Raman scattering from mixtures of poly(ethylene oxide) 2000 with poly(ethylene oxide) 200

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The longitudinal acoustic mode fundamental (ν_1) and third harmonic (ν_3) in 2000 *MW* PEO with both hydroxy- and methody-end-groups have been observed in the Raman spectrum as a function of 200 *MW* PEO oligomer content. Measurements of small-angle X-ray spacing l_x permit interpretation using a composite rod model. A good fit to the measured quantities $\nu_1 l_x$ and ν_3/ν_1 is obtained with crystal length $l_c \sim 9$ nm, crystal modulus $E_c = 9 \times 10^{10}$ N/m^2 and amorphous modulus $E_a = 1 \times 10^{10}$ N/m^2. The value of l_c implies a crystalline content of ~70% for the pure polymer; the value of E_c is larger than static determinations and similar discrepancies in other materials are discussed.

INTRODUCTION

Low frequency Raman scattering from the longitudinal acoustic mode (*LAM*) in crystalline low molecular weight poly(ethylene oxide) (PEO) fractions has been reported recently[1]. The Raman mode has a frequency ν_1 cm^{-1} which varies with lamella thickness l_xm as determined by small-angle X-ray scattering. The product $\nu_1 l_x$ is roughly constant in the range (110–130) x 10^{-9}. The ratio of the frequency of the overtone ν_3 to that of the fundamental is in the range 1.5–2.5. Representative results are listed in *Table 1*. The variation of $\nu_1 l_x$ and, more particularly, the values of ν_3/ν_1 indicate that these results cannot be interpreted in terms of the vibration of isolated uniform rods. In this simple case $\nu_1 l_x$ would be constant and ν_3/ν_1 constant and equal to 3. It seems likely therefore that the frequencies of the Raman bands are considerably affected by the non-crystalline layers in the stacked lamella poly(ethylene oxide) crystals. The effect of the amorphous layer between crystals has also been observed by Raman scattering in other polymers, for instance polyethylene[2], polypropylene[3] and polyoxymethylene[4].

A structure of alternating crystalline and non-crystalline layers is established for bulk crystallized low molecular weight poly(ethylene oxide) fractions[5–8], although the proportion of non-crystalline material is disputed, e.g. 20–40% [9,10] or about 10% [11,12]. Terrisse, Mathis and Skoulios[13] have shown that it is possible to swell the non-crystalline layers of crystalline α,ω-hydroxy-poly(ethylene oxide) polymers. Swelling provides a method of changing the thickness of the non-crystalline layer l_a independently of the thickness of the crystalline layer l_c, and so provides a means of investigating the dependence of ν_1 and ν_3 on l_a. In this paper we present Raman studies of the *LAM* and X-ray measurements of the lamellar dimensions in 2000 *MW* PEO containing variable quantities of 200 *MW* oligomer.

EXPERIMENTAL

Samples of α,ω-hydroxy-poly(ethylene oxide) were gifts from Hoechst Chemicals Ltd ($M_n \simeq 2000$, denoted 2000H) and Shell Chemicals Co. Ltd ($M_n \simeq 200$, denoted 200H). Sample 2000H was purified by recrystallization from solution (70% toluene/30% isooctane). Sample 200H was used as supplied.

Both samples were methoxylated by means of a modified Williamson synthesis as described elsewhere[14]. The conversion of hydroxy-to-methoxy-end-groups exceeded 99%. Methoxylated samples are denoted 2000M and 200M.

The molecular weight distributions of samples 2000H and 2000M were practically identical and were narrow (gel permeation chromatography, spreading correction via reverse flow, $M_w/M_n \simeq 1.03$).

Mixtures were made up by weight (as indicated in *Table 2*). The polymers were mixed by melting at 70°C and shaking vigorously several times for a period exceeding 30 min. Gel permeation chromatography of the mixtures showed no detectable degradation during the mixing process. Two independent sets of mixtures were prepared for the system 2000H/200H.

Samples were crystallized by immersion of the hot flasks in a water thermostat held at 25°C (2000H/200H: set A), or otherwise by cooling the hot flasks to room temperature on the bench top.

Raman spectra were obtained at room temperature by use of a Cary 82 spectrometer and an argon ion laser operating at 514.05 nm with 600 mW power. The general features of the low frequency Raman spectra of crystalline

Table 1 Experimental results for α,ω-hydroxy-poly(ethylene oxide) fractions crystallized at 25°C

Approximate M_n	ν_1 (cm^{-1})	$\nu_1 l_x \times 10^9$	ν_3/ν_1
1000	18	128	–
1500	12.5	123	1.6
2000	9.2	121	2.1
4000	7.8	120	2.4
20 000	7.0	118	2.6

Table 2 Experimental results for mixtures

W_{200}	ν_1 (cm^{-1})	ν_3 (cm^{-1})	l_x (nm)	Δh* (J/g)	T_m (°C)
2000H/200H/A:					
0.00	9.3	19.0	12.6	173 (173)	54
0.04	8.5	18.5	13.4	165 (174)	53
0.10	8.3	18.5	13.8	146 (163)	52
0.14	8.0	18.0	13.9	139 (164)	51
0.16	7.6	18.0	14.6	133 (161)	51
0.23	7.4	17.5	14.8	124 (165)	50
0.30	6.7	17.5	15.4	115 (159)	49
2000H/200H/B:					
0.00	9.3	19	12.6	–	54
0.05	8.2	18	13.4	–	53
0.10	8.0	18	13.9	–	51
0.19	7.0	17	15.0	–	49
0.42	6	–	16.3	–	–
0.62	–	–	16.9	–	–
0.80	–	–	18.1	–	–
2000M/200M:					
0.00	8.4	19	13.1	–	54
0.04	7.8	19	13.8	–	52
0.10	7.3	18	13.9	–	52
0.17	6.8	–	14.5	–	–
0.22	6.3	17	15.0	–	–
0.36		–	15.3	–	–
0.46		–	16.2	–	–

* See text for explanation of values in parentheses

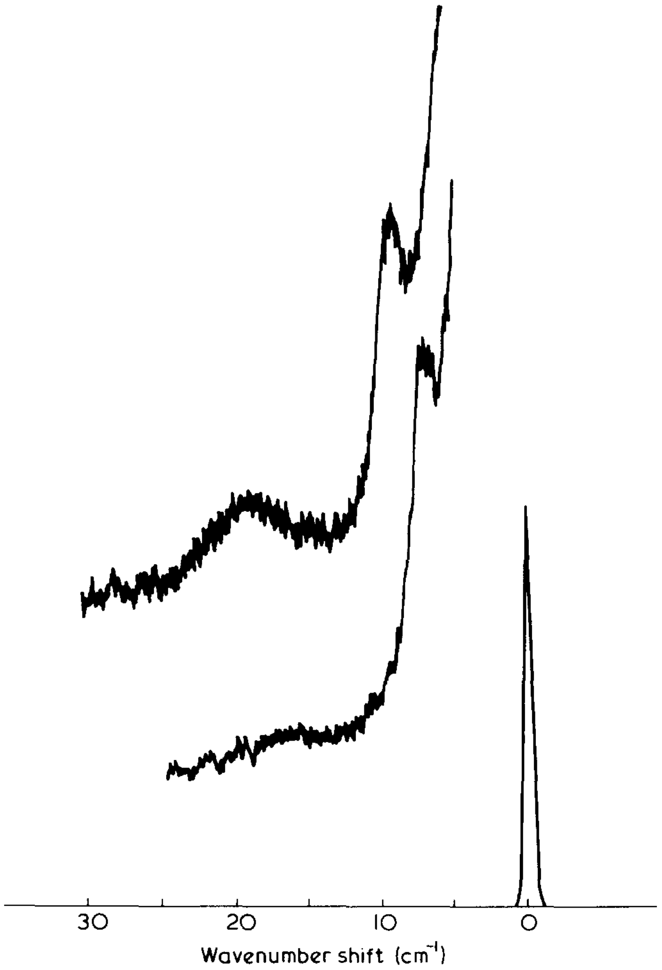

Figure 1 Low frequency Raman spectra for crystalline PEO M_n = 2000 mixed with 200 molecular weight oligomer. Both polymer and oligomer have hydroxy-end-groups. The upper curve was obtained from pure polymer sample and the lower curve from a sample containing a weight fraction 0.19 of oligomer. Shifts in the frequencies of the two observed bands are clearly visible. The Rayleigh peak was recorded at reduced gain

poly(ethylene oxide) fractions have been described earlier[1]. Two peaks can be distinguished at frequencies below 25 cm^{-1} corresponding to the fundamentals (*LAM*-1) and the overtones (*LAM*-3) of the longitudinal acoustic modes of the lamella crystals. Typical spectra are shown in *Figure 1*. The *LAM*-1 peaks of our samples had widths at half-height of about 2 cm^{-1} irrespective of the weight fraction of oligomer (W_{200}) and we were able to determine their frequencies to ±0.2 cm^{-1}. The *LAM*-3 peaks were broader (width at half-height $\simeq$5 cm^{-1} for 2000H) and became very broad as W_{200} was increased: their peak frequencies were determined to no better than ±1 cm^{-1}.

Small-angle X-ray scattering photographs were obtained at room temperature by use of a Rigaku–Denki camera as described elsewhere[8,9]. Two or more Bragg peaks were visible. The peaks were diffuse for mixtures with $W_{200} > 0.15$ (as noted earlier by Terrisse *et al.*[13]) and lamella spacings could be determined to ±0.1 nm ($W_{200} < 0.15$) or ±0.2 nm ($W_{200} > 0.15$).

Heats of fusion were determined from endotherm peak areas observed by differential scanning calorimetry (Perkin–Elmer DSC-2) in comparison with those observed for melting indium, Freshly crystallized samples gave single-peaked endotherms (heating rate = 2.5 K/min).

Melting points were measured by differential scanning calorimetry (2000H/200H, set A) or otherwise by hot-stage polarizing microscopy. Calibration was principally by the known melting point (54°C) of sample 2000H [8,9]. Temperatures quoted are those of the disappearance of the last trace of crystallinity.

RESULTS AND DISCUSSION

The experimental results are summarized in *Table 2*: these are the frequencies of the fundamentals (ν_1) and the overtones (ν_3) of the *LA* modes, the lamella spacing (l_x), the heat of fusion (Δh) and the melting point (T_m).

In *Figure 2a* we plot the increase in l_x due to swelling by oligomer (Δl_x) against the volume ratio (200/2000) for the system 2000H/200H*. This plot has been used by Terrisse *et al.*[13] and is a convenient way to compare the work: the agreement between the two laboratories is good. The line drawn on *Figure 2a* is that expected if all the oligomer enters the non-crystalline layers of the stack: the adherence of the initial results ($W_{200} < 0.15$) to this line is good evidence that the oligomer swells the non-crystalline layers and leaves the crystalline layers intact. The corresponding plot for the system 2000M/200M* is shown in *Figure 2b*, together with a few results obtained for the systems 2000H/200M and 2000M/200H in which swelling is slight. The maximum increase in l_x is about 4.3 nm for 2000H/200H and about 3.0 nm for 200M/200M. The similarity in behaviour of the two systems is of interest since the underlying molecular explanation of the swelling effect must be seen as a dilution (entropic) effect rather than an

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* Assuming the following specific volumes (cm^3/g, room temperature): 200H(liq.) = 0.89; 200M(liq.) = 1.00; 2000H(cryst.) = 0.83; 2000M(cryst.) = 0.84.

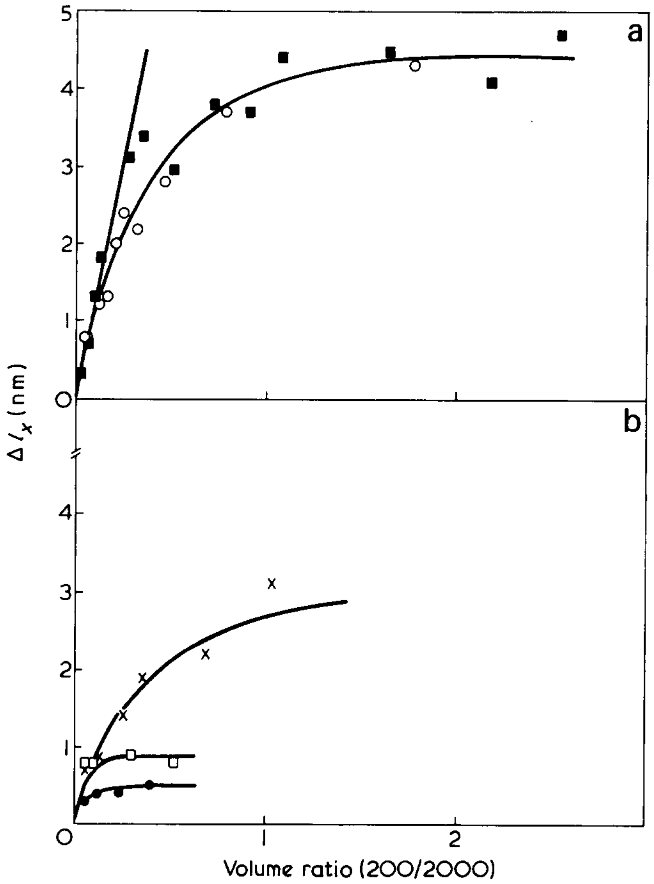

Figure 2 The measured increase in X-ray spacing l_x in PEO 2000/200 mixtures plotted as a function of sample composition (a) ○, 2000H/200H; ■, data of Terrisse *et al.* ref 13. (b) x, 2000M/200M; □, 2000M/200H; ●, 2000H/200M. The straight line on (a) represents the situation where all the oligomer enters the non-crystalline layer

adsorption effect at specific polar (hydrogen bonding) sites.

The calorimetric results (*Table 2*) can be used to calculate the heat of fusion per gram of crystallizable poly(ethylene oxide) by dividing the measured Δh by W_{2000} ($= 1 - W_{200}$), and these values can be adjusted to a standard temperature using $\Delta C_p \simeq 0.7$ J/K/g. This procedure leads to Δh (54°C) = 167 ± 6 J/(g of 2000): the values for the individual samples are given in parentheses in *Table 2*. The near constancy of these values is consistent with a constant extent of crystallinity of the 2000H in the mixtures with 200H.

The Raman frequencies ν_1 and ν_3 are much affected by swelling the non-crystalline layers of the poly(ethylene oxide) crystal (*Table 2*). The products $\nu_1 l_x$ and the quotients ν_3/ν_1 are plotted against l_x in *Figure 3*. The similarity of behaviour of the two systems, hydroxy- and methoxy-ended polymer, is apparent. The systematic variation of $\nu_1 l_x$ and ν_3/ν_1 with l_x is of considerable interest and forms the basis of our interpretation of the Raman results in terms of the composite rod model of Olf, Peterlin and Peticolas[2].

The composite rod has been used[2] to model a lamella crystal with non-crystalline surface layers and has been applied to Raman scattering from polyethylene. The rod has a crystalline core of length l_c, density ρ_c and elastic modulus E_c and has symmetrical non-crystalline ends of length $l_a/2$, density ρ_a and elastic modulus E_a. Coupling between adjacent rods (lamellae) is neglected and both core and ends are assumed to be perfectly elastic at the frequency of the vibration, i.e. 10^{11}–10^{12} Hz. With these assumptions the equation for determining the normal frequencies of the composite rod is[2]:

$$(\rho_c E_c)^{1/2} \cot\left(\frac{\pi \rho_c^{1/2} l_c \nu}{E_c^{1/2}}\right) = (\rho_a E_a)^{1/2} \tan\left(\frac{\pi \rho_a^{1/2} l_a \nu}{E_a^{1/2}}\right) \quad (1)$$

We set $\rho_c = 1.23$ g/cm^3 and $\rho_a = 1.12$ g/cm^3 [10] and so, given $l_x = l_c + l_a$, the equation contains three unknowns: l_c, E_c and E_a. The data summarized in *Figure 3* enable us to fix these unknowns within meaningful limits.

We have examined the possibility of fitting the results for the system 2000H/200H with l_c taken to be either 90, 80 or 70% of the lamella spacing of 2000H, i.e. either 11.3 nm, 10.1 nm, or 8.8 nm. The experimental values of $\nu_1 l_x$ lie between 117×10^{-9} ($l_x = 12.6$ nm) and 98×10^{-9} ($l_x = 16.3$ nm). We show in *Figure 4a* that a fairly wide choice of parameters E_c and E_a serve to approximate this behaviour when l_c is chosen to be 8.8 nm. The corresponding values of ν_3/ν_1 lie between 2.0 and 2.6. We show in *Figure 4b* that the need to fit both sets of data with the same values of l_c, E_c and E_a narrows the choice considerably. A comparison of the calculated curves for l_c = 8.8 nm, $E_c = 9 \times 10^{10}$ N/m^2 and $E_a = 1 \times 10^{10}$ N/m^2 with the experimental results for 2000H/200H is shown in *Figure 5* (solid lines). The uncertainty of the experimental data is such that values of E_c and E_a within ±25% of those above give equivalent results. A similar fitting of equation

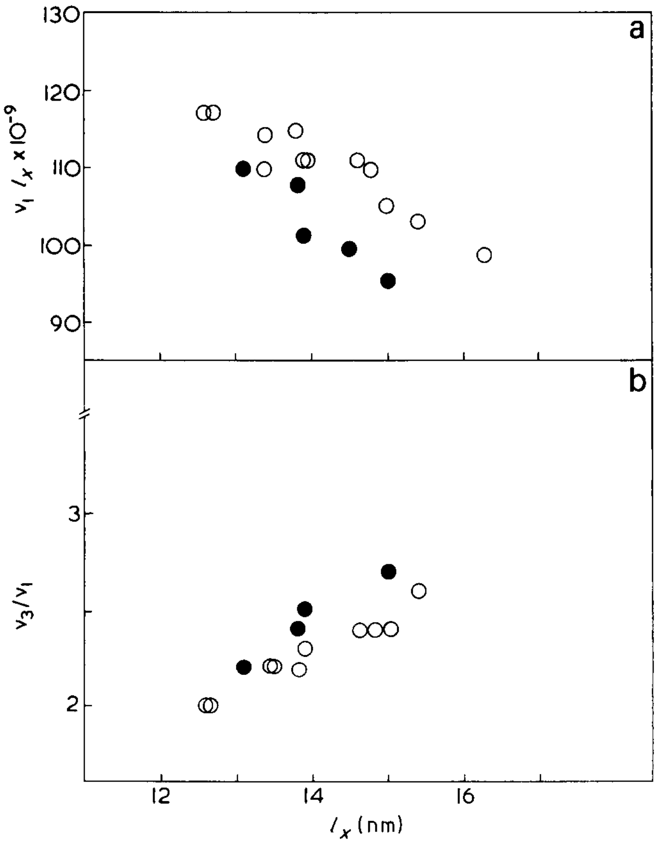

Figure 3 (a) The measured product of Raman *LAM* fundamental ν_1 cm^{-1} and X-ray spacing l_x m plotted *versus* l_x. (b) The ratio of third Raman overtone frequency ν_3 to the fundamental ν_1 plotted *versus* l_x. ○, 2000H/200H; ●, 2000M/200M

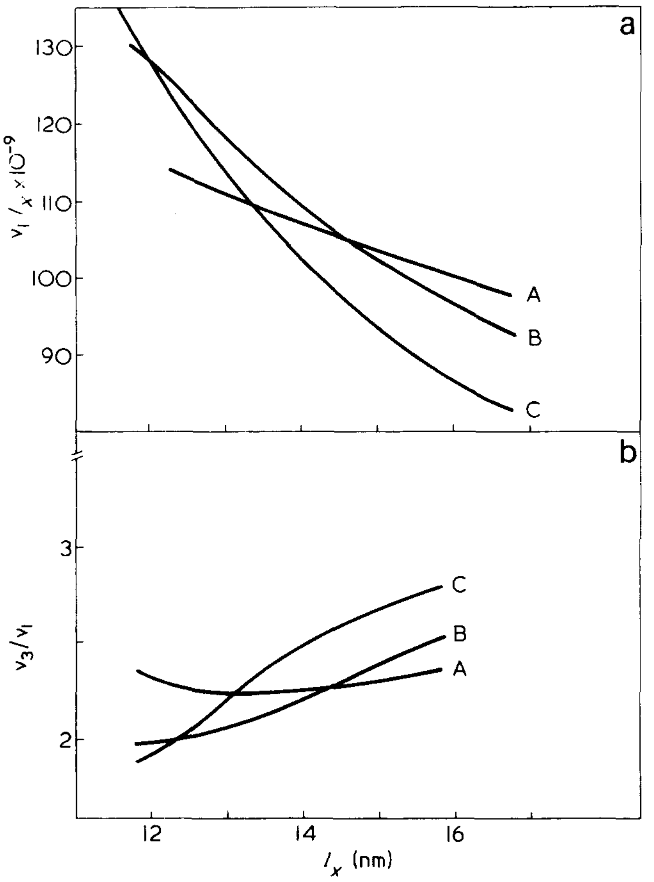

Figure 4 (a) Product of Raman *LAM* fundamental ν_1 cm^{-1} and X-ray spacing l_x m and (b) quotient of Raman third overtone ν_3 and ν_1 calculated as functions of l_x according to the composite rod model. The crystal length, l_c, in each case is 8.8 nm; the amorphous and crystalline moduli, E_a and E_c, have the following values: A, $E_c = 6.0 \times 10^{10}$ N/m^2; $E_a = 1.0 \times 10^{10}$ N/m^2; B, $E_c = 9.0 \times 10^{10}$ N/m^2, $E_a = 1.5 \times 10^{10}$ N/m^2; C, $E_c = 12 \times 10^{10}$ N/m^2, $E_a = 7.0 \times 10^9$ N/m^2

(1) to the experimental results with l_c fixed at 10.1 nm or 11.3 nm proves to be impossible. The situation for l_c = 11.3 nm is illustrated in *Figure 5* (broken lines). Any combination of values of E_c and E_a which fits the results for $\nu_1 l_x$ fails dramatically to fit the ν_3/ν_1 data, and *vice versa.*

In terms of this composite rod model our results are best approximated by $l_c \sim 9$ nm ($l_a \sim 4$ nm), $E_c \sim 9 \times 10^{10}$ N/m^2 and $E_a \sim 10^{10}$ N/m^2. These values are best for both hydroxy- and methoxy-ended PEO 2000. Several authors have reported data consistent with a substantial non-crystalline component in solid low molecular weight fractions[9,10,15], though the heats of fusion are inconsistent with our result if the heat of fusion of perfectly crystalline PEO is substantially less than 230 J/g at 54°C. The ratio $E_a/E_c \sim 0.1$ is similar to that used by Olf *et al.*[2] to explain the Raman spectra of polyethylene using the composite rod model. Sakurada *et al.*[16] have used lattice extension measurements to obtain a value of 10^{10} N/m^2 for the static elastic modulus of crystalline PEO in the chain direction, which is much smaller than the value we obtain from Raman data. Similar discrepancies have been found in other helical materials. In the case of polyoxymethylene (POM) values of 1.89×10^{11} N/m^2 and 0.54×10^{11} N/m^2 were deduced by Raman[4] and X-ray[17] methods, respectively and neutron scattering data[18] give a value of 1.5×10^{11} N/m^2. Theoretical estimates are also in broad agreement with Raman, falling in the range 0.95–2.2 × 10^{11} N/m^2 [19–21]. In the case of melt crystallized isotactic polypropylene (IPP) there is also a discrepancy between the modulus measured by X-ray techniques[17] (0.42×10^{11} N/m^2) and by Raman[4] (0.88×10^{11} N/m^2) although extruded IPP gives a value[3] of 0.37×10^{11} N/m^2 from Raman data. A useful tabulation of other experimental and theoretical results can be found in the review by Holliday and White[22]. Differences between static and high frequency measurements of modulus are not unexpected in complicated chain structures because of the possibility of relaxations at intermediate frequencies. However, the agreement between experimental values in POM and theoretical estimates based on static parameters casts doubt on the assumptions inherent in the static determination in this case. Relaxation measurements would clearly be of help in understanding these differences for each polymer system.

There are two major assumptions in our interpretation. The first is that E_a is a constant, independent of the amount of oligomer present. This is a first approximation and amounts to the supposition that liquid PEO 2000 and 200 have identical elastic properties in the frequency range 10^{11}–10^{12} Hz, though this begs the question of the orientation of chains within the amorphous layer. The second assumption is that the coupling between adjacent lamellae can be neglected so that each rod can be treated as an isolated unit. This leads to great simplification in the calculations and has been adopted in most work to date. Recent theoretical work[23] has examined the effect on the fundamental frequency of perturbing forces at the chain ends; these forces are taken to represent coupling either between chains

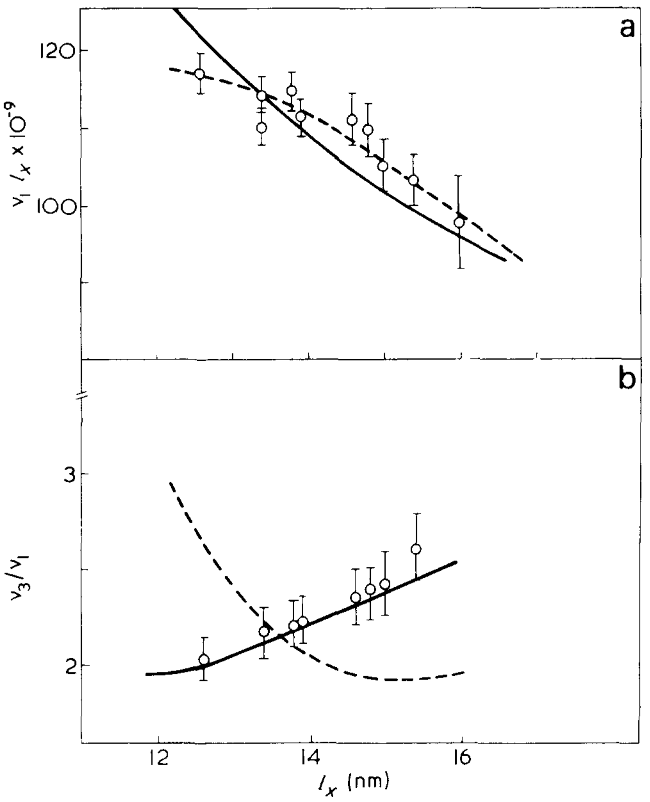

Figure 5 Comparison of measured data of *Figure 3* (2000H/200H only) with calculations based on the composite rod model. ——, correspond to values of l_c = 8.8 nm, $E_c = 9.0 \times 10^{10}$ N/m^2 and $E_a = 1.0 \times 10^{10}$ N/m^2 and represent the best fit to both sets of data. — — —, represent the closest fit possible with l_c = 11.3 nm. The errors in the experimental data along the ordinate are indicated; the error in l_x is approximately ±0.11 nm

in the same crystal or between adjacent lamellae. Calculations as a function of E_a/E_c show a weak dependence of ν_1 on the perturbing force for $E_a/E_c \lesssim 1$, but large effects are possible for $E_a/E_c > 1$ which depend also on the degree of crystallinity. Estimates of the magnitude of the force, which have been made for IPP[23], depend on accurate knowledge of the parameters E_c, l_x, l_a. A further effect of coupling should be to cause observable broadening of the fundamental Raman band. There is also the possibility of longer wavelength excitations incorporating several lamellae which will appear at lower frequencies. These will be outside the range of Raman techniques but could be studied by Fabry–Perot spectroscopy[24]. Refinements to the model to take account of the effect of crystalline defects have also been considered[25,26]. In the case of polyethylene the inclusion of a *gauche* isomer in an all *trans* chain is shown to decrease the intensity of the *LAM*[25]. The more complicated case of a helical system has not yet been treated.

CONCLUSIONS

The *LAM* fundamental and third harmonic vibrations in PEO 2000 with both hydroxy- and methoxy-end-groups have been observed as a function of 200 PEO oligomer content. Interpretation based on a composite rod model leads to the conclusion that the length of crystalline chain l_c must be about 9 nm, the modulus along the chain axis $E_c \sim 9 \times 10^{10}$ N/m^2 and the amorphous modulus $E_a \sim 1 \times 10^{10}$ N/m^2. The value of l_c implies a crystalline content of 70%; the value of E_c is an order of magnitude larger than static determinations, and similar discrepancies in other materials have been discussed. The assumption that the liquids of both molecular weight 2000 and 200 have the same elastic properties appears reasonable and experiments are underway to test this by swelling with oligomers of molecular weight >200. The assumption that each rod is isolated is valid in this case because $E_a/E_c < 1$.

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