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Effect of Temperature on Low-frequency Raman Scattering from Crystalline Pentadecaethylene Glycol di-n-Octadecyl Ether†

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Raman spectra have been recorded for a homogeneous sample of pentadecaethylene glycol di-n-octadecyl ether at several temperatures in the range 77-293 K. The crystalline material comprises helical oxyethylene and planar zig-zag n-alkyl blocks in a contiguous structure. Five scattering peaks are found with frequency (ν) dependent on temperature (T). One peak at 88-80 cm^{-1} with a linear variation of ν with T is assigned to a lattice mode. The other peaks, with more complex variations of ν with T, are assigned to the longitudinal acoustical mode, LAM-1, of the n-alkyl block (130-125 cm^{-1}), to the LAM-3 and LAM-1 of the oxyethylene block (46-41 and 18-14 cm^{-1}) and, with less certainty, to a transverse acoustical mode, TAM-1 (14-10 cm^{-1}).

Monodisperse (homogeneous) triblock oligomers of general formula

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

have been prepared with $m = 9$ or 15 and have been found[1,2] to crystallise completely at 25 °C when the alkyl end blocks have chain lengths in the range $12 \leqslant n \leqslant 18$. The completely crystalline structure, denoted II in earlier work,[1-3] is a layer structure in which the central oxyethylene blocks are helices oriented normal to the layer end plane and packed similarly to the helices in polyoxyethylene[4] and the n-alkyl end blocks are planar zig-zags oriented at an angle to the layer end plane and packed in a novel manner.[5] The di-n-octadecyl ether of pentadecaethylene glycol, which we denote 18-15-18,‡ forms a typical type-II structure.

The observation[6] of low-frequency Raman scattering from the longitudinal acoustical mode (LAM-1) of the n-alkyl end block, as well as from the central oxyethylene block,[6,7] has considerably aided the characterisation of the type-II structure since the elongational modulus of the alkyl end block is essentially identical to that found[8,9] for the planar zig-zag chains of the crystalline n-alkanes.

The frequencies of the scattering peaks of oligo-oxyethylene have been shown[10] to be temperature dependent, and this effect has been used[10] to distinguish acoustical and lattice modes from intramolecular modes. In addition to the LAM-1 and LAM-3

† Systematic name: α-octadecyl-ω-octadecaoxypentadeca(oxyethylene); formula: $H(CH_2)_{18}O[CH_2CH_2O]_{15}(CH_2)_{18}H$.

‡ Samples are denoted by their alkyl-end-block length in number of carbon atoms (n, here 18) and their nominal oxyethylene-central-block length in number of oxyethylene units (m, here 15). Note that sample 18-15-18 has an overall chain length of 82 chain atoms (C and O).

peaks at frequencies dependent on chain length, first assigned by Hartley *et al.*,[11] observations over a range of temperatures (77–310 K) show[10] two other temperature-dependent scattering peaks: one at 92–80 cm^{-1}, which is unaffected by changes in chain length and assigned to a lattice mode, and one at very low frequencies, which is dependent on chain length and provisionally assigned to a transverse acoustical mode. These are additional to the prominent scattering peak at 80 cm^{-1}, assigned by Rabolt *et al.*[12] to CO internal rotation, and other small peaks at 107, 61, 34–35 and 13–16 cm^{-1}, some previously described,[12] all of which are at frequencies which are independent of temperature and, largely, of sample.

Here we report a systematic investigation of the temperature dependence of Raman scattering from sample 18-15-18, supported by results obtained at 293 K for other samples in the homologous series *n*-15-*n*.

EXPERIMENTAL

MATERIALS

The homogeneous pentadecaethylene glycol and its di-n-alkyl ethers were prepared and purified as described earlier.[2,13] The purity of 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 earlier[10] using a Cary 82 spectrometer. Low-frequency spectra (100–5 cm^{-1}) were recorded with narrow spectral bandwidths (down to 0.7 cm^{-1}), which allowed close approach to the Rayleigh-scattering peak. Otherwise the spectral bandwidth 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, and spectra were recorded with the samples maintained to ±5 K at temperatures in the range 293–77 K using an Oxford Instruments CF104 vacuum cryostat (±5 K). Small corrections to the scattering-peak frequency were made as described earlier[6,7,10] for the background of Rayleigh scattering and also for frequency and temperature.

RESULTS

Samples of 18-15-18 were investigated at 9 temperatures within the range 77–310 K. The other samples were investigated at 293 K only. It is convenient to describe separately the scattering observed in the frequency ranges 1500–150 and 150–5 cm^{-1}. The lower frequency range has been the most thoroughly studied, since this contains the scattering from both the n-alkyl end-block LAM-1 and the oxyethylene central-block LAM-1. Corrected frequencies are quoted.

FREQUENCY RANGE 1500–150 cm^{-1}

A spectrum of sample 18-15-18 at 293 K, over the frequency range 1500–700 cm^{-1}, is illustrated in fig. 1. Apart from sharpening of the peaks, the spectra in this range are essentially unchanged on lowering the temperature to 77 K. Compared with the spectra of the oligo-oxyethylenes,[10,14] a new intense scattering peak is observed at 1295 ± 2 cm^{-1}, and additional scattering is observed at 1468–1444 and at 892 ± 2 cm^{-1}. Spectra of sample 18-15-18 at (*a*) 293 and (*b*) 77 K, over the frequency range 700–30 cm^{-1}, are illustrated in fig. 2. Splitting of the peak at 231 cm^{-1}, apparent in fig. 2(*b*), has been observed[10] in the low-temperature spectra of oligo-oxyethylenes.

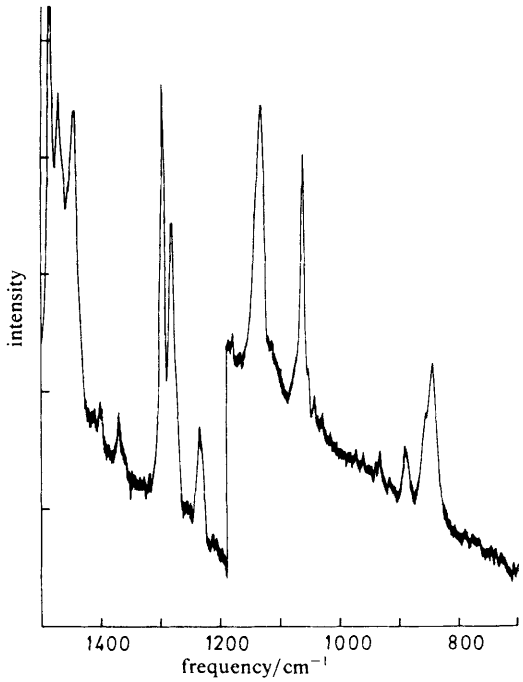

Fig. 1. Raman spectrum of sample 18-15-18 at 293 K. The intensity scale and zero were chosen arbitrarily. The discontinuity at *ca.* 1170 cm^{-1} is a zero adjustment.

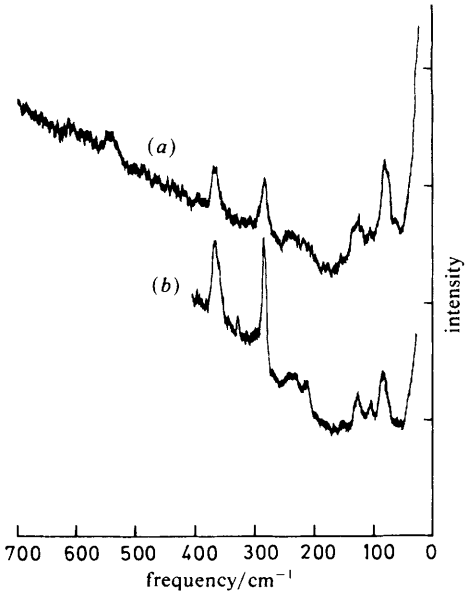

Fig. 2. Intermediate-frequency Raman spectra of sample 18-15-18 at (*a*) 293 and (*b*) 77 K. The intensity scales and zeros were chosen arbitrarily.

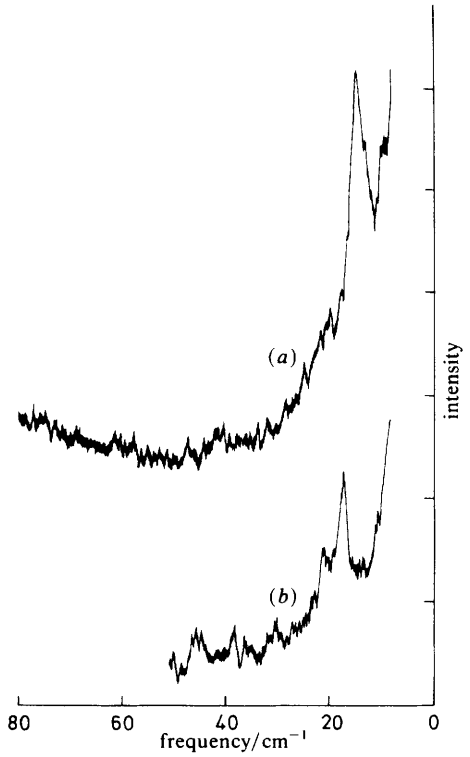

Fig. 3. Low-frequency Raman spectra of sample 18-15-18 at (*a*) 293 and (*b*) 77 K. The intensity scales and zeros were chosen arbitrarily.

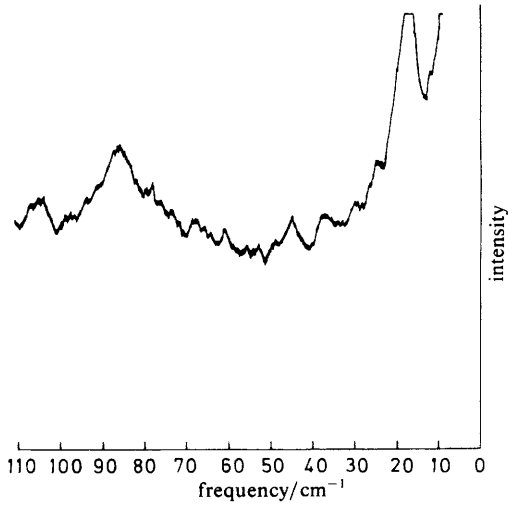

Fig. 4. Low-frequency Raman spectrum of sample 18-15-18 at 103 K. The intensity scale and zero were chosen arbitrarily.

Table 1. Corrected peak frequencies (ν) for sample 18-15-18[a]

frequency, ν/cm^{-1}		
293 K	77 K	assignment
9.8	14.0	oxyethylene TAM-1
14.5	17.6	oxyethylene LAM-1
21.3	21.6	—
—	30.3	—
—	38.3	—
41.0	45.9	oxyethylene LAM-3
61	61	oxyethylene chain deformation
80	79	oxyethylene CO internal rotation
80	88	oxyethylene lattice
—	97	—
106	105	oxyethylene CO internal rotation
125	130	n-alkyl LAM-1

[a] Uncertainty in frequencies: LAM-1, ±0.2 cm^{-1}; other peaks, ±1 cm^{-1}.

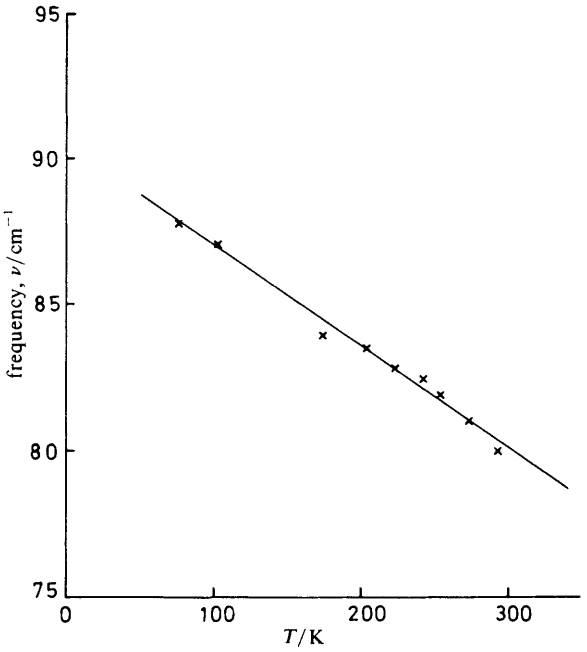

Fig. 5. Temperature dependence of frequency (ν) of the peak at 88-80 cm^{-1} in the Raman spectrum of sample 18-15-18.

FREQUENCY RANGE 150-5 cm^{-1}

Spectra of sample 18-15-18 are illustrated in fig. 2-4. Frequencies of peaks averaged over many spectra and corrected for baseline *etc.* are listed in table 1. The frequencies of five of the scattering peaks are temperature dependent: *i.e.* those at

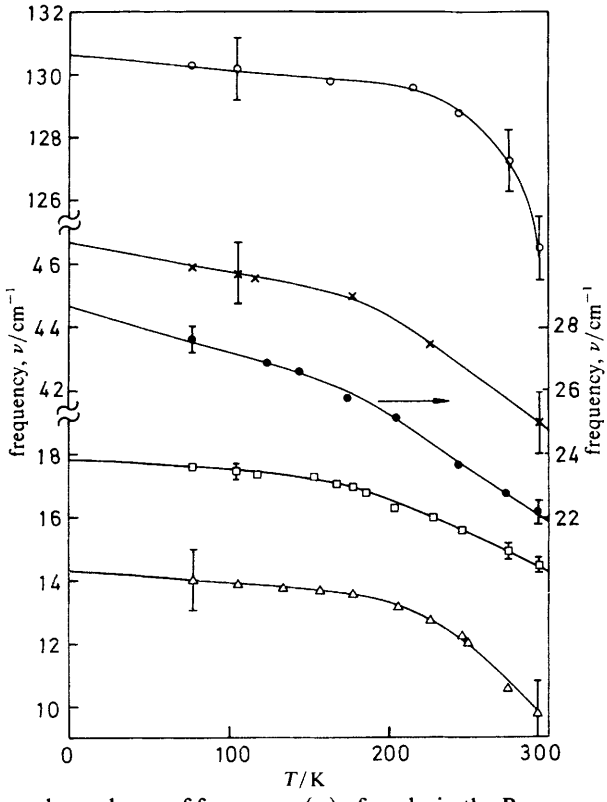

Fig. 6. Temperature dependence of frequency (ν) of peaks in the Raman spectrum of sample 18-15-18 assigned as follows: ○, n-alkyl-block LAM-1; ×, oxyethylene-block LAM-3; □, oxyethylene-block LAM-1; △, oxyethylene-block TAM-1. Comparison is made with the temperature dependence of frequency of LAM-1; ●, in the Raman spectrum of the oligo-oxyethylene sample 2-15-2,[10] the values for which are referred to the right-hand ordinate. The estimated errors of determination are indicated on each curve.

9-14, 14-18, 41-46, 80-88 and 125-130 cm^{-1}. The remainder are at frequencies which are independent of temperature or are observed only at the lowest temperature (see table 1). The temperature dependence of the peak at 88 (77 K) to 80 cm^{-1} (293 K) is shown in fig. 5: the data fit a straight line, $\nu/cm^{-1} = 90.5 - 0.035T$. The temperature dependences of the other peaks are more complex. Plots of peak frequency against temperature are non-linear in all cases: see fig. 6.

By repeated recording of spectra, the lowest-frequency peak has been defined in the spectra of several samples of the series n-15-n at 293 K, examples of which are shown in fig. 7. The frequencies of the peaks assigned to oxyethylene LAM-1 and TAM-1 (see table 1) are plotted against n-alkyl block length in fig. 8; the results for LAM-1 have been published previously.[6]

DISCUSSION

ASSIGNMENTS OF SCATTERING PEAKS

The spectra in the high-frequency range (1500-150 cm^{-1}) show no significant changes of band frequencies with temperature. This observation is evidence that

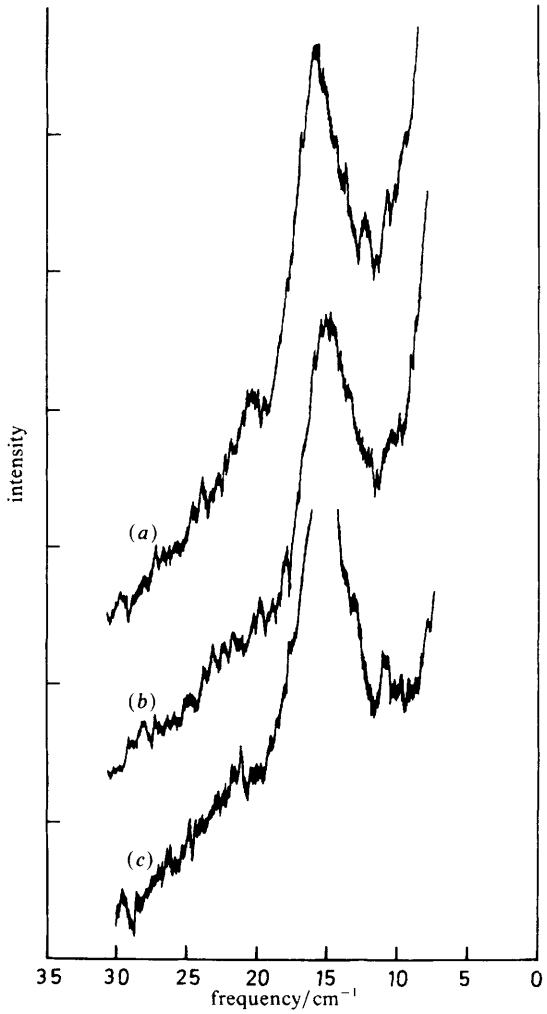

Fig. 7. Very-low frequency Raman spectra of samples (*a*) 13-15-13, (*b*) 15-15-15 and (*c*) 16-15-16 at 293 K. The intensity scales and zeros were chosen arbitrarily.

the chain conformations (helical oxyethylene, planar zig-zag alkyl) and the chain packing do not change significantly in the temperature range 293–77 K. Most of the observed scattering is from the crystalline oxyethylene block and these bands can be assigned according to Koenig and Angood.[14] The additional scattering (*e.g.* at 1295 and 1468–1444 cm^{-1}) can be ascribed to crystalline n-alkyl end blocks, by analogy[1] with scattering from crystalline triclinic n-alkanes.

The assignment, where possible, of scattering peaks in the low-frequency spectra of the samples (summarised for sample 18-15-18 in table 1) rests on earlier work.[6,7,10–12] The peaks may be categorised as follows.

FREQUENCY INDEPENDENT OF TEMPERATURE AND SAMPLE

Peaks at 61, 80–79 and 105–104 cm^{-1} (table 1) can be identified with the peaks observed in the spectra of oligo-oxyethylenes[7,10,12] and assigned by Rabolt *et al.*[12]

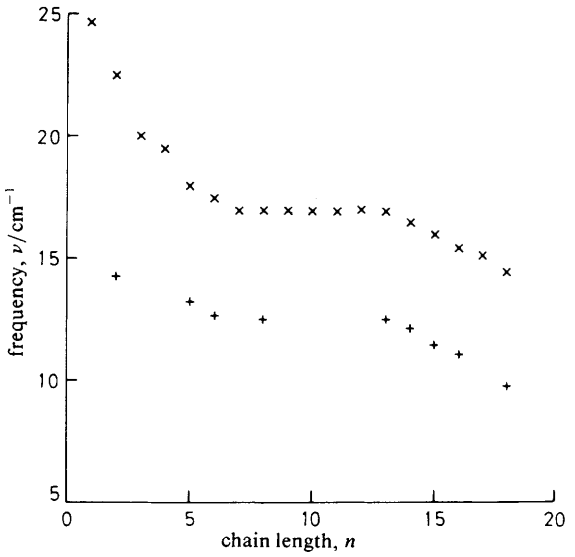

Fig. 8. Comparison of the frequency (ν) at 293–298 K of ×, the LAM-1 peak and +, the low-frequency temperature-dependent TAM-1 peak for the series of pentadecaethylene glycol di-n-alkyl ethers with alkyl chain length n.

to internal deformations of the oxyethylene chain. That at 22–21 cm^{-1} (table 1) has not been observed in Raman scattering from oligo-oxyethylenes, possibly because of overlap of more intense scattering from the LAM,[7,10] but is apparent in the low-frequency spectra of all the samples (see fig. 3–6).

FREQUENCY DEPENDENT ON TEMPERATURE BUT INDEPENDENT OF SAMPLE

The peak at 88–80 cm^{-1} can be identified with that observed in the spectra of oligo-oxyethylenes and assigned to a lattice mode.[10] The temperature coefficient of the frequency, $d\nu/dT = 0.035$, is lower than those found for oligo-oxyethylenes (*i.e.* $d\nu/dT = 0.055$).

FREQUENCY DEPENDENT ON TEMPERATURE AND SAMPLE

The assignment of scattering peaks to oxyethylene-block LAM-1 and LAM-3 rests upon the chain-length dependence of frequency found for a range of oligo-oxyethylenes,[7] and also upon the large perturbation of the frequency of scattering from a given oxyethylene block by the n-alkyl end groups in the homologous series, as illustrated in fig. 8. The assignment of the low-frequency temperature-dependent peak to an oxyethylene-block transverse acoustical mode, TAM-1, is based on more limited results. In the previous investigation[10] the assignment to TAM-1 rested mainly on the temperature dependence of its frequency. Here we have additional evidence of an acoustical mode, since the perturbation of the LAM-1 frequency by the n-alkyl end groups of the di-n-alkyl ethers 2-15-2 to 18-15-18 is mirrored by the perturbation of the TAM-1 frequency, as seen in fig. 8. The assignment of the n-alkyl-block LAM-1 is more straightforward, being based upon the dependence of frequency on n-alkyl chain length in the series of ethers with $12 \leqslant n \leqslant 26$,[3,6] the perturbation of the n-alkyl-block LAM by the adjacent oxyethylene block being slight.[6]

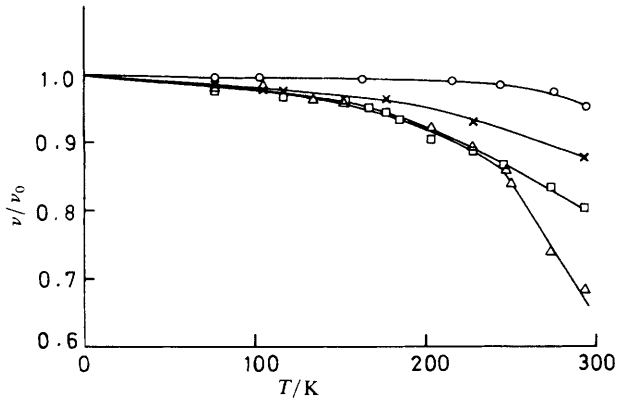

Fig. 9. Temperature dependence of frequency (ν) relative to the value obtained by extrapolation to 0 K (ν_0, see fig. 6) of peaks in the Raman spectrum of sample 18-15-18 assigned as follows: ○, n-alkyl-block LAM-1; ×, oxyethylene-block LAM-3; □, oxyethylene-block LAM-1; △, oxyethylene-block TAM-1.

TEMPERATURE AND SAMPLE DEPENDENCE OF FREQUENCY NOT DETERMINED

One of the two small peaks in the frequency range 38–30 cm^{-1} may be related to those found[12] for PEO 20 000 at 37 cm^{-1} and PEO 2000 at 35–34 cm^{-1}.

TEMPERATURE DEPENDENCE OF THE ACOUSTICAL MODES

Sample 18-15-18 is completely crystalline at room temperature.[2,5] Except for the slight differences noted earlier, the high-frequency Raman spectra are essentially unchanged from room temperature down to 77 K. The spectra of homogeneous oligo-oxyethylenes (*e.g.* sample 2-15-2) are also little changed over the same temperature range.[10] Consequently a change in crystallinity will not contribute to the change in LAM frequency with temperature.

The temperature dependence of LAM-1 frequency in the monodisperse oligo-oxyethylene sample 2-15-2 has been attributed[10] in large part to the effect of changes in end-group interactions. As discussed earlier,[6,7] the effect of given perturbing forces on the end groups of a triblock chain will be large, relative to LAM-1 frequency, for the low-modulus oxyethylene block compared with the high-modulus alkyl block. Indeed a better representation of the results than that in fig. 6 is obtained by plotting a relative frequency, ν/ν_0, against temperature, where ν_0 is the frequency of the mode at some convenient reference temperature, say 0 K. Such a plot is shown in fig. 9. As expected the effect of changing the temperature is smallest for the n-alkyl-block LAM-1 and smaller for the oxyethylene-block LAM-3 than for the oxyethylene-block LAM-1.[7,10,15] The temperature dependence of the oxyethylene-block TAM-1 is identical with that of the oxyethylene-block LAM-1, except at the highest temperatures (> 200 K). The relative change with temperature of the n-alkyl-block LAM-1 frequency is *ca.* −4% from 77 to 293 K, which is similar to that found[9,16] for the n-alkanes (*ca.* −2% from 168 to 298 K). That for the oxyethylene-block LAM-1 of *ca.* −18% from 77 to 293 K is almost identical to that found[10] for the oligo-oxyethylene sample 2-15-2 (−19%, 77 to 293 K).

Fig. 6 and 9 indicate a change in behaviour at 160–200 K from a slight and linear temperature dependence of frequency below 160 K to a larger and less regular temperature dependence of frequency above 200 K. This change in behaviour at

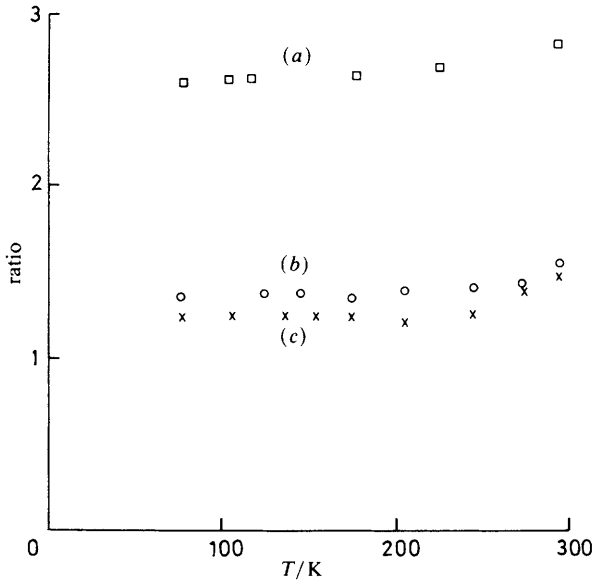

Fig. 10. Temperature dependence of the ratio of frequencies of the peaks in the Raman spectra of samples 18-15-18 and 2-15-2: (*a*) oxyethylene-block LAM-3/LAM-1 for sample 18-15-18; (*b*) LAM-1/TAM-1 for oligo-oxyethylene sample 2-15-2; (*c*) oxyethylene-block LAM-1/TAM-1 for sample 18-15-18.

ca. 200 K can also be seen if the ratio of frequencies LAM-1/TAM-1 for sample 18-15-18 is plotted against temperature or if the ratio of frequencies LAM-1/LAM-3 is similarly plotted, as shown in fig. 10. Comparable results for the oligo-oxyethylene sample 2-15-2 show similar changes at a similar temperature (see fig. 10). Regularity in the low-frequency Raman spectra can be assured only when the temperature of the sample is < 200 K.

THE LOW-FREQUENCY MODE

The nature of the low-frequency mode, provisionally assigned to a transverse acoustical mode of the oxyethylene block (TAM-1), has not been defined. Normal coordinate calculations for the planar zig-zag poly(methylene) chain indicate[17] a torsional mode at frequencies below that of LAM-1. The corresponding calculations for the helical poly(oxyethylene) chain have not been made. The sensitivity of the frequency of vibration to temperature and end group and the difficulty in assigning moduli count against the use of a rod model.

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