

Low-Frequency Raman-Active Modes in Methoxy-Ended and Hydroxy-Ended Oligo(oxyethylene)s

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SYNOPSIS

Low-frequency Raman spectra were recorded for α -methyl, ω -methoxy-oligo(oxyethylene)s, $C_1E_mC_1$ with m in the range 4–25 (i.e., 15–78 atoms). Longitudinal acoustical mode (LAM-1) frequencies were identified and compared with those determined previously for α -hydro, ω -hydroxy-oligo(oxyethylene)s. Nonlinear relationships between LAM-1 frequency and reciprocal chain length were explained as an effect of intermolecular end forces.

Keywords: Raman spectra in methoxy or hydroxy-ended oligo(oxyethylene)s • oxyethylene oligomers, methoxy- or hydroxy-ended, Raman spectra of

INTRODUCTION

Studies of the crystalline n -alkanes (see, e.g., refs. 1–3) by low-frequency Raman spectroscopy have led to an understanding of their whole-molecule vibrational modes, particularly the longitudinal acoustical mode (LAM) which derives from bond angle and bond length distortion of the trans-planar chains. More recently⁴ we have investigated in detail the effects of end groups on the LAM-1 of α , ω -disubstituted n -alkanes. Corresponding studies of the low-frequency bands in the Raman spectra of crystalline oligo(oxyethylene)s pertain to vibrations of helical chains, with the LAM deriving predominantly from rotational angle distortion, a much lower energy process.

Commercially available polyethylene glycols [PEG, systematic name α -hydro, ω -hydroxy-poly(oxyethylene)s] have distributions of chain lengths. Although the distributions are narrow (typically $M_w/M_n < 1.1$), they complicate the interpretation of spectra for samples of short chain length, since the low-frequency bands are broadened by a crystal-stem length distribution. At room temperature, samples longer in chain length than PEG3000 ($M_n = 3000$, corresponding to a number-average chain

length of 68 oxyethylene units, i.e., about 200 chain atoms) crystallize in folded-chain conformations, while samples shorter than PEG1000 ($M_n = 1000$, corresponding to a number-average chain length of 23 oxyethylene units, i.e., about 70 chain atoms) undergo fractional crystallization, with substantial rejection of short chains.⁵ Consequently, the range of chain lengths available for convenient study of the LAM by Raman spectroscopy is limited, and the effective lower limit of 70 chain atoms is particularly irksome. In this work the difficulty has been resolved by making use of specially synthesized uniform oligomers, covering the range 2–25 oxyethylene units (i.e., 9–78 chain atoms, including end groups).

The present study is concerned mainly with methoxy-ended oligomers [α -methyl, ω -methoxy-oligo(oxyethylene)s]. This avoids large end forces due to hydrogen bonding, which are known to affect the frequencies and intensities of the LAMs of oligomers.^{4,6} An advantage of the use of uniform samples is uniformity of environment of the end groups in the end planes of layer crystals. In contrast, the chain ends in PEGs have a variety of environments in the rough end surfaces of their lamellar crystals, including hydrogen bonding with both hydroxy and ether oxygen:⁷ the resulting nonuniformity of end forces is an additional factor broadening the Raman band.

The literature of the low-frequency Raman spectroscopy of oligo(oxyethylene)s and low-molecular

weight poly(oxyethylene)s dates from the first report⁸ of the LAM in these materials in 1976, and includes our own reports^{5,8-10} and those of Krimm and co-workers.¹¹⁻¹⁵ Related information has also emerged from studies by Raman spectroscopy of other materials containing oxyethylene blocks, particularly oligo(oxyethylene) alkyl ethers.¹⁶⁻¹⁹ However, the important relationship between LAM-1 frequency and chain length for short oligo(oxyethylene)s has not yet been empirically defined.

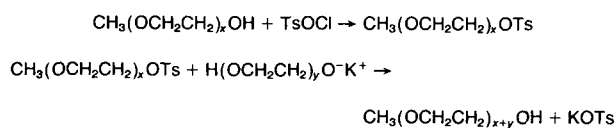
The dependence of LAM-1 frequency on length for oligo(oxyethylene)s is less straightforward than that for *n*-alkanes. The low energy change on elongation of the oxyethylene chain means that inter-chain forces are important, a point made in the recent papers of Song and Krimm.¹³⁻¹⁵ Also the repeat length for the helical conformation, with the *tgt* sequence of bonds O—CH₂—CH₂—O, is 3 oxyethylene units (9 chain atoms), which implies the possibility of perturbations of crystal structure due to differences in end group packing within the homologous series resulting in a more complex effect on the LAM than the even-odd effect in the *n*-alkanes.²

EXPERIMENTAL

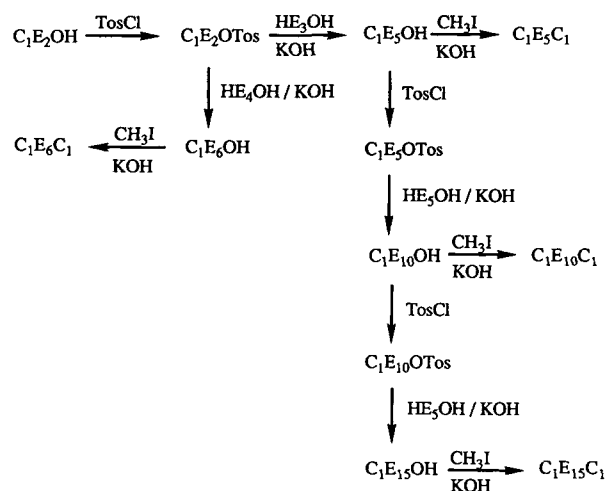
Materials

The α -methyl, ω -methoxy-oligo(oxyethylene)s were prepared from the corresponding α -methyl, ω -hydroxy-oligomers, the spectroscopy of which will be reported later.

The preparation started from commercially available oligoethylene glycols, H(OCH₂CH₂)_mOH where *m* = 2–5, and the monomethyl ethers of the lower two glycols, CH₃(OCH₂CH₂)_mOH where *m* = 2, 3. The method used, described elsewhere^{20,21} for related syntheses, involved ascending the homologous series by reaction of the tosylate of a methyl ether with the monopotassium salt of a glycol: i.e.

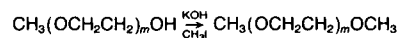


The required product was isolated from small amounts of higher oligomers and residues of the reactants by preparative gel-permeation chromatography,²² and characterized by infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy



Scheme 1: Synthesis of α -methyl, ω -methoxy-oligo(oxyethylene)s: examples C₁E₅C₁, C₁E₆C₁, C₁E₁₀C₁, C₁E₁₅C₁

and chemical analysis. The hydroxyl group was subsequently methylated by a modified Williamson procedure: i.e.



Examples of the synthetic routes are outlined in Scheme 1.

The products were characterized by a number of methods:

Chemical analysis. C and H analyses were consistent with molecular formulae.

IR spectroscopy (Perkin-Elmer FTIR Model 1710). Spectra showed no bands at 3200–3500 cm⁻¹, indicating complete conversion to the dimethyl ether.

¹H-NMR spectroscopy (Bruker 300 MHz spectrometer, CDCl₃ solvent, TMS reference). Spectra showed the expected resonances at δ = 3.35 (—CH₃OCH₂CH₂O—), 3.35 (CH₃—OCH₂CH₂O—) and 3.65 (interior CH₂), but not as δ = 3.75 (HOCH₂CH₂O—), again indicating complete conversion to the dimethyl ether.

Analytical GPC. GPC curves, obtained using a system suited to oligomers²³ with tetrahydrofuran eluent at 30°C, showed narrow single peaks with no indication of oligomeric impurities.

Mass spectroscopy (Kratos MS-25 with chemical ionization, NH₄⁺, *M* < 700). Spectra showed molecular ions (*M* + 1 and *M* + 18) corre-

sponding to the molecular formulae, and with no indication of higher oligomers.

Raman Spectroscopy

Raman scattering at 90° to the incident beam was recorded by means of a Spex Ramalog spectrometer fitted with a 1403 double monochromator and a 1442U third monochromator and operated in scanning mode. The operation of the instrument was controlled by a DM1B Spectroscopy Laboratory Coordinator computer. The light source was a Coherent Innova 90 argon-ion laser operated at 514.5 nm and 450 mW. Typical operating conditions for low frequencies ($5\text{--}150\text{ cm}^{-1}$) were bandwidth = 1.5 cm^{-1} , scanning increment = 0.1 cm^{-1} , integration time = 2 s. On occasion, for very low frequencies, the conditions were bandwidth = 0.8 cm^{-1} , scanning increment = 0.05 cm^{-1} , integration time = 5 s. The frequency scale was calibrated by reference to the spectra of L-cystine and *n*-hexacosane, the latter being used immediately before recording a spectrum. Generally high-frequency spectra were recorded immediately after the low-frequency spectra, in order

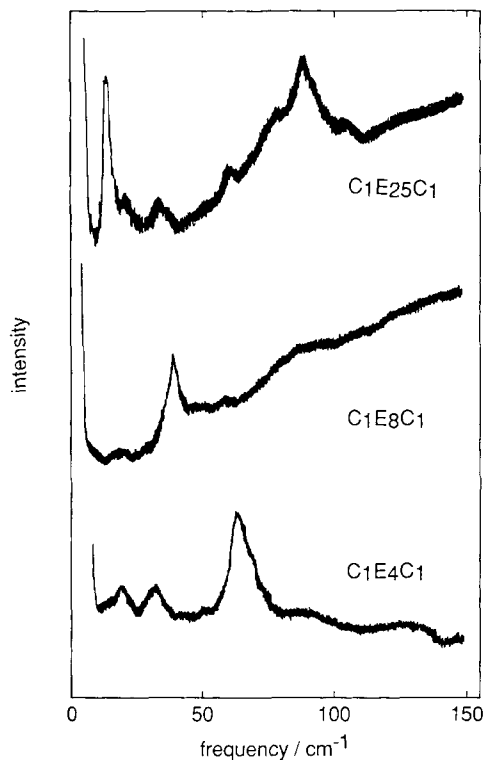


Figure 1. Low-frequency Raman spectra of methoxy-ended oligo(oxyethylene)s at 173 K: (a) $C_1E_{25}C_1$ (b) $C_1E_8C_1$ (c) $C_1E_4C_1$. The intensity scales and zeros are arbitrary.

to confirm that samples were unchanged by exposure to the laser beam.

Samples were enclosed in a capillary tube and held at a constant temperature ($\pm 1\text{ K}$) in the range 153–298 K by means of a Harney-Miller cell (Spex Industries Inc.).

RESULTS

The oligomers are denoted as follows: a di-methyl ether, α -methyl, ω -methoxy-oligo(oxyethylene) with m oxyethylene units in the chain, by $C_1E_mC_1$, and a corresponding diol, α -hydro, ω -hydroxy-oligo(oxyethylene), by HE_mOH . [The chain lengths (C and O atoms) are $x = 3m + 3$ and $3m + 1$, respectively.] New results are presented for $C_1E_2C_1$ to $C_1E_{12}C_1$ inclusive, $C_1E_{15}C_1$, $C_1E_{16}C_1$ and $C_1E_{25}C_1$, and for HE_2OH to HE_6OH inclusive. Results quoted for other samples are taken from earlier work.⁹

High Frequency Spectra

The high frequency Raman spectra ($100\text{--}1800\text{ cm}^{-1}$) of the oligomers were examined for evidence of the conformation of the oxyethylene chain. Following recent work by Matsuura and Fukuhara,¹⁹ the indicators used were the bands at 291, 936, and 1231 cm^{-1} . The spectra of all samples with oxyethylene chain length $m \geq 4$, irrespective of chain length, were consistent with crystallization of chains in the helical conformation, i.e., the *tgt* sequence of bonds $O\text{--}CH_2\text{--}CH_2\text{--}O$. Samples of shorter chain length ($C_1E_2C_1$ and $C_1E_3C_1$, HE_2OH and HE_3OH) had significantly different spectra in the relevant frequency ranges. Accordingly only spectra of samples with $m \geq 4$ were considered for calibration of the LAM-frequency/chain-length relationship.

Low-Frequency Spectra of Methoxy-Ended Oligo(oxyethylene)s

The spectra of some samples showed evidence of fluorescence, in which case the effect was minimized (but not eliminated; see Fig. 1) by exposure of the sample to the laser beam for a period of time before recording the spectrum.

A low-frequency spectrum ($5\text{--}150\text{ cm}^{-1}$) of sample $C_1E_{25}C_1$ at 173 K is shown in Figure 1. The spectrum is typical of published spectra¹⁰ of low-molecular weight poly(oxyethylene)s at low temperature, with bands at 33, 50, 61, 79, 90, and 107 cm^{-1} in addition to the LAM-1 band at 15.8 cm^{-1} . As expected,^{9,10} the spectrum of the sample at room tem-

Table I. Low-Frequency Raman Spectra of α -Methyl, ω -Methoxy-Oligo(Oxyethylene)s: Frequencies for Samples at 173 K

Sample	Chain Atoms	Chain Length l/nm	Other Bands, ν/cm^{-1}								
			LAM-1 ν_1/cm^{-1}	9	21	34	—	52	85	92	—
$C_1E_4C_1$	15	1.39	64.5	9	21	34	—	52	85	92	—
$C_1E_6C_1$	18	1.67	55	—	23	—	—	—	80	—	—
$C_1E_8C_1$	21	1.95	50	11	23	32	61	—	83	—	—
$C_1E_7C_1$	24	2.23	50.5	12	23	34	61	—	—	91	—
$C_1E_8C_1$	27	2.51	42	12	22	—	—	—	—	89	—
$C_1E_9C_1$	30	2.78	43	—	22	—	—	—	83	—	—
$C_1E_{10}C_1$	33	3.06	33	—	—	—	63	—	—	88	—
$C_1E_{11}C_1$	36	3.34	31.5	—	21	—	61	—	—	91	—
$C_1E_{12}C_1$	39	3.62	28.5	—	21	—	61	—	—	91	—
$C_1E_{15}C_1$	48	4.45	25	—	21	—	61	—	—	89	—
$C_1E_{16}C_1$	51	4.73	21.5	—	—	—	—	—	—	89	—
$C_1E_{25}C_1$	78	7.24	15.8	—	21	33	61	50	79	90	107

perature (not shown) was similar except that the bands at 79 and 90 cm^{-1} merged into a single broad band centered on 80 cm^{-1} and the LAM-1 band was at lower frequency.

The spectra of the lower oligomers at the same low temperature (173 K) showed similar features. Scattering from LAM-1 was always the most prominent feature in the low-frequency spectra, particularly as the intensity of the 80–90 cm^{-1} peak decreased relative to that from LAM-1 as chain length was decreased (see Fig. 1, $C_1E_8C_1$, $C_1E_4C_1$). As a consequence, the LAM-1 band was clearly seen even in spectra which were otherwise of poor quality because of fluorescence. A band at 20–23 cm^{-1} , irre-

spective of chain length, was observed in the spectra of the lower oligomers (see Fig. 1).

Spectra were recorded several times in order to define the LAM-1 frequencies as precisely as possible, and other frequencies wherever possible. The values obtained are listed in Table I: no corrections were applied, particularly as the LAM-1 peaks were very narrow. The chain lengths listed in Table 1 were calculated for $C_1E_mC_1$ assuming the helical conformation²⁴ as follows:

$$1/\text{nm} = xd$$

where the chain length in chain atoms, is $x = 3m + 3$ and the interatomic distance in the longitudinal direction is $d = 0.0928 \text{ nm}$.

Effect of Temperature

Spectra were recorded over the temperature range 153–298 K. No large changes were observed in the

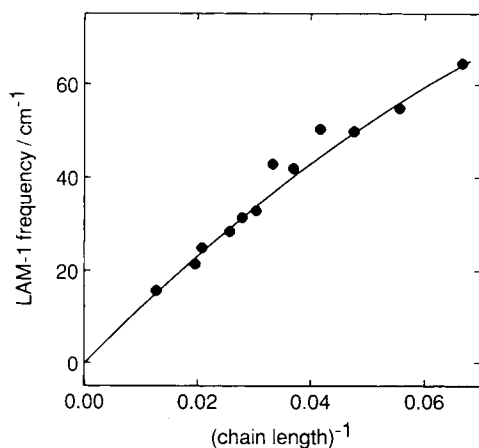


Figure 2. (●) LAM-1 frequency (ν) versus reciprocal chain length (x^{-1}) for methoxy-ended oligo(oxyethylene)s ($C_1E_mC_1$) at 173 K. The curve is: $\nu/\text{cm}^{-1} = 1248x^{-1} - 4287x^{-2}$.

Table II. Low-Frequency Raman Spectra of α -Hydro, ω -Hydroxy-Oligo(Oxyethylene)s: LAM-1 Frequencies for Samples at 293 K^a

Sample	LAM-1 ν_1/cm^{-1}	$x/\text{Chain Atoms}$	Chain Length l_a/nm
HE_9OH	49.5	28	2.60
$HE_{15}OH$	31.7	46	4.27
$HE_{25}OH$	20.0	76	7.05
$HE_{35}OH$	14.0	106	9.83

^a Values taken from ref. 9: chain length $x = 3m + 1$, $l = 0.0928x \text{ nm}$.

spectra, showing that the crystal structure was unchanged across the temperature range. The LAM-1 frequency decreased as temperature increased at a rate of -1 to -2 cm^{-1} per 100 K. Temperature dependences of this magnitude have been found for *n*-alkanes² and their derivatives.⁴ More extensive studies¹⁰ of the temperature dependences of LAM-1 frequencies of oligo(oxyethylene)s have shown that the frequency/temperature relationship is almost linear for alkyl-ended uniform oligomers, but not for poly(oxyethylene)s and hydroxy-ended uniform oligo(oxyethylene)s.

Low-Frequency Spectra of Hydroxy-Ended Oligo(oxyethylene)s

As described earlier,^{9,10} for samples HE_9OH and higher oligomers, the intensity of Raman scattering from the LAM-1 of a uniform hydroxy-ended oligo(oxyethylene) is very low. This is consistent with the force acting on the ends of these hydrogen-bonded chains being comparable with the internal force resisting elongation of the oxyethylene helix. The shorter the oxyethylene chains, the more uniform will be the hydrogen bonding across the end-planes of the layer crystals,⁷ so that very low intensities of Raman scattering from LAM-1 would be expected from samples HE_4OH to HE_6OH . In fact we have been unable to identify scattering from LAM-1 in these oligomers. The small intensities observable with higher oligomers probably reflect end-melting²⁵ of longer chains.

DISCUSSION

Frequency/Chain Length Relationship for Methoxy-Ended Oligomers

The LAM-1 frequencies listed in Table I for the methoxy-ended oligomers at 173 K are plotted against chain length (in chain atoms) in Figure 2. The results define an acceptably smooth curve, except that the points for oligomers $\text{C}_1\text{E}_7\text{C}_1$ and $\text{C}_1\text{E}_9\text{C}_1$ lie above the curve. Care was taken to confirm the frequencies for these samples by repeat experiments: a high value for the LAM-1 frequency of oligomer $\text{C}_1\text{E}_9\text{C}_1$ has been observed before.⁹ The presumption is that the oligomers with the anomalous LAM-1 frequencies have different crystal structures from the rest, though the same helical chain conformation.

It is known from studies of x-ray scattering from the long spacings of the longer oligomers, such as $\text{C}_1\text{E}_{15}\text{C}_1$, $\text{C}_1\text{E}_{25}\text{C}_1$, $\text{C}_1\text{E}_{45}\text{C}_1$ and related block oligo-

mers,²⁶⁻²⁹ that the usual orientation of the helical chains in the layer crystals is normal to the end-group plane. However, oligomer $\text{C}_1\text{E}_9\text{C}_1$ is known to be an exception,²⁶ as in this case the x-ray data indicate that the helix is tilted with respect to the end-group plane. The tilt angle is about 60° , corresponding to a longitudinal displacement of one chain relative to its neighbor of three oxyethylene units (i.e., a turn of the helix). Interestingly, the corresponding oligomer with ethyl end groups, $\text{C}_2\text{E}_9\text{C}_2$, conforms to the general rule of normal orientation and exhibits unexceptional Raman scattering. Unfortunately we have not had an opportunity to study oligomer $\text{C}_1\text{E}_7\text{C}_1$ by x-ray scattering as it is liquid at room temperature. However, the present results (Fig. 2) indicate that oligomer $\text{C}_1\text{E}_7\text{C}_1$ should be classified together with $\text{C}_1\text{E}_9\text{C}_1$. Their relatively high LAM-1 frequencies are consistent either with the methyl end-groups being more closely packed in tilted structures, leading to a larger end intermolecular force, or with a larger contribution of lateral intermolecular interactions^{13,15} in the tilted structure, or both.

Frequency/Chain Length Relationship for Hydroxy-Ended Oligomers

LAM-1 frequencies obtained previously⁹ for a number of uniform hydroxy-ended oligo(oxyethylene)s at 298 K are listed in Table II and plotted against chain length in Figure 3. The frequency/chain length relationship established for methoxy-ended oligo(oxyethylene)s by the present work (Fig. 2) is represented by the full curve. The dashed curve represents results² for *n*-alkanes. The higher frequency found for a hydroxy-ended oligo(oxyethylene), compared to a methoxy-ended oligo(oxyethylene) of the same chain length, must be ascribed to the hydrogen bonds between end groups. The generally lower frequencies of the oligo(oxyethylene)s compared to the trans-planar *n*-alkanes result from the lower longitudinal modulus of the helical chain. These effects are discussed next.

Calculation of LAM-1 Frequencies

Song and Krimm^{13,15} have calculated LAM-1 frequencies for oligo(oxyethylene) via normal coordinate analysis and shown that lateral interchain forces, as well as end interchain forces, are important for the helical chains. The calculations reported here are based on the assumption that the large differences in behavior of methoxy-ended and hydroxy-ended oligomers can be ascribed to end forces, with

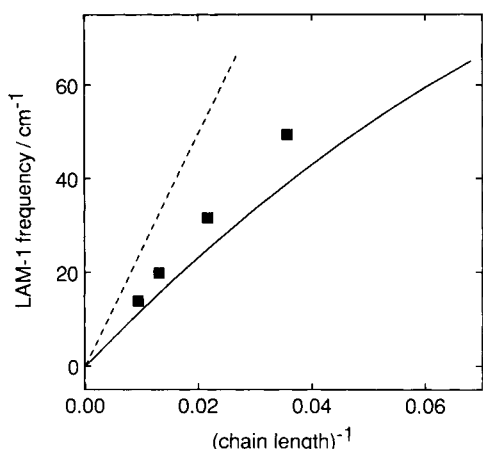


Figure 3. (■) LAM-1 frequency (ν) versus reciprocal chain length (x^{-1}) for hydroxy-ended oligo(oxyethylene)s (HE_mOH) at 293 K. The full curve is the plot for the dimethyl ethers at 173 K taken from Fig. 2; the dashed curve represents results² for n -alkanes at 297 K.

the effect of lateral forces being subsumed into a composite longitudinal modulus (in the perturbed-rod model of Hsu, Ford, and Krimm³⁰) or a composite chain force constant (in the chain model of Minoni and Zerbi³¹), both of which are independent of chain length.

Application of the Perturbed Uniform Rod Model

It is assumed that the different behaviors of the hydroxy-ended and methoxy-ended oligomers reflect the difference in magnitude of hydrogen-bonded and van der Waals end forces. The frequencies found for the hydroxy-ended oligomers are considerably greater than those found for the methoxy-ended oligomers (see Fig. 3). Such a large effect of end forces cannot be ignored.

Calculation of the frequency of vibration of a rod (longitudinal modulus E) perturbed by an end force (force constant f_e) has been carried out using the equation of Hsu, et al.³⁰ (see Appendix). Since more than one combination of E and f_e can be used to fit the data, it was necessary to choose a value for one of the parameters. A value of the modulus $E = 2.5 \times 10^{10} \text{ N m}^{-2}$ determined^{9,10} from the results obtained earlier for hydroxy-ended oligo(oxyethylene)s has been used^{16-18,32} to describe a number of related systems. The use of this value will be justified further below.

The present results for the LAM-1 frequencies of the methoxy-ended oligomers are well represented by the model. A comparison of calculated and experimental results is shown in Figure 4. The end-

force constants used to fit the data are $f_e = 5 \text{ N m}^{-1}$ for the methoxy-ended oligomers and $f_e = 20 \text{ N m}^{-1}$ for the hydroxy-ended oligomers. The calculated curves lie between those expected for unperturbed uniform rods ($f_e = 0$) and highly perturbed uniform rods ($f_e \rightarrow \infty$, effectively rods with fixed ends). It is apparent from Figure 4 that for lengthy chains the curves for $f_e = 20 \text{ N m}^{-1}$ and $f_e = \infty$ (chains with fixed ends) practically coincide.

A value of $f_e = 5 \text{ N m}^{-1}$ was determined by Hsu and Krimm³³ for n -alkanes at low temperatures. The fitting of data by the same value here, i.e., for oligomers with the same (methyl) ends, is satisfactory. Obviously, it would have been possible to have used Hsu and Krimm's result for f_e as the basis of the fitting procedure and arrived at a value of $E = 2.5 \times 10^{10} \text{ N m}^{-2}$. A value of $f_e = 20 \text{ N m}^{-1}$ (i.e., 4 times larger) to fit the results for the hydroxy-ended oligo(oxyethylene)s is in keeping with the relative strengths of hydrogen bonds and van der Waals interactions: Song and Krimm have used a value of $f_e = 15 \text{ N m}^{-1}$ in their work.¹³

The application of the uniform perturbed rod to these results serves to show that the pronounced curvature of the plots of LAM-1 frequency against inverse chain length, particularly seen in the results for the methoxy-ended oligomers which cover a wider range, can be attributed (at least in major part) to the effect of end forces acting on a chain of low modulus.

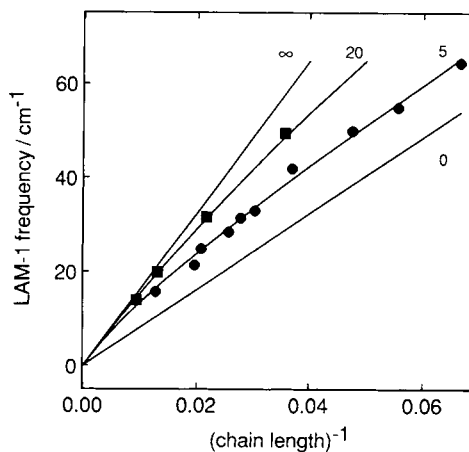


Figure 4. Effect of end forces on the LAM-1 frequencies of oligo(oxyethylene)s: application of the perturbed uniform rod model. The curves represent the results of calculation for rods of modulus $E = 2.5 \times 10^{10} \text{ N m}^{-2}$ and appropriate lengths (see Tables I and II) and with the end forces indicated: see Text and Appendix for details. Experimental results are for (●) methoxy-ended oligomers at 173 K and (■) hydroxy-ended oligomers at 293 K.

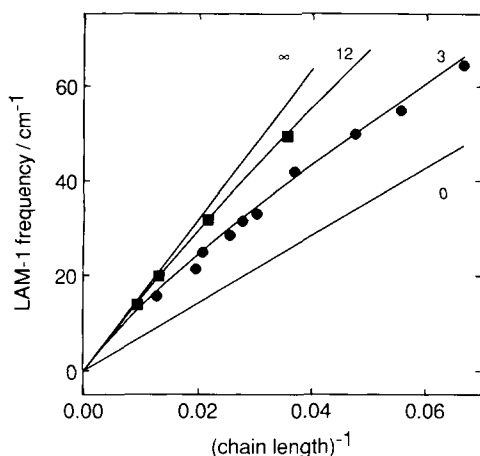


Figure 5. Effect of end forces on the LAM-1 frequencies of oligo(oxyethylene)s: application of the Minoni-Zerbi model. The curves represent the results of calculation for chains with force constant $f_c = 55 \text{ N m}^{-1}$ and appropriate lengths (see Tables I and II) and with the end forces indicated: see text and Appendix for details. Experimental results are for (●) methoxy-ended oligomers at 173 K and (■) hydroxy-ended oligomers at 293 K.

Application of the Model of Minoni and Zerbi

Calculations have also been carried out using the linear chain model of Minoni and Zerbi³¹ (see Appendix). This model allows for the fact that the molecules are packed into layer crystals, and treats the case of the infinite one-dimensional crystal with an oligomeric repeat unit. Because of this feature, the Minoni-Zerbi chain might be expected to yield more realistic predictions than the perturbed but isolated rod.

In this work, since exact fitting of results was not required, calculations were carried out with a rounded value of $f_c = 55 \text{ N m}^{-1}$. The data could then be adequately fitted (see Fig. 5) using values of $f_e = 3 \text{ N m}^{-1}$ for the methoxy-ended oligomers and $f_e = 12 \text{ N m}^{-1}$ for the hydroxy-ended oligomers.

The pronounced curvature of the plots of LAM-1 frequency against inverse chain length is predicted by the model, and, as remarked above, can be attributed (at least in major part) to the effect of end forces acting on a chain of low chain-force constant. The proximity of the results for the hydroxy-ended oligomers to the line for $f_e = f_e \rightarrow \infty$ (effectively LAM-2) is also reproduced.

The two models predict different values for the end-force constants. This is because the rod model treats a single perturbed vibrator, while the Minoni-Zerbi model treats an infinite linear array of coupled vibrators. The results of Tables I and II could be equally well fitted by Minoni and Zerbi's equation with $f_e = 5 \text{ N m}^{-1}$ (methoxy-ended oligomers) or $f_e = 20 \text{ N m}^{-1}$ (hydroxy-ended oligomers) provided that $f_c = 45 \text{ N m}^{-2}$ (equivalent to $E \sim 2.0 \times 10^{10} \text{ N m}^{-2}$).

LAM-3

In principle, values of the LAM-3 frequency provide a means of distinguishing between pairs of values of f_c and f_e . In the case of the hydroxy-ended oligomers, the Minoni-Zerbi theory predicts ratios of frequencies (LAM-3/LAM-1) of $r < 2.01$ irrespective of the value of f_e (12 or 20 N m^{-1}). However, in the case of the methoxy-ended oligomers, the value of r is sensitive to choice of f_c and f_e ,

Oligomer	$C_1E_4C_1$	$C_1E_8C_1$	$C_1E_{15}C_1$	$C_1E_{25}C_1$
$r (f_e = 3, f_c = 55 \text{ N m}^{-1})$	2.42	2.28	2.14	2.07
$r (f_e = 5, f_c = 45 \text{ N m}^{-1})$	2.20	2.10	2.03	2.01

The required parameters are the force constants between intrachain groups (f_c) and between end groups (f_e). It seems logical to use a value of f_c which is consistent with the modulus ($2.5 \times 10^{10} \text{ N m}^{-2}$) used in applying the perturbed rod model, i.e.

$$f_c = AE/d = 57 \text{ N m}^{-1}$$

where A is the area of cross-section of the chain (0.214 nm^2) and d is the interatomic spacing in the chain direction (0.0928 nm).

Unfortunately, our spectra are not of sufficient quality to allow the distinction to be made: the predicted values of LAM-3 (using either set of values of the force constants) generally overlap other bands.

We thank Mr. Peter Kobryn for help with the experimental work. The Royal Society and the Science and Engineering Research Council provided financial support.

APPENDIX

Perturbed Rod Model

Hsu, Ford, and Krimm³⁰ allow for perturbation of the longitudinal vibrational of a uniform rod by end forces. For an elastic rod of length l , area of cross-section A , density ρ , and longitudinal modulus E , with forces (force constant f_e) acting symmetrically at its ends, the LAM frequencies can be conveniently calculated from.³⁰

$$2f_e q(p^2 - 1) + 2p(f_e^2 - q^2) = 0,$$

where $p = \cot(\pi\nu/2\nu_0)$ and $q = 2\pi\nu A(E\rho)^{1/2}$ with $\nu_0 = E^{1/2}/2l\rho^{1/2}$. In applying the equation to oligo(oxyethylene)s, the values of the parameters used were:

$$\begin{aligned} A &= 0.214 \times 10^{-18} \text{ m}^2 \\ \rho &= 1.23 \times 10^3 \text{ kg m}^{-3} \\ E &= 2.5 \times 10^{10} \text{ N m}^{-2} \\ l &= 0.0928 \times 10^{-9} x \text{ m} \end{aligned}$$

where x is the chain length of the oligomer in chain atoms. These values are fixed by x-ray²⁴ and Raman^{9,10,13,18} results.

Infinite Chain Model

Minoni and Zerbi³¹ allow for perturbation of the longitudinal vibrational of a linear chain by inter-chain forces caused by its incorporation into a one-dimensional crystal. In the model, chain and end groups are represented by point masses (m_c and m_e , respectively) connected by intergroup forces within the chain and between end groups (force constants f_c and f_e , respectively). The phase angle (θ) of the longitudinal vibration can be conveniently calculated from eq. (16) of ref. 31: i.e.

$$\begin{aligned} &\sin\{(x-1)\theta\} \{\cos\theta - 1\} [\cos\theta(2K-1-2K^2) \\ &+ (2K^2 - 2K + G - 2KG)] + \cos\{(x-1)\theta\} \\ &\times \sin\theta[(1-2K)(\cos\theta - 1) - G] + G \sin\theta = 0 \end{aligned}$$

where x is the chain length in chain atoms, $K = m_e/m_c$, $G = f_e/f_c$. The LAM frequency (ν) is obtained from:

$$(2\pi\nu)^2 = (2f_c/m_c)(1 - \cos\theta)$$

In applying the equation to the oligo(oxyethylene)s, the CH₂ and O units of the chain were each assigned

an average mass of 2.4385×10^{-26} kg, the CH₃ units of the methoxy-ended oligomers each a mass of 2.4967×10^{-26} kg, and the end of OH groups of the hydroxy-ended oligomers each a mass of 2.8243×10^{-26} kg. In fact, LAM-1 frequencies were not significantly affected by these niceties, and the assumption $m_e = m_c$ sufficed for the calculations. The chain-force constant was assigned a value of 55 N m⁻¹ (see text).

REFERENCES AND NOTES

1. S. Mizushima and T. Shimanouchi, *J. Am. Chem. Soc.*, **71**, 1320 (1949).
2. H. G. Olf and B. Fanconi, *J. Chem. Phys.*, **59**, 534 (1973).
3. J. F. Rabolt, *CRC Crit. Rev., Solid State Mater. Sci.*, **12**, 165 (1977).
4. K. Viras, F. Viras, C. Campbell, T. A. King, and C. Booth, *J. Phys. Chem.*, **93**, 3479 (1989).
5. A. Marshall, R. C. Domszy, H. H. Teo, R. H. Mobbs, and C. Booth, *Eur. Polym. J.*, **17**, 885 (1981).
6. G. Minoni, G. Zerbi, and R. F. Rabolt, *J. Chem. Phys.*, **81**, 4782 (1984).
7. H. H. Teo, A. Marshall, and C. Booth, *Makromol. Chem.*, **183**, 2265 (1982).
8. A. J. Hartley, Y. K. Leung, C. Booth, and I. W. Shepherd, *Polymer*, **17**, 354 (1976).
9. K. Viras, H. H. Teo, A. Marshall, R. C. Domszy, T. A. King, and C. Booth, *J. Polym. Sci., Polym. Phys. Ed.*, **21**, 919 (1983).
10. K. Viras, T. A. King, and C. Booth, *J. Polym. Sci., Polym. Phys. Ed.*, **23**, 471 (1985).
11. S. Krimm and S. L. Hsu, *J. Polym. Sci., Polym. Phys. Ed.*, **16**, 2105 (1978).
12. K. Song and S. Krimm, *Macromolecules.*, **22**, 1504 (1989).
13. K. Song and S. Krimm, *J. Polym. Sci., Polym. Phys. Ed.*, **28**, 35 (1990).
14. K. Song and S. Krimm, *J. Polym. Sci., Polym. Phys. Ed.*, **28**, 51 (1990).
15. K. Song and S. Krimm, *J. Polym. Sci., Polym. Phys. Ed.*, **28**, 63 (1990).
16. K. Viras, T. A. King, and C. Booth, *J. Chem. Soc., Faraday Trans. 2*, **81**, 491 (1985).
17. K. Viras, T. A. King, and C. Booth, *J. Chem. Soc., Faraday Trans. 2*, **81**, 1477 (1985).
18. T. G. E. Swales, H. H. Teo, R. C. Domszy, K. Viras, T. A. King, and C. Booth, *J. Polym. Sci., Polym. Phys. Ed.*, **21**, 1501 (1983).
19. H. Matsuura and K. Fukuhara, *J. Phys. Chem.*, **91**, 6139 (1987).
20. S. G. Yeates, H. H. Teo, R. H. Mobbs, and C. Booth, *Makromol. Chem.*, **185**, 1559 (1984).
21. J. R. Craven, R. H. Mobbs, C. Booth, E. J. Goodwin, and D. Jackson, *Makromol. Chem.*, **190**, 1207 (1989).
22. H. H. Teo, R. H. Mobbs, and C. Booth, *Eur. Polym. J.*, **18**, 541 (1982).

23. J. R. Craven, H. Tyrer, S. P. L. Li, C. Booth, and D. Jackson, *J. Chromatogr.*, **387**, 233 (1987).
24. Y. Takahashi and H. Tadokoro, *Macromolecules.*, **6**, 672 (1973).
25. P. J. Flory and A. J. Vrij, *J. Am. Chem. Soc.*, **85**, 3548 (1963).
26. R. C. Domszy and C. Booth, *Makromol. Chem.*, **183**, 1051 (1982).
27. H. H. Teo, T. G. E. Swales, R. C. Domszy, F. Heatley, and C. Booth, *Makromol. Chem.*, **184**, 861 (1983).
28. T. G. E. Swales, R. C. Domszy, R. L. Beddoes, C. Price, and C. Booth, *J. Polym. Sci., Polym. Phys. Ed.*, **23**, 1585 (1985).
29. S. G. Yeates and C. Booth, *Makromol. Chem.*, **186**, 2663 (1985).
30. S. L. Hsu, G. W. Ford, and S. Krimm, *J. Polym. Sci. Polym. Phys. Ed.*, **15**, 1769 (1977).
31. G. Minoni and G. Zerbi, *J. Phys. Chem.*, **86**, 4791 (1982).
32. F. Viras, K. Viras, C. Campbell, T. A. King, and C. Booth, *J. Chem. Soc., Faraday Trans. 2*, **83**, 927 (1987).
33. S. L. Hsu and S. Krimm, *J. Appl. Phys.*, **47**, 4265 (1976).
34. The Raman spectroscopy of α -methyl, ω -hydroxy-oligo(oxyethylene)s mentioned in this paper has been published in *J. Phys. Chem.*, **95**, 4647 (1991).

Received September 11, 1990

Accepted May 9, 1991