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The effect of swelling on the longitudinal acoustic mode in crystalline α,ω-methoxy-poly(ethylene oxide)

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Low molecular weight poly(ethylene oxide) crystallizes into well defined layer structures. Raman scattering from the longitudinal acoustic mode (*LAM*) of vibration of the lamellae is readily detected[1–3]. The experimental evidence[1–6] favours a structure in which crystalline and non-crystalline layers alternate. It is possible to swell the non-crystalline layers with low molecular weight liquids, and oligomers of ethylene oxide have been used for this purpose[2,3,7]. For α,ω-hydroxy-poly(ethylene oxide) of molecular weight 2000 g mol^{-1} swollen with α,ω-hydroxy-oligomers of various molecular weights less than $\bar{M}_n$ = 600 g mol^{-1}, it is found[2,3] that the *LAM* frequencies vary systematically with the lamella spacing (l_x = thickness of crystalline plus non-crystalline layer) determined by small-angle X-ray scattering (SAXS). These results are given in *Figures 1(a)* and *2(a)*, where the hydroxy ended samples are denoted by molecular weight and suffix H. We plot $\nu_1 l_x$ and ν_3/ν_1 against l_x (ν_1 is the frequency of the *LAM* fundamental and ν_3 that of the third overtone). For the ideal case of crystalline lamellae vibrating independently of the non-crystalline layer, $\nu_1 l_x$ would increase with l_x and ν_3/ν_1 would be constant and equal to 3. Our results show a considerable effect of the non-crystalline layer on the *LAM*.

For the α,ω-hydroxy systems the effect of swelling is independent of the molecular weights of the oligomers studied (M = 106 to $\bar{M}_n$ = 600: see *Figures 1* and *2*). However the liquid properties of α,ω-hydroxy-poly(ethylene oxide) may be insensitive to molecular weight. For example[8,9] the liquid density of α,ω-hydroxy-oligomers of ethylene oxide is constant at 1.12 g cm^{-3} (20°C). This is in contrast to the liquid densities of α,ω-methoxy-oligomers which increase from 0.94 g cm^{-3} (M = 134 g mol^{-1}) to 1.08 g cm^{-3} ($\bar{M}_n$ = 600 g mol^{-1}) and to 1.12 g cm^{-3} only in the high molecular weight limit of extrapolation. Hydrogen bonding, principally of hydroxy to ether oxygen, provides a rationalization of this effect. Consideration of this point prompted us to reinvestigate the effect of molecular weight of the swelling agent on the *LAM* under conditions where hydrogen bonding is absent.

Samples of α,ω-hydroxy-poly(ethylene oxide) of molecular weights $\bar{M}_n$ = 2000, 600 and 200 g mol^{-1}, obtained from various commercial sources, were methoxylated by the procedure described elsewhere[9]. Methoxylated samples are denoted by the original molecular weight with suffix *M*. Conversion of hydroxy to methoxy was better than 98%. Molecular weight distributions were checked by gel permeation chromatography and were essentially unchanged by the methoxylation process. The crystallizable α,ω-methoxy-poly(ethylene oxide) 2000M had a narrow molecular weight distribution, $\bar{M}_w/\bar{M}_n$ = 1.03. Dimethyldigol (M = 134 g mol^{-1}) was SynchemicA grade (Hopkins and Williams) used without further purification. Mixtures were prepared by melting at 70°C and shaking several times over a period of 30 min. Crystallization was at 25°C. *LAM* frequencies and lamella spacings were determined by laser Raman spec-

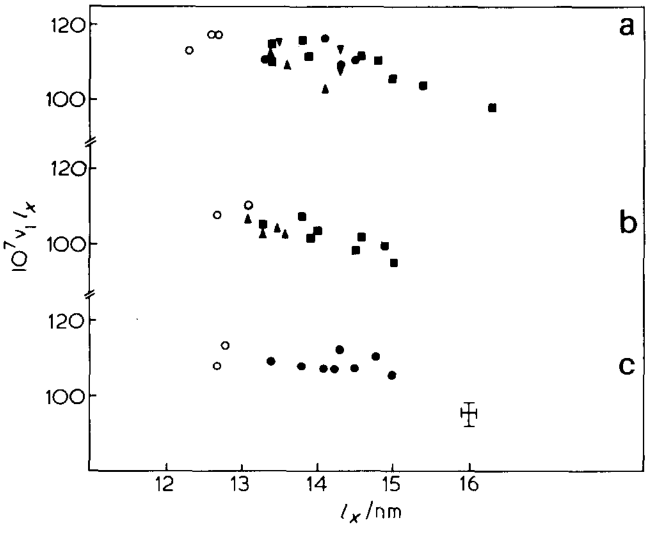

Figure 1 The variation of $\nu_1 l_x$ with l_x for mixtures of: (a) 2000H (○) with 106H (●), 200H (■), 400H (▼) and 600H (▲); (b) 2000M (○) with 200M (■) and 600M (▲); (c) 2000M (○) with 134M (●). The experimental error is indicated

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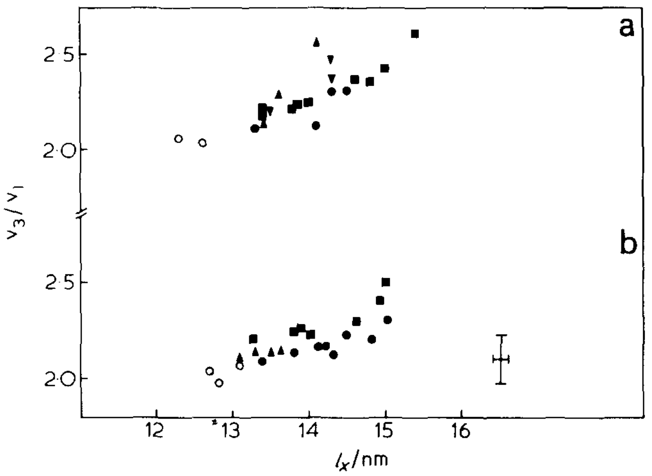

Figure 2 The variation of ν_3/ν_1 with l_x for mixtures of: (a) 2000H (○) with 106H (●), 200H (■), 400H (▼) and 600H (▲); (b) 2000M (○) with 134M (●), 200M (■) and 600M (▲). The experimental error is indicated

Table 1 Lamella spacing (l_x) and LAM fundamental ($\bar{\nu}_1$) and third overtone ($\bar{\nu}_3$) for poly(ethylene oxide) 2000

	α,ω-hydroxy			α,ω-methoxy		
Sample	l_x/nm	$\bar{\nu}_1$/cm^{-1}	$\bar{\nu}_3$/cm^{-1}	l_x/nm	$\bar{\nu}_1$/cm^{-1}	$\bar{\nu}_3$/cm^{-1}
1	12.6	9.3	19.0	13.1	8.4	19.0
2	12.3	9.2	19.0	12.8	8.8	19.0
3	12.3	9.2	19.0	12.7	8.5	19.0

troscopy and small-angle X-ray scattering as described earlier[1,2].

The experimental results are given in *Tables 1* and *2*. The estimated experimental errors are ±0.2 nm (l_x), ± 0.2 cm^{-1} ($\bar{\nu}_1$) and ± 1 cm^{-1} ($\bar{\nu}_3$). We have investigated 3 different samples of 2000M: one set of results for 2000M (1)/200M has been published earlier[2]. Methoxylation has the effect of increasing l_x by about 0.5 nm and decreasing $\bar{\nu}_1$ by about 0.6 cm^{-1} in comparison with the α,ω-hydroxy precursor (see *Table 1*). In *Figures 1 (b,c)* and *2(b)* the product $\nu_1 l_x$ and the quotient ν_3/ν_1 are plotted against l_x. The results for 2000M/200M and 2000M/600M are indistinguishable and are comparable in most respects with those found for the α,ω-hydroxy systems. The variation of $\nu_1 l_x$ with l_x (but not ν_3/ν_1 with l_x) is less marked for 2000M/134M than for the other systems. We infer that swelling with oligomers of molecular weight 200 g mol^{-1} or more suffices, in this experiment, to model the limit of high polymer in the non-crystalline layer.

We have used[2,3] the composite rod model with free ends[10] to rationalize our results for α,ω-hydroxy-poly (ethylene oxide). Clearly the same model can be used for α,ω-methoxy-poly(ethylene oxide). The fit to the data[2] requires a degree of crystallinity of the crystallizable poly(ethylene oxide) 2000 of 70% and an elastic modulus ratio (E_a/E_c) near 0.1. However the crystalline elastic modulus needed for the fit is $E_c \simeq 9 \times 10^{10}$ N ½m^{-2} which is much larger than the value of 10^{10} N ½m^{-2} found by lattice extension measurements[11]. Recent theoretical work of Hsu *et al.*[12] permits prediction of the LAM frequencies of composite rods with perturbing forces at the ends. A uniform rod of elastic modulus 1.0 × 10^{10} N ½m^{-2} with fixed ends (very large forces) would have $\nu_1 l_x = 96 \times 10^{-7}$ ($\rho = 1.21 \times 10^3$ kg m^{-3}) compared to an experimental value of about 110 × 10^{-7}. It is not obvious why a rod with fixed ends should model the behaviour of our polymers. It may be that adjacent lamellae in low molecular weight poly(ethylene oxide) are coupled[12], though this is not found for other systems[13]. The possibility of a detailed theoretical[12] fit of our results, incorporating an acceptable value of E_c, is under consideration.

Table 2 Lamella spacing (l_x) and LAM fundamental ($\bar{\nu}_1$) and third overtone (ν_3) for α,ω-methoxy-poly(ethylene oxide) 2000 swollen by different weight fractions of low molecular weight oligomers

Weight fraction	l_x/nm	$\bar{\nu}_1$/cm^{-1}	$\bar{\nu}_3$/cm^{-1}
2000M(2)/134M			
0.08	14.3	7.8	18.0
0.14	14.5	7.4	18.0
0.18	14.8	7.4	17.8
0.20	15.0	7.0	17.5
2000M(3)/134M			
0.07	13.4	8.1	18.5
0.12	13.8	7.8	18.2
0.16	14.1	7.6	18.0
0.19	14.2	7.5	17.8
2000M(3)/200M			
0.04	13.3	7.9	19.0
0.09	14.0	7.4	18.0
0.15	14.6	7.0	17.5
0.20	14.9	6.7	17.5
2000M(3)/600M			
0.06	13.1	8.2	18.4
0.12	13.3	7.9	18.4
0.18	13.5	7.7	18.0
0.22	13.6	7.6	17.8

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