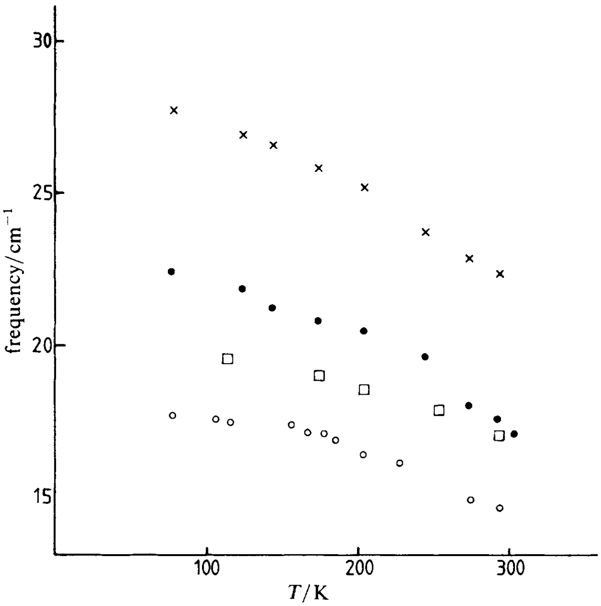

Fig. 5. Temperature dependence of the LAM-1 mode in samples 2-15-2 (×), 6-15-6 (●, table 1), 8-15-8 (□), 18-15-18 (○). The most intense LAM component is plotted for 6-15-6 and 8-15-8.

difference is that the samples investigated earlier are completely crystalline, whereas the present samples are partly crystalline, with crystalline oxyethylene blocks sandwiched between liquid-crystalline n-alkyl blocks. The broadening and splitting is towards higher frequencies, hence a possible origin of the effect is a more restricted chain end.

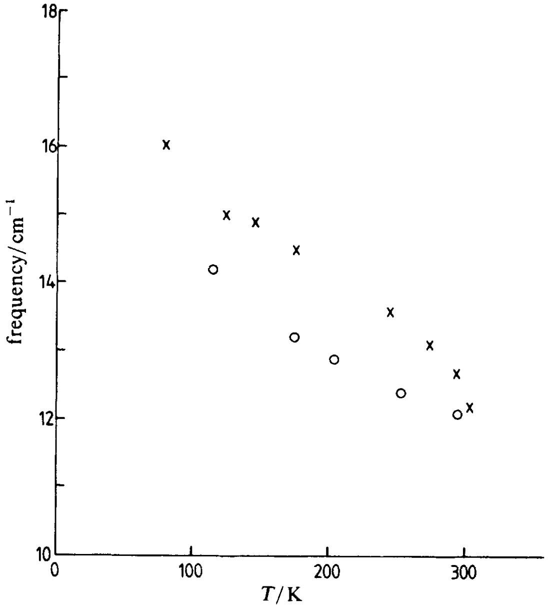

Fig. 6. Temperature dependence of the TAM-1 mode in 6-15-6 (×) and 8-15-8 (O).

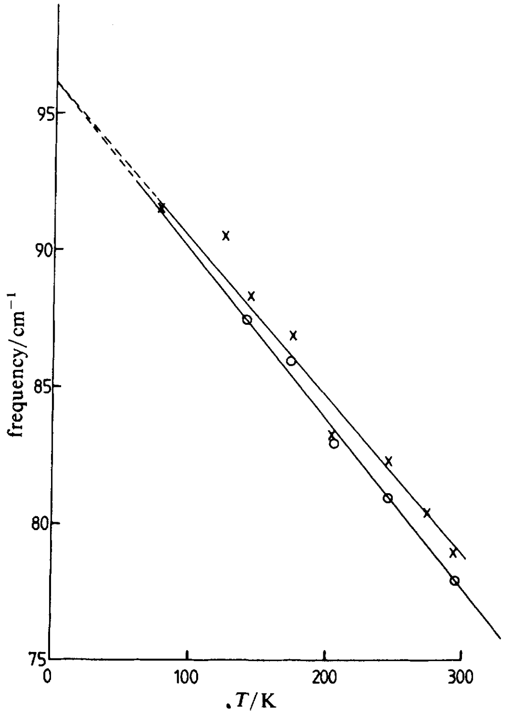

Fig. 7. Dependence of the band at 80-90 cm^{-1} with temperature: sample 6-15-6 (×), frequency dependence $\nu = 96.1 - 0.057T$; sample 8-15-8 (O), frequency dependence $\nu = 96.0 - 0.060T$.

End interactions are important in determining the LAM in oligo(oxyethylene)s and their ethers. This has been demonstrated in several ways: by changing end-groups,[2,6] crystallinity[6] and temperature[3,4] and by swelling end-layers.[10] It is likely that a type I structure will undergo reorganisation within the n-alkyl layer when the temperature is reduced, leading to changes in structure and symmetry. Unfortunately we have no crystallographic information at low temperatures.

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