# Poly(oxyethylene) Chains and Rings Studied by Raman Spectroscopy and Differential Scanning Calorimetry

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ABSTRACT: Crystalline poly(ethylene glycol)s (PEG) of number-average molar mass 1000, 1500, 2000, and 3000 g mol$^{-1}$ and the cyclic analogues were studied by low-frequency laser-Raman spectroscopy and differential scanning calorimetry. The frequencies of the single-node longitudinal acoustic modes (LAM-1) of the rings were higher than those of the corresponding unfolded methoxy-ended chains by a factor of *ca.* 1.8. Melting points and enthalpies of fusion of the rings were lower than those of unfolded-chain crystals. The structural implications of the results are discussed.

## Introduction

Comparative studies of the solid-phase properties of crystallizable rings and chains have been reported previously: e.g., a lengthy listing, which includes melting points, is available[1] for uniform oligomers (i.e., samples with chains or rings all exactly the same size). However, structural studies of crystalline cyclic oligomers, whether by X-ray diffraction or by Raman spectroscopy, are uncommon. In those studies reported, specific effects of composition often affect the crystallinity, e.g., odd−even effects in cyclic oligoacetals,[2,3] packing restrictions caused by hydrogen bonding in oligourethanes,[4] etc. Studies by Wegner and co-workers[5,6] of the solid-state properties of lengthy linear and cyclic alkanes are particularly interesting, since they relate to the packing of uncomplicated methylene chains and rings.

Studies of the properties of oligo(oxyethylene) rings and chains should be equally interesting, particularly since an oxyethylene chain crystallizes in a helical conformation rather than in the trans-planar conformation characteristic of a methylene chain. Surprisingly, the solid-state properties of large cyclic oligo(oxyethylen)s (large crown ethers) have received little attention. Crown ethers comprising as many as 20 oxyethylene units have been prepared and purified, and melting points have been reported,[7,8] but structural studies have not been carried out. Similarly, there are no reports of the solid-state properties of nonuniform, cyclic poly(oxyethylene)s. This is despite much interest in the crystallization of nonuniform, linear poly(oxyethylene)s, stimulated by the studies of the Strasbourg School in the late 1960s[9,10] and continued there[11,12] and elsewhere,[13−16] including our own laboratories.[17−21]

LAM-1 and LAM-3 bands were first observed[19] in the low-frequency Raman spectra of low-molar-mass poly-(oxyethylene) chains in Manchester in 1976. Since that time, low-frequency Raman spectra of poly(oxyethylene) glycols with $M_n \leq 2000$ g mol$^{-1}$ have been published on

several occasions.[18,20,21] Most recently, Song and Krimm[15,16] have reported refined normal-mode calculations for poly(oxyethylene) chains and, from a detailed reexamination of the low-frequency spectra of poly-(oxyethylene) glycols 1000−5000, have assigned LAM-1 and LAM-3 for both unfolded and folded chains. Particularly important for the present work was the assignment[16] of the band at 5.5 cm$^{-1}$ in the spectrum of PEG3000 to LAM-1 of unfolded chains, as this very-low-frequency band was not detected previously.[19]

Recently, we have reported[22] the preparation of cyclic polymers starting from poly(ethylene glycol) precursors with number-average molar masses in the range 1000−3000 g mol$^{-1}$. A Williamson reaction of a PEG with dichloromethane under alkaline conditions in very dilute solution was used to form an oxymethylene-linked cyclic polymer $\overline{\text{OCH}_2(\text{OCH}_2\text{CH}_2)_m}$, where $m$ has a number-average value in the range 23−68. This paper describes a comparative study of the solid-state properties of the rings and their linear precursor chains. From previous work (e.g., refs 11, 14, 16, and 17) it was known that either chain folding or fractionation (or both) could be important during crystallization at normal temperatures. The results reported below were obtained with these complications in mind.

## Experimental Section

**Materials.** The preparation of cyclic poly(oxyethylene)s starting from poly(ethylene glycol)s PEG1000, -1500, -2000, and -3000 (Fluka AG) has been described previously.[22] Williamson reaction of PEGs with dichloromethane under alkaline conditions in very dilute solution resulted in formation of oxymethylene-linked cyclic polymers in excellent yield. Under the conditions of preparations and purification used, little or no unreacted PEG impurity was present in the product and any high-molar-mass linked polymer was readily separated from the rings by fractional precipitation.

The four linear and four cyclic polymers used in the present study were identical with those described previously.[22] For the chains, $^{13}$C NMR gave ratios of intensities of resonances assigned to oxyethylene chain units and end units which were consistent with the manufacturer's specification of $M_n$, while a similar comparison of oxyethylene chain units to linking

units showed that no detectable fractionation occurred during preparation of the rings. Both the rings and their chain precursors had narrow chain length distributions: $M_w/M_n \leq$ 1.1, as checked by GPC.[22] In what follows the chains and rings are denoted by their number-average molar masses, with the rings distinguished from the chains by an appropriate suffix: i.e., 2000C, 2000R, etc.

**Differential Scanning Calorimetry (DSC).** A Perkin-Elmer DSC-4 was used. Known weights (<10 mg) of the samples, which had been crystallized and stored at room temperature (*ca.* 20 °C), were sealed into aluminum pans and heated at 1 K min$^{-1}$ to 70–80 °C. Samples with low melting points were quenched (−320 K min$^{-1}$) in the calorimeter to 0 °C before heating. The sample was then quenched to a temperature *ca.* 30 K below the melting point and reheated, this cooling–heating cycle being repeated several times, possibly including faster heating rates. Certain samples were annealed in the calorimeter at a temperature 2 K or so below the measured melting point, quenched, and reheated: details are given below.

The DSC curves were analyzed using the data station of the DSC-4. Approximate values of the enthalpy of fusion were obtained from peak areas, and melting temperatures from the temperature at the peak, both with reference to the enthalpy of fusion and melting temperature of pure indium at the same heating rate. The power and temperature scales of the calorimeter were checked against the melting temperatures and enthalpies of fusion of PEG2000 (2000C, 52.7–53.8 °C and 168–175 J g$^{-1}$, respectively), both of which have been reported many times.[9,11,16–18] Corrections were made to the melting temperature to account for thermal lag.

**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 with a third (1442U) monochromator 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 500 mW. Typical operating conditions for the low-frequency range under investigation were as follows: bandwidth 1.0 cm$^{-1}$, scanning increment 0.05 cm$^{-1}$, integration time 4 s. The low-frequency scale was calibrated to ±0.1 cm$^{-1}$ reference to the 9.6 and 14.9 cm$^{-1}$ bands in the spectrum of L-cystine. High-frequency spectra were also recorded for each sample.

Samples 1000, 1500, and 2000 (C and R) were enclosed in capillary tubes, in which they were melted and cooled rapidly to room temperature to crystallize. Spectra were recorded with the samples at a constant temperature of 15 ± 1 °C, achieved by means of a Harney–Miller cell (Spex Industries Inc). The intensity of a Raman band was observed over a period of time to ensure equilibration of the sample at a given temperature. Samples 3000C and 3000R were melted in the hollowed end of a stainless-steel rod and crystallized by cooling to room temperature (*ca.* 20 °C). Spectra were recorded with these two samples at room temperature. Temperature corrections between 15 and 20 °C were not required, as the temperature derivative of frequency is known[21] to be small for the LAM bands of poly(oxyethylene).

## Results and Discussion

**Thermal Analysis.** The DSC curves of samples of 1500C and 2000C crystallized at room temperature contained single narrow melting peaks. The curves of quenched samples were essentially the same. Sample 1000C was not investigated by DSC, as it was too hygroscopic to be used in this technique without rigorous drying.

DSC curves of sample 3000C (quenched or crystallized at room temperature) obtained at high heating rates showed two peaks, while corresponding curves obtained at 1 K min$^{-1}$ showed a narrow peak with a low-$T$ shoulder: see Figure 1. Melting points of the two species, from DSC curves obtained at high heating rates
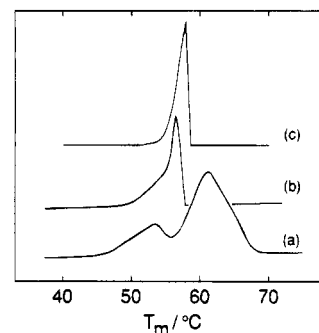


**Figure 1.** DSC curves for sample 3000C: (a) crystallized at 20 °C, quenched to 0 °C, and heated at 20 K min$^{-1}$; (b) crystallized at 20 °C, quenched to 0 °C, and heated at 1 K min$^{-1}$; (c) crystallized at 20 °C, annealed at *ca.* 56 °C for 2 h, quenched to 0 °C, and heated at 1 K min$^{-1}$.
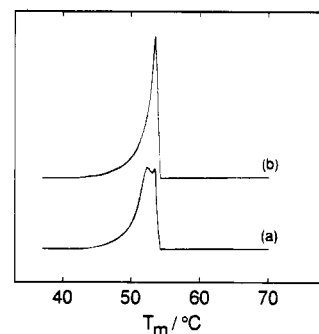


**Figure 2.** DSC curves for sample 3000R: (a) melted at 70 °C, quenched to 0 °C, and heated at 1 K min$^{-1}$; (b) crystallized at 20 °C, stored at room temperature, quenched to 0 °C, and heated at 1 K min$^{-1}$;

corrected for thermal lag, were *ca.* 51 and 59 °C. Following previous work,[12,16] and low-$T$ peak was assigned to once-folded-chain crystals, and the high-$T$ peak to unfolded-chain crystals. The shoulder seen on the low-$T$ side of the melting peak in the DSC curve obtained at 1 K min$^{-1}$ (see Figure 1, curve b) was similar to that reported by Song and Krimm[16] and assigned by them to once-folded chains in bilayers. Annealing a sample at *ca.* 56 °C for 2 h served to eliminate the shoulder (see Figure 1, curve c), yielding a crystalline sample with no folded chains, as discussed further below.

The DSC curves (heating rate 1 K min$^{-1}$) of the samples 1500R, 2000R, and 3000R which had been crystallized and stored at *ca.* 20 °C contained signle narrow melting peaks. Corresponding DSC curves of quenched samples showed splitting of the melting peak by *ca.* 1 K. Examples are given in Figure 2. A quenched sample of 3000R heated at 10 K min$^{-1}$ gave a DSC curve (not illustrated) with only one peak with a maximum, corrected for thermal lag, at the lower melting temperature observed when heating at 1 K min$^{-1}$. These observations indicate that quenching led to formation of metastable crystals and that these annealed to a more stable form on storage at room temperature. It is known from studies of copolymers that a co-unit can enter a lattice as a metastable defect,[23] and we speculate that the oxymethylene units, which close the rings, were randomly incorporated into the lattice on rapid crystallization but rejected on annealing.

The DSC curves of sample 1000R (not illustrated), whether quenched from 60 °C or from room temperature, had two peaks as a result of premelting in the range 15–20 °C and recrystallization in the range 20–25 °C. This complication was not investigated further.
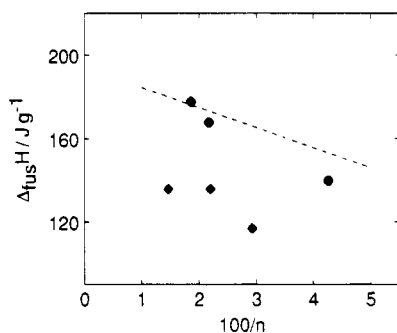
**Table 1. Poly(oxyethylene) Chains and Rings: Melting Points, Enthalpies of Fusion, and Entropies of Fusion by DSC (Heating Rate 1 K min⁻¹)**

| sample | $T_m$/°C ($T_m \approx 20$ °C) | $T_m$/°C (quenched) | $T_m$/°C (annealed) | $\Delta_{fus}H$/ (J g⁻¹) | $X$ | $\Delta_{fus}S$/ (J K⁻¹ g⁻¹) |
|---|---|---|---|---|---|---|
| 1000C | | | | | | |
| 1500C | 49.5 | 48.3 | | 155 | 0.77 | 0.480 |
| 2000C | 53.3 | | | 172 | 0.85 | 0.527 |
| 3000C | 58.6 | 50.8,ᵃ 58.5 | 58.8 | 176 | 0.86 | 0.530 |
| | | | | | | |
| 1000R | 34 | 34 | | | | |
| 1500R | 42.8 | 42.2, 42.7 | | 117 | 0.59 | 0.370 |
| 2000R | 50.5 | 49.2, 49.9 | | 136 | 0.68 | 0.420 |
| 3000R | 55.9 | 54.7, 55.4 | | 136 | 0.67 | 0.413 |

ᵃ Shoulder on low-$T$ side of melting peak: see Figure 1.
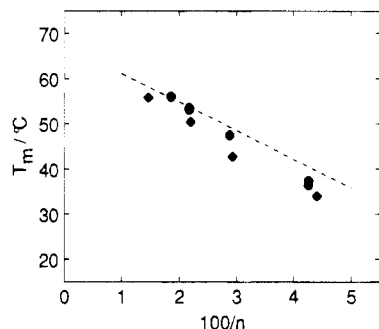


**Figure 3.** Melting temperatures versus $100/n$, where $n$ = average number of oxyethylene units in the molecules, for crystals of (●) unfolded methyl-ended poly(oxyethylene) chains and (◆) poly(oxyethylene) rings. The dashed line is a least-squares fit to results for unfolded hydroxy-ended chains. Results are taken from refs 11, 16–18, 24, and 25 and from the present work.



**Figure 4.** Enthalpies of fusion versus $100/n$, where $n$ = average number of oxyethylene units in the molecules, for crystals of (●) unfolded methyl-ended poly(oxyethylene) chains and (◆) poly(oxyethylene) rings. The dashed line is a least-squares fit to results for unfolded hydroxy-ended chains. Results are taken from refs 11, 17, 18, and 25 and from the present work.

However, because of this behavior samples were crystallized and held at 15 °C before and during the recording of Raman spectra.

Melting points (to ±1 °C) are listed in Table 1. These varied with crystallization conditions, as indicated. Enthalpies of fusion (±5 J g⁻¹), also listed in Table 1, were not greatly affected by crystallization conditions, and the values obtained for samples crystallized at room temperature are listed. Comparisons with published[11,16–18,24,25] melting points and enthalpies of fusion of poly(ethylene glycol)s are made in Figures 3 and 4. The dashed lines represent published data for hydroxy-ended poly(oxyethylene)s and illustrate the effect of hydrogen bonding of hydroxy end groups in elevating melting temperatures and enthalpies of fusion of short chains, an effect which has been explored previously.[26]

Compared with methyl-ended chains, the values of $T_m$ and $\Delta_{fus}H$ obtained for rings were lower than those obtained for methyl-ended chains: $T_m$ by *ca.* 3 K and $\Delta_{fus}H$ by *ca.* 30 J g⁻¹. Calculation of the entropy of fusion from

$$\Delta_{fus}S = \Delta_{fus}H/T_m$$

yielded values some 0.11 J K⁻¹ g⁻¹ lower for the rings than for the chains (see Table 1), as might be anticipated considering the greater conformational restriction of the rings in their melt state.

Also listed in Table 1 are apparent fractional crystallinities, calculated as $X = \Delta_{fus}H/\Delta_{fus}H°$, where $\Delta_{fus}H°$ is the thermodynamic enthalpy of fusion of poly(oxyethylene), which was calculated from[27]

$$\Delta_{fus}H° = 175 + 0.650T - 2.53 \times 10^{-3}T^2$$

with $T$ put equal to the measured melting temperature of the sample. As can be seen, the apparent crystallinities of the rings calculated in this way are significantly lower than those of chains of comparable length. This may arise in several ways: (i) a significant difference in chain packing in the crystalline rings compared to the chains; (ii) an increased positive contribution to the enthalpy of formation of the lamellar surface layers of the rings; (iii) a decreased fraction of each chain incorporated into the crystalline layers of the rings; (iv) rejection of a greater fraction of small molecules from the crystalline lamellae of the rings. The evidence from high-frequency Raman spectroscopy and wide-angle X-ray scattering (referred to below) suggests that (i) is not an important factor, while that from low-frequency Raman spectroscopy (see below) favors a significant contribution from (iii) and (iv).

Melting temperatures published[5] for uniform alkane chains and rings show almost identical values for the two systems at corresponding chain lengths. Values of $\Delta_{fus}H$ have not been published, making it difficult to comment on this identity. By analogy with the present system, we would speculate that it involves compensating reductions in both $\Delta_{fus}H$ and $\Delta_{fus}S$.

**Raman Spectroscopy.** The high-frequency Raman spectra recorded were all similar, one to another and to published spectra.[28] The indicators used (bands at 291, 936, and 1231 cm⁻¹) confirmed the crystal structure as one of poly(oxyethylene) helices, packed in the expected way,[29] across the range of samples studied. These spectra, taken before and after recording the low-frequency spectra, also confirmed the stability of the samples under the conditions of the experiments. They are not discussed further below.

Examples of low-frequency Raman spectra of the chains are shown in Figure 5 and 6. They are essentially identical with spectra described previously by ourselves[18–21] or by Song and Krimm.[16] Our assignments to LAM-1 and LAM-3 are made in Table 2, where the frequencies of other bands are noted: all frequencies reported are the averages of the Raman shifts taken from a number of spectra. The band at 9 cm⁻¹ in the spectrum of sample 1000C is probably related to that observed by Song and Krimm at 8.1 cm⁻¹ in the spectrum of their sample and assigned to a "LAM-like" mode.[16] Bands in the low-frequency region have been recognized previously in the spectra of uniform pentadeca(oxyethylene) dialkyl ethers,[30] e.g., *ca.* 15 cm⁻¹ for the dimethyl ether, and provisionally assigned to torsional modes. The band at 10.8 cm⁻¹ in the spectrum
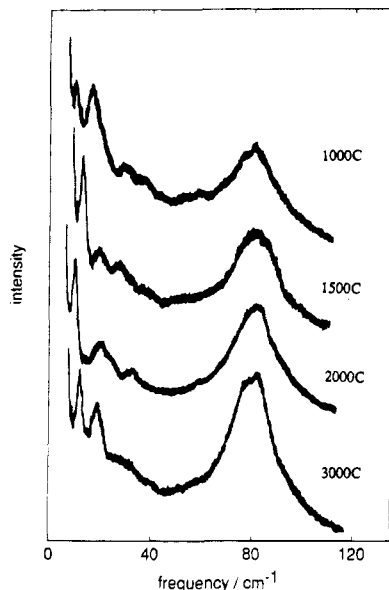
**Figure 5.** Low-frequency Raman spectra of poly(oxyethylene) chains: samples 1000C to 3000C, as indicated. Samples 1000C, 1500C, and 2000C were crystallized and examined at 15 °C; sample 3000C was crystallized at 20 °C, annealed at 56 °C, and examined at 20 °C. Intensity scales and zeros are arbitrary.
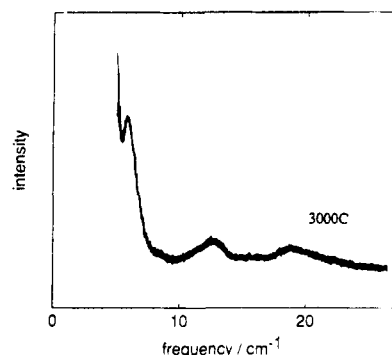


**Figure 6.** Very-low-frequency Raman spectra of sample 3000C, crystallized at room temperature, annealed at 56 °C, and examined at 20 °C. The intensity scale and zero are arbitrary.

**Table 2. Poly(oxyethylene) Chains and Rings: Low-Frequency Raman Frequencies (cm⁻¹) of Samples Crystallized at 15–20 °C (LAM-1 and LAM-3 Frequencies Denoted $\nu_1$ and $\nu_3$, Respectively)**

| sample | $\nu_1$/cm⁻¹ | $\nu_3$/cm⁻¹ | $\nu_3/\nu_1$ | $\nu_{1R}/\nu_{1C}$ | other bands/cm⁻¹ |
|---|---|---|---|---|---|
| 1000C | 16.5 | 38.0 | 2.30 | | 9.0, 31, 78, 81 |
| 1500C | 12.4 | 27.9 | 2.25 | | 19.0, 78, 81 |
| 2000C | 9.3 | 21.5 | 2.31 | | 19.5, 31, 78, 81 |
| 3000C[a] | 5.7 | 12.7 | 2.23 | | 19.0, 33, 78, 81 |
| 1000R | 27.7 | | | 1.68 | 10.8, 78, 81 |
| 1500R | 20.6 | 46.6 | 2.26 | 1.66 | 81 |
| 2000R | 16.1 | 39.4 | 2.36 | 1.73 | 81 |
| 3000R | 9.5 | 23.0 | 2.42 | 1.67 | 48, 78, 81 |

[a] Crystallized at 20 °C and annealed at 56 °C.

of sample 1000R may well be related, though its stem-length dependence is not obvious. The bands at 19.0–19.5, 31–33, 78, and 81 cm⁻¹ are characteristic of crystalline poly(oxyethylene). That at 78 cm⁻¹ is assigned[31] to a CO torsional mode of the helical chain, while the others are assigned to lattice modes.[16,21]

Sample 3000C crystallized either at room temperature or at 35 °C gave spectra which were similar, though not identical, to those reported by Song and Krimm.[16]

**Table 3. Poly(oxyethylene) 3000C: Effect of Crystallization Conditions on Raman Frequencies**

| crystallization conditions[a] | $\nu_1$/cm⁻¹ | other modes/cm⁻¹ |
|---|---|---|
| $T_c$ = 20 °C | 10.1 (folded) | 19.8, 33, 54, 78, 81 |
| $T_c$ = 35 °C | 11.1 (folded) | 20.0, 33, 54, 78, 81 |
| $T_c$ = 20 °C, $T_a$ = 56 °C | 5.7 (unfolded) | 12.7, 19.0, 30, 78, 81 |

[a] $T_c$ = crystallization temperature, $T_a$ = annealing temperature.
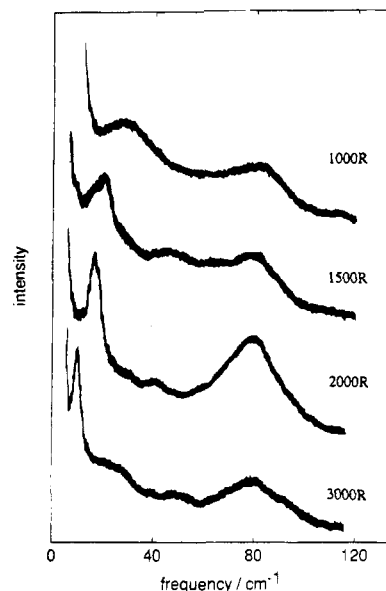


**Figure 7.** Low-frequency Raman spectra of poly(oxyethylene) rings: samples 1000R to 3000R, as indicated. Samples 1000R, 1500R, and 2000R were crystallized and examined at 15 °C; sample 3000R was crystallized and examined at 20 °C. Intensity scales and zeros are arbitrary.

Selected results are given in Table 3. The bands at 10–11 cm⁻¹ can be identified with the LAM-1 bands of once-folded chains, the different frequencies reflecting evolution of more perfect structures. Song and Krimm have assigned bands in this range to noninteger folded chains. Annealing a crystalline sample of 3000C at 56 °C resulted in a spectrum characteristic of the unfolded-chain form (see Figures 5 and 6). This was judged by the disappearance of the characteristic band at 10–11 cm⁻¹, the band at 12.7 cm⁻¹ being sufficiently different in frequency to permit its assignment to LAM-3 of unfolded-chain crystals. In support of this assignment, the ratios of the LAM-3 to LAM-1 frequencies ($\nu_3/\nu_1$; see Table 2) found for the crystalline chains, including that of annealed sample 3000C, were consistently in the range 2.2–2.3. A low value of the frequency ratio has been established many times previously for low-molar-mass poly(oxyethylene)s, and has been explained as an effect of end forces[20,32] and predicted by normal mode calculations.[16] The relatively high intensity of this band for our annealed sample, compared with those of the LAM-3 bands of the other samples, would be consistent with the presence of a proportion of folded chains, but the evidence from DSC (discussed above) is not consistent with that explanation.

Examples of low-frequency Raman spectra of the rings are shown in Figure 7. Assignments to LAM-1 and LAM-3 are made in Table 2, where the reported frequencies are averages taken from a number of spectra. Observation of the band at 81 cm⁻¹ in the spectra of the crystalline rings confirms the helical conformation.
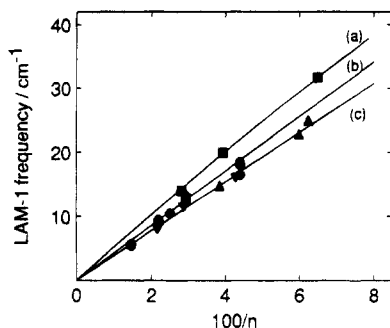
**Figure 8.** LAM-1 frequency versus reciprocal chain length ($n$ = average number of oxyethylene units in the molecules) for linear oligo(oxyethylene)s: (■) uniform hydroxy-ended chains; (●) nonuniform hydroxy-ended chains; (▲) uniform methoxy-ended chains; (▼) nonuniform methoxy-ended chains. Data points are from refs 16 and 18–21 and from the present work. The curves through the points are for (a) uniform hydroxy-ended chains, (b) nonuniform hydroxy-ended chains, and (c) uniform and nonuniform methoxy-ended chains.

Samples of 3000R crystallized at 20 or 37 °C had essentially identical spectra with a LAM-1 frequency of 9.5 cm$^{-1}$. Similarly, the spectrum of a sample crystallized at 20 °C and annealed at 52 °C was essentially unchanged, apart from a shift of the LAM-1 frequency to a slightly lower value of 8.9 cm$^{-1}$, consistent with slight thickening of lamellar crystals. Thus, in agreement with the results of DSC, Raman spectroscopy shows that the crystallization of sample 3000R is less complicated than that of sample 3000C, no doubt because the only conformation attainable under the conditions used is the "folded" conformation, i.e., two crystal stems with a fold at each lamellar end surface.

The ratios of the LAM-1 frequencies found for the unfolded chains and the rings ($\nu_{IR}/\nu_{1C}$; see Table 2) were in the range 1.67 ± 0.04. This result contrasts with that of Lee and Wegner[5] for the LAM-1 frequencies to alkane chains and rings: i.e., $\nu_{IR}/\nu_{1C} \approx 2.0$. The latter result allowed direct interpretation, each stem in the crystals of a ring being halved in length compared to a chain with the same number of atoms.

One obvious complication in the present results is that comparison of the LAM-1 frequencies of rings with those of hydroxy-ended chains is in itself misleading, since hydrogen bonding of the hydroxy groups with hydroxy and ether oxygen is known to increase the LAM-1 frequency. The effect of illustrated in Figure 8. The largest effect of H-bonding is found for uniform oligomers, where the end groups are crystallographically ordered in the end-group plane and the OH groups are cooperatively bonded.[26] The effect in polydisperse samples is smaller, since the end groups are in a disordered surface layer, and H-bonding between hydroxy groups and ether oxygens is relatively weak. Limited polydispersity in itself has little effect on the LAM-1 frequency, as is shown in Figure 8 by the results for uniform and polydisperse oxyethylene chains with methoxy end groups, which fall onto a single line. Compared with methoxy-ended chains, the LAM-1 frequencies of hydroxy-ended chains are raised by ca. 10% for polydisperse samples and by ca. 25% for uniform samples.

Comparison of the LAM-1 frequencies of the crystalline rings with those of methoxy-ended chains increases the value of $\nu_{IR}/\nu_{1C}$. Considerating the published[20,21] result for samples of methyl-ended 2000C, 1500C, and 1000C ($\nu_{1C}$ = 8.6, 11.9, and 16.5 cm$^{-1}$, respectively), comparison with the results for rings (see Table 2) leads,

on average, to apparent stem lengths some 10% longer for the rings than expected. Presumably this result could reflect variation in the chain lengths of samples supplied, as well as fractionation during preparation of methyl-ended samples, and fractionation during crystallization, i.e., rejection of smaller molecules to the interlamellar layer, this being more important for the thinner lamellae of the rings compared to those of the chains and for the smaller rings and chains compared to the larger. However, since end forces and end masses are known to have large effects on the LAM-1 vibrations of oxyethylene chains, it is equally possible that the connected stems are mutually damping their longitudinal vibrations. Clearer elucidation of the direct effect of folds (of the rings) versus ends (of the chains) in determining the LAM-1 frequencies may well have to wait on the preparation of large but uniform cyclic oligo-(oxyethylene)s.

## Additional Remarks

The primary purpose of this paper is to report the first measurements by low-frequency Raman spectroscopy on new model polymers, cyclic poly(oxyethylene)s. Comparison is made with the vibrational properties of their linear-chain counterparts as a convenient means of connection to the considerable literature on that topic; see, e.g., reports on nonuniform low-molar-mass polymers[15,16,18–21] and uniform oligomers.[20,21,32,33] The detailed discussions of the properties of the crystalline chains which can be found in those papers are not repeated here.

At the time of writing, the cyclic polymers are under examination by wide-angle X-ray crystallography, making use of the facilities at the SERC Daresbury Laboratory, Warrington, U.K. Details of the technique used have been given elsewhere.[34] A preliminary investigation of sample 2000R has yielded a scattering pattern essentially identical to that published previously[18] for a sample of hydroxy-ended poly(oxyethylene) with $M_n$ = 1000 g mol$^{-1}$ (PEG1000 or 1000C in present notation), i.e., Bragg peaks consistent with an identical monoclinic subcell[29] for rings and chains. A full account of X-ray scattering from the range of samples will be published. Here we use the one result presently available to add weight to our conclusion, based on the high-frequency Raman spectroscopy, that the rings and chains have identical crystal structures.

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