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Application of the Perturbed-elastic-rod Model to the Longitudinal Acoustical Modes of Poly(oxyethylene)s and their n-Hexadecyl Ethers

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The LAM-1 frequencies of low-molecular-weight poly(oxyethylene) dimethyl and diethyl ethers and methyl-n-hexadecyl ethers are interpreted by modelling the chain molecules as elastic rods perturbed by end masses and end forces. In the case of the n-hexadecyl ethers the important factor is the damping effect of the alkyl block acting as an inertial mass.

Longitudinal acoustical modes were first observed[1] in the low-frequency Raman spectra of crystalline n-alkanes, and the chain-length dependence of the LAM-1 frequency was interpreted[1] in terms of a uniform elastic rod. A more generally applicable model, in which the elastic rod is perturbed by end forces and end masses, was introduced[2-4] in order to interpret the LAM-1s of the n-alkanes in more detail, and also to interpret the more complex chain-length dependences of LAM-1 found for helical chain molecules, *e.g.* crystalline polypropylene.

The perturbed elastic rod has proved a useful model for crystalline oxyethylene chains[5-7] and their di-n-alkyl ethers.[8] This includes members of the homologous series of uniform oligo(oxyethylene) dimethyl ethers, which are helical analogues of the planar zig-zag n-alkanes. Since the longitudinal modulus of a helical chain is very much lower than that of a planar zig-zag, owing to the lower energies associated with rotational-angle rather than bond-angle distortion, the effects of end forces (interlamellar or interlayer forces) are particularly important in this case, so much so that the unperturbed elastic rod is a very poor model indeed for oligo-oxyethylenes.

In the preceding paper[9] we have reported the LAM-1 frequencies of a number of crystalline poly(oxyethylene) methyl-n-alkyl ethers, covering a fairly wide range of chain lengths. In this paper we interpret these results in terms of the perturbed-elastic-rod model. Since the samples studied[9] were non-uniform in chain length, albeit with narrow distributions of chain lengths, the molecular parameters for the model are defined in the light of a preliminary comparison of the chain-length dependences of uniform and non-uniform samples of methyl-ended poly(oxyethylene), *i.e.* poly(oxythylene) dimethyl and diethyl ethers.

LAM-1 Frequencies

Observed Frequencies

LAM-1 frequencies from the low-frequency Raman spectra of poly(oxyethylene) dimethyl and diethyl ethers[5-7] [$H(CH_2)_n(OCH_2CH_2)_mO(CH_2)_nH$, *m* in the range 15-45,

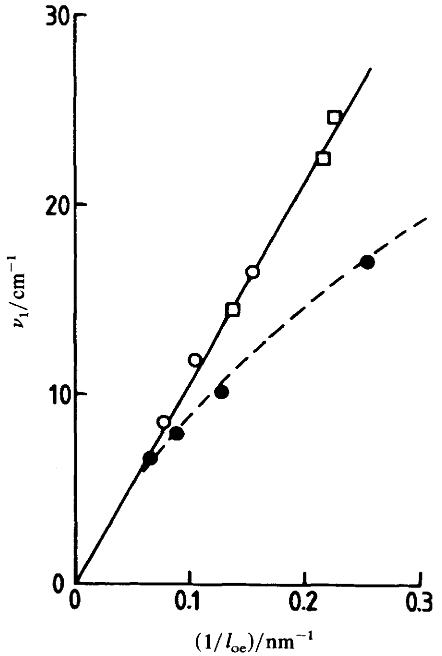

Fig. 1. LAM-1 frequency (ν_1) of unfolded chains *vs.* reciprocal oxyethylene-block length ($1/l_{\mathrm{oe}}$): □, uniform oligo(oxyethylene) dimethyl and diethyl ethers; ○, polydisperse poly(oxyethylene) dimethyl ethers; ●, polydisperse poly(oxyethylene) methyl-n-hexadecyl ethers. The lines drawn are based only on the experimental data.

$n = 1$ or 2] and methyl-n-hexadecyl ethers[9] [$CH_3(OCH_2CH_2)_mO(CH_2)_nH$, m in the range 13-53, $n = 16$] are plotted against oxyethylene-block length [$l_{\mathrm{oe}} = 0.0928(3m+3)$] in fig. 1. The results for the methyl-n-hexadecyl ethers are representative of results obtained[9] for a number of n-alkyl ethers in the range $n = 12$ to 21. The frequencies correspond to chains in their unfolded helical conformation, as indicated[5,10-12] by X-ray diffraction and infrared spectroscopy as well as by Raman spectroscopy.[5-7,9]

Calculated Frequencies

For an elastic rod of length l, area of cross-section A, density ρ and longitudinal modulus E, with forces (force constant f) acting symmetrically on its ends and with point masses (M_1, M_2) at its ends, the LAM frequencies can be conveniently calculated from:[3]

$$(p^2q - q)(2f - r) + 2p(f^2 - q^2 - fr + s) = 0$$

where $p = \cot(\pi\nu/2\nu_0)$, $q = 2\pi\nu A(E\rho)^{1/2}$, $r = (2\pi\nu)^2(M_1 + M_2)$, $s = (2\pi\nu)^4 M_1 M_2$ and $\nu_0 = E^{1/2}/2l\rho^{1/2}$. In applying this equation to oxyethylene helices, values of $A = 2.17 \times 10^{-19}\ \mathrm{m}^2$ and $\rho = 1.23 \times 10^3\ \mathrm{kg\ m}^{-3}$ were fixed by X-ray crystallographic results[13] and of $E = 2.5 \times 10^{10}\ \mathrm{N\ m}^{-2}$ by previous Raman spectroscopic results.[6-8] The other parameters (l, f, M_1, M_2) were given values which conformed to the sample under consideration, as described later. The equation was solved numerically.

Poly(oxyethylene) Dimethyl and Diethyl Ethers

The poly(oxyethylene) dimethyl and diethyl ethers considered are of two types; either uniform or non-uniform (polydisperse) in chain length, as indicated in fig. 1, where the squares denote uniform samples and the circles polydisperse samples. The chain-length distributions of the polydisperse samples are narrow, $M_w/M_n \approx 1.05$. Irrespective of end group ($n = 1$ or 2) the uniform chains are completely crystalline.[5,10-12] The polydisperse chains are partly crystalline, and the extent of crystallinity varies with chain length. For poly(oxyethylene) dimethyl ethers crystallised into unfolded-chain lamellae, the observed[5] extents of crystallinity at 20 °C are *ca.* 75% when $m = 25$ and *ca.* 85% when $m = 45$. These values roughly correspond to 3 non-crystalline oxyethylene units at each chain end.

The results of fig. 1 show that the LAM-1 frequencies of the poly(oxyethylene) dimethyl and diethyl ethers are practically independent of their nature, *i.e.* their extent of crystallinity. This finding, surprising at first sight, can be rationalised in terms of the perturbed-elastic-rod model.

Two limiting cases are considered.

(*i*) *Rigid End Blocks*

The partly crystalline molecule consists of a helical inner block and short non-helical end blocks. The modulus of the end block will exceed that of the inner helix, and in the limit of an all-*trans* end block will be some 10 to 20 times higher. [Compare the moduli reported[6-8,14] for helical poly(oxyethylene), *i.e.* $(1\text{-}2.5)\times10^{10}$ N m^{-2}, with those[2,14,15] reported for the planar zig-zag poly(methylene), *i.e.* $(24\text{-}29)\times10^{10}$ N m^{-2}.] In this limiting case the end blocks are effectively inextensible and the increase in LAM-1 frequency owing to the shortened helical stem length of the partly crystalline molecule is compensated by the damping effect of the inertial masses of the end blocks.

(*ii*) *Flexible End Blocks*

Interlamellar forces are important in determining LAM frequencies in crystalline low-molecular-weight poly(oxyethylene)s. This has been demonstrated in several ways: by changing the end groups[5,6] or the temperature,[7,16,17] or by swelling the lamellar surface layer.[18] The forces acting on the ends of uniform (completely crystalline) oligo(oxyethylene) ethers can be assigned similar force constants (f) to those which act on crystalline n-alkanes[2] (*e.g.* $f \approx 3$ N m^{-1}) and since the modulus of the oxyethylene helix is much lower than that of the methylene planar zig-zag the effect of the forces is correspondingly greater. The LAM-1 frequencies of the uniform oligomers of fig. 1 can be reproduced by the vibration of an elastic rod of modulus 2.5×10^{10} N m^{-2} with end force constant of the expected magnitude: *e.g.* for pentadeca(oxyethylene) dimethyl ether ($m = 15$, denoted 1-15-1†) the observed LAM-1 frequency is 24.7 cm^{-1}, while that calculated with $f = 3$ N m^{-1} is 24.8 cm^{-1} (with $l = 4.45$ nm and $M_1 = M_2 = 0$). Since the end forces in the uniform crystalline oligomers derive from crystallographically packed methyl groups, a smaller value of f is expected[6] to act on the chain ends in a disordered lamellar surface layer formed in a polydisperse sample. In this case the increase in LAM-1 frequency due to the shortened helical stem length of the partly crystalline molecule is compensated by a decrease in the forces acting on the chain ends.

Illustrative calculations for these two limiting cases, applied to a polydisperse poly(oxyethylene) dimethyl ether with $m = 23$ (sample 1-23-1) are set out in table 1. In both calculations f was used as an adjustable parameter to bring the calculated frequency into rough correspondence with that observed (*i.e.* 16.5 cm^{-1}). Neither limiting case is likely correctly to describe the molecule, but rather some intermediate combination of masses and forces. However, any sensible choice of end masses (*i.e.* within the range

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† Samples are denoted by their oxyethylene block length (m) in oxyethylene units and their alkyl block lengths (n) in methylene units. Thus 1-27-1 denotes the dimethyl ether and 1-27-16 the methyl-n-hexadecyl ether of an oxyethylene of chain length 27 units.

Table 1. Calculated LAM-1 frequencies of unfolded polydisperse poly(oxyethylene) dimethyl ether 1-23-1[a]

model	$f/\mathrm{N\,m^{-1}}$	$M/10^{-25}\,\mathrm{kg}$	LAM-1 frequency[b]/$\mathrm{cm^{-1}}$
(i) rigid end blocks	2.5	2.21	16.5
(ii) flexible end blocks	0.4	0	16.7

[a] Calculations based on a rod with end forces and end masses and with the following properties: modulus $E = 2.5 \times 10^{10}\,\mathrm{N\,m^{-2}}$, cross-sectional area $A = 2.17 \times 10^{-19}\,\mathrm{m^2}$, density $\rho = 1.23 \times 10^3\,\mathrm{kg\,m^{-3}}$, length $l_{oe} = 5.01$ nm (corresponding to 18 oxyethylene units). The end-masses in model (i) correspond to 3 oxyethylene units (*i.e.* 9 chain atoms). [b] Observed LAM-1 frequency $= 16.5 \pm 0.5\,\mathrm{cm^{-1}}$.

Table 2. Calculated LAM-1 frequencies of unfolded polydisperse poly(oxyyethylene) methyl-n-hexadecyl ether 1-27-16[a]

model	$f/\mathrm{N\,m^{-1}}$	$M_1, M_2/10^{-25}\,\mathrm{kg}$	LAM-1 frequency[b]/$\mathrm{cm^{-1}}$
(i) rigid end blocks	2.5	2.21, 3.50	13.3
(ii) flexible end blocks	0.4	0, 0	12.4

[a] Calculations based on a rod with end forces and end masses and with the following properties: modulus $E = 2.5 \times 10^{10}\,\mathrm{N\,m^{-2}}$, cross-sectional area $A = 2.17 \times 10^{-19}\,\mathrm{m^2}$, density $\rho = 1.23 \times 10^3\,\mathrm{kg\,m^{-3}}$, length $l_{oe} = 6.96$ nm (corresponding to 25 oxyethylene units). The end masses in model (i) correspond to 9 chain atoms (M_1, oxyethylene) or 15 chain atoms (M_2, methylene). [b] Observed LAM-1 frequency $= 10.0 \pm 0.3\,\mathrm{cm^{-1}}$.

of the limiting cases) can be matched by end forces (also within the range described) to produce the desired result.

Poly(oxyethylene) Methyl-n-hexadecyl Ethers

An explanation of the large differences in LAM-1 frequency between the dimethyl and diethyl ethers on the one hand and the methyl-n-hexadecyl ethers on the other (see fig. 1) can be sought either in damping due to the mass of the n-alkyl block, or in a diminution of the end forces due to an extra component (the n-alkyl block) in the disordered surface layer, or in a combination of these effects.

Some revision of the model is needed.

The samples are polydisperse and the ends of their oxyethylene blocks are in the non-crystalline lamellar-surface layers. The relatively stiff n-alkyl block will be aligned in the surface layer in the general direction of the axis of the oxyethylene helix and will suppress the disordering of the helix at the end to which it is attached. In other words some conformational ordering of the adjacent units of the oxyethylene block will be induced by the n-alkyl block. Accordingly a useful model for the molecule is an oxyethylene helix of $m-2$ units with a non-helical block of 3 oxyethylene units at one end and an n-alkyl block at the other.

As before, two limiting cases of (i) rigid end blocks and (ii) flexible end blocks are considered.

The calculation of LAM-1 frequency for sample 1-27-16 is illustrated in table 2 and values for the four methyl-n-hexadecyl ethers are plotted against reciprocal oxyethylene chain length in fig. 2. The parameters used match those of table 1. The agreement between calculated and observed values is not exact, but it must be remembered that in these calculations the force constant is taken from table 1 and not adjusted to obtain

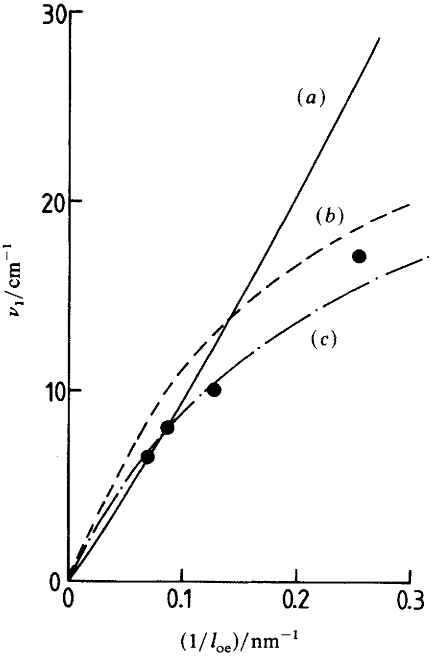

Fig. 2. LAM-1 frequency (ν_1) of unfolded poly(oxyethylene) methyl-n-hexadecyl ethers *vs.* reciprocal oxyethylene-block length ($1/l_{oe}$). The points represent the experimental results. The curves are calculated for model block oligomers with end forces (f) and end masses (M_1, M_2): (*a*) flexible end blocks, $f = 0.4\ \text{N m}^{-1}$, $M_1 = M_2 = 0$; (*b*) rigid end blocks, $f = 2.5\ \text{N m}^{-1}$, $M_1 = 2.21 \times 10^{-25}$ kg, $M_2 = 3.50 \times 10^{-25}$ kg; (*c*) rigid end blocks, $f = 1\ \text{N m}^{-1}$, $M_1 = 2.21 \times 10^{-25}$ kg, $M_2 = 3.50 \times 10^{-25}$ kg. Other parameters are as described in table 2.

a fit. However, it is clear that the dependence of LAM-1 frequency on reciprocal oxyethylene chain length is reasonably well described only by curve (*b*) of fig. 2, *i.e.* model (i) with rigid end blocks. Moreover, further reduction of the force constant in model (ii), even to zero, does not enforce agreement. We take this as evidence that the large deviation from linear dependence on inverse oxyethylene block length observed for the LAM-1 frequencies of poly(oxyethylene) methyl-n-alkyl ethers is to be attributed mainly to a damping effect of the n-alkyl end block and not to dilution of the surface layer by flexible ends.

The agreement between experiment and theory can be improved by adjusting the parameters. As an example a curve calculated for a lower end force ($f = 1\ \text{N m}^{-1}$ rather than $f = 2.5\ \text{N m}^{-1}$) is included in fig. 2.

Folded Chains

Sample 1-53-16 crystallises[9] in an unfolded-chain conformation at high crystallisation temperature ($T_c = 40$ °C) but in a folded-chain conformation at room temperature ($T_c = 20$ °C).

In modelling a once-folded 1-53-16 chain by an elastic rod the two stems will be almost identical since the non-crystalline n-alkyl block at the end of one stem will be matched by a non-crystalline oxyethylene block at the end of the other. The model used earlier for unfolded 1-*m*-*n* chains defined 9 oxyethylene chain atoms (3 oxyethylene units) at one end and $n - 1$ alkyl chain atoms at the other as non-crystalline. A 1-53-16 chain with 6 non-crystalline oxyethylene units at the fold and 5 non-crystalline oxyethylene units at the end will have a crystallinity of *ca.* 80% (based on oxyethylene), *i.e.* much as expected. Ignoring the connection at the fold, each stem of such a 1-53-16 chain will be equivalent to the single stem of a 1-24-16 chain. This is in keeping with the observed[9] LAM-1 frequencies; *i.e.* 10.6 cm^{-1} for folded 1-53-16, 10.1 cm^{-1} for unfolded 1-27-16.

Conclusions

The dependence of the LAM-1 frequencies of poly(oxyethylene) methyl-n-hexadecyl ethers on oxyethylene block length can be explained by modelling the chain molecules as elastic rods perturbed by end masses and end forces. The important factor is the damping effect of the n-alkyl block acting as an inertial mass. The observation that the LAM-1 frequencies of uniform and non-uniform samples of poly(oxyethylene) dimethyl and diethyl ethers have identical dependences on chain length in spite of having different crystallinites can also be explained in terms of the perturbed-elastic-rod model.

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References

1 S. Mizushima and T. Shimanouchi, *J. Am. Chem. Soc.*, 1949, **71**, 1320.
2 S. L. Hsu and S. Krimm, *J. Appl. Phys.*, 1977, **48**, 4013.
3 S. L. Hsu, G. W. Ford and S. Krimm, *J. Polym. Sci., Polym. Phys. Ed.*, 1977, **15**, 1769.
4 S. Krimm, *J. Polym. Sci., Polym. Phys. Ed.*, 1978, **16**, 2105.
5 A. Marshall, R. C. Domszy, H. H. Teo, R. H. Mobbs and C. Booth, *Eur. Polym. J.*, 1981, **17**, 885.
6 K. Viras, H. H. Teo, A. Marshall, R. C. Domszy, T. A. King and C. Booth, *J. Polym. Sci., Polym. Phys. Ed.*, 1983, **21**, 919.
7 T. G. E. Swales, H. H. Teo, R. C. Domszy, K. Viras, T. A. King and C. Booth, *J. Polym. Sci., Polym. Phys. Ed.*, 1983, **21**, 1501.
8 K. Viras, T. A. King and C. Booth. *J. Polym. Sci., Polym. Phys. Ed.*, 1985, **23**, 471.
9 K. Viras, F. Viras, C. Campbell, T. A. King and C. Booth, *J. Chem. Soc., Faraday Trans. 2*, 1987, **83**, 917.
10 R. C. Domszy and C. Booth, *Makromol. Chem.*, 1981, **182**, 1051.
11 H. H. Teo, T. G. E. Swales, R. C. Domszy, F. Heatley and C. Booth, *Makromol. Chem.*, 1983, **184**, 861.
12 S. G. Yeates and C. Booth, *Makromol. Chem.*, 1985, **186**, 2663.
13 Y. Takahashi and H. Tadokoro, *Macromolecules*, 1973, **6**, 672.
14 F. Sakurada, T. Ito and K. Nakamae, *J. Polym. Sci., Part C*, 1966, **15**, 75.
15 G. R. Strobel and R. Eckel, *J. Polym. Sci., Polym. Phys. Ed.*, 1976, **14**, 913.
16 K. Viras, T. A. King and C. Booth, *J. Chem. Soc., Faraday Trans. 2*, 1985, **81**, 491.
17 K. Viras, T. A. King and C. Booth, *J. Chem. Soc., Faraday Trans. 2*, 1985, **87**, 1477.
18 A. J. Hartley, Y. K. Leung, J. McMahon, C. Booth and I. W. Shepherd, *Polymer*, 1977, **18**, 386.

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