J. Chem. Soc., Faraday Trans. 2, 1987, **83**, 917-925

Morphology of Poly(oxyethylene) Methyl-n-alkyl Ethers as determined by Small-angle X-Ray and Raman Scattering

Kyriakos Viras
Physical Chemistry Laboratory, University of Athens, 13A Navarinou Street, Athens, Greece

Fotini Viras
Department of Physics, University of Athens, 104 Solonos Street, Athens, Greece

Carl Campbell, Terence A. King* and Colin Booth
Departments of Chemistry and Physics, University of Manchester, Manchester M13 9PL

Poly(oxyethylene) methyl-n-alkyl ethers with oxyethylene block lengths of 13, 27, 40 or 53 oxyethylene units and n-alkyl end-block lengths in the range 12 to 21 methylene units have been studied in their solid state by low-frequency Raman scattering and small-angle X-ray diffraction. The low-frequency Raman transitions observed are assigned to longitudinal acoustical modes of unfolded chains in either monolayer or bilayer lamellae or of folded chains probably in bilayer lamellae, the morphology being dependent on the molecular structure and the crystallisation conditions.

The solid-state structures of poly(oxyethylene) n-alkyl ethers are of interest in themselves and also for the information they provide concerning the chain conformations in molecules which consist of naturally helical (oxyethylene) and planar zig-zag (methylene) blocks. Recent studies of mono-n-alkyl[1] and di-n-alkyl[2-4] ethers have concentrated upon homogeneous oligomers, which are crystallographically most tractable.[1,5-7] However, poly(oxyethylene) n-alkyl ethers of commercial concern, for use as surfactants, have polydisperse poly(oxyethylene) blocks and studies of materials of this type in the solid state are less plentiful. Early work of Rösch[8] has been supplemented by a study of poly(oxyethylene) di-n-alkyl ethers.[9,10] However, a detailed structural study of poly(oxyethylene) mono-n-alkyl ethers has not been made, although some methyl-n-alkyl ethers have been examined.[11]

In connection with studies of micellisation of poly(oxyethylene) n-alkyl ethers[12-14] we have available in Manchester four series of methyl-n-alkyl ethers with number-average oxyethylene block lengths in the range 13 to 53 oxyethylene units and alkyl end-blocks from 12 to 21 methylene units. In this paper we report on the morphology of these compounds as revealed by small-angle X-ray diffraction and Raman spectroscopy. The low-frequency Raman spectra are especially interesting since the identification and interpretation of the scattering from the longitudinal acoustical modes (LAM) of the blocks is potentially a rich source of structural information.[15]

Experimental

Materials

As described elsewhere[11-14] methyl-n-alkyl ethers of formula $H(CH_2)(OCH_2CH_2)_mO(CH_2)_nH$ with number-average oxyethylene block lengths $m = 13, 27, 40$ or 53 and n in the range 12-21, were prepared by Drs H. H. Teo and M. G. Styring from preformed samples of α-methyl,ω-hydroxypoly(oxyethylene) with narrow

Table 1. Lamellar spacings and melting points of poly(oxyethylene) methyl n-alkyl ethers[a]

		low T_c		high T_c	
sample	$T_m/°C$	l_x/nm	l_x/l	l_x/nm	l_x/l
1-13-16	30	12.2	2.06	—	—
1-13-18	30	13.5	2.18	—	—
1-27-12	40	9.5	1.02	9.6	1.03
1-27-14	40	9.6	1.00	10.0, 17.5	1.04, 1.83
1-27-16	40	9.8	0.99	10.2, 18.4	1.04, 1.87
1-27-18	39	10.1	1.00	10.0, 18.8	0.99, 1.87
1-27-21	30	10.4	0.99	10.6, 18.8	1.01, 1.80
1-40-12	50	12.5	0.97	13.0	1.00
1-40-14	49	12.5	0.95	13.3	1.01
1-40-16	49	12.9	0.96	13.5	1.00
1-40-18	49	12.1	0.88	13.5	0.99
1-53-12	54	14.7, 9.9	0.89, 0.60	15.4, 10.3	0.93, 0.62
1-53-14	54	10.0	0.59	16.1, 11.3	1.01, 0.71
1-53-16	54	9.8	0.57	15.7, 11.9	0.92, 0.70
1-53-18	53	10.0	0.58	16.1, 11.9	0.93, 0.69
1-53-21	53	10.2	0.58	17.5	0.99

[a] T_m, melting point; T_c, crystallisation temperature; low $T_c \approx 20$ °C; high $T_c \approx 37$-38 °C for series 1-27-*n*, 44-45 °C for series 1-40-*n* and 1-53-*n*; l_x, lamellar spacing; *l*, molecular length calculated from eqn (1); estimated error in $l_x = \pm 0.3$ nm.

molecular weight distributions ($M_w/M_n \leqslant 1.05$) and n-alkyl bromides. Because of this choice of preparative method the oxyethylene block length distribution is constant within a given series of ethers.

Samples are denoted 1-*m*-*n*: *e.g.* 1-27-12 denotes the methyl-n-alkyl ether of a poly(oxyethylene) of number average block length $m = 27$ oxyethylene units, of n-alkyl block length $n = 12$ and of overall length 95 chain atoms (C or O).

Crystallisation

Melting points of solid samples were measured on the hot stage of a Reichert polarising microscope. The melting point (T_m) was taken to be the temperature at which the last trace of birefringence disappeared at the heating rate of 2-3 K min^{-1} starting from *ca.* 20 K below T_m. Values of T_m are listed in table 1. For investigation of solids by X-ray and Raman scattering each sample was heated above T_m and then crystallised by cooling rapidly either to room temperature ($T_c \approx 20$ °C, all samples) or to $T_c = 37$-38 °C (samples of series 1-27-*n*) or 44-45 °C (samples of series 1-40-*n* and 1-53-*n*).

Small-angle X-Ray Diffraction (SAXD)

SAXD photographs of samples at room temperature (*ca.* 20 °C) were obtained by means of a Rigaku-Denki slit-collimated camera with nickel-filtered Cu *Kα* radiation from a Philips PW1130 generator and broad-focus tube operated at 40 kV and 20 mA. Solid samples were powdered and supported as thin (*ca.* 1 mm) films between Melinex polyester sheets. Exposure times were 12 h or less for Kodak NoScreen film with a sample-to-film distance of 25 cm. The method was calibrated with n-octadecane and sodium stearate.

Raman Spectroscopy

Raman scattering at 90° to the incident beam from samples at room temperature was recorded by means of a Spex Ramalog spectrometer fitted with a 1403 double monochromator and, for low-frequency work, a 1442U third monochromator and 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 either 150 mW for the low-melting samples of series 1-13-*n* or 450 mW otherwise. The bandwidth and scanning parameters were chosen to suit the frequency range of the spectrum: *e.g.* low-frequency range ($<40\ \mathrm{cm}^{-1}$), bandwidth = $1.0\ \mathrm{cm}^{-1}$, scanning increment = $0.05\ \mathrm{cm}^{-1}$, integration time = 5 s; high-frequency range ($<1700\ \mathrm{cm}^{-1}$), bandwidth = $5.0\ \mathrm{cm}^{-1}$, scanning increment = $0.5\ \mathrm{cm}^{-1}$, integration time = 2 s. For the low-frequency spectra the third monochromator was in the scanning mode. The frequency scale was calibrated by reference to the spectrum of L-cystine.

Generally high-frequency spectra were recorded immediately after determining low-frequency spectra in order to confirm that the samples were unchanged by exposure to the laser beam.

Results

Small-angle X-Ray Diffraction

SAXD photographs showed lines corresponding to one or more orders of scattering from the lamellar spacing (or, in some instances, from two distinct spacings). Bragg's equation was used directly to obtain the lamellar spacings (l_x) which are listed in table 1. Comparison is made with the molecular length in the crystal (l) calculated, as described elsewhere,[7] from crystallographic data *via* the formula

$$l/\mathrm{nm} = 0.0928(3m+3) + 0.127n$$

wherein it is assumed that the helical oxyethylene block comprises all methylene groups adjacent to oxygen, that the methylene block is planar zig-zag and that the chain ends contribute 0.127 nm. The values of l_x/l fall into three groups which are identified (as discusssed later) with lamellar structures as follows:

$l_x/l \approx 1.8\text{–}2.2$, unfolded chains in bilayers;

$l_x/l \approx 0.9\text{–}1.1$, unfolded chains in monolayers;

$l_x/l \approx 0.6\text{–}0.7$, folded chains probably in bilayers.

High-frequency Raman Spectra

Spectra were recorded across the frequency range $50\text{–}1700\ \mathrm{cm}^{-1}$ for samples of series 1-27-*n* to 1-53-*n* crystallised at $T_c \approx 20$ °C: examples are shown in fig. 1. Samples of series 1-13-*n*, which had low melting points, were not investigated this way. The spectra recorded for samples of series 1-40-*n* and 1-53-*n* were practically indistinguishable from published[16–18] spectra of poly(oxyethylene)s: an example is shown in fig. 1(*a*). A sharp scattering peak at $1295\ \mathrm{cm}^{-1}$ was evident in the spectra of samples of series 1-27-*n* with $n = 16\text{–}21$, as illustrated in fig. 1(*b*), otherwise scattering at this frequency was weak [see, *e.g.* fig. 1(*c*)]. (A sharp peak at $1295\ \mathrm{cm}^{-1}$ has been used[2-4] as an indicator of n-alkyl blocks crystallised in planar zig-zag conformation: the scattering can be assigned to a methylene twisting mode.) Scattering from LAM-1 of the planar zig-zag n-alkyl blocks was not observed. Such scattering has been observed[19,20] in the spectra of highly crystalline samples of uniform oligo(oxyethylene) di-n-alkyl ethers, and its absence in the present spectra indicates that the n-alkyl blocks are imperfectly crystallised. The

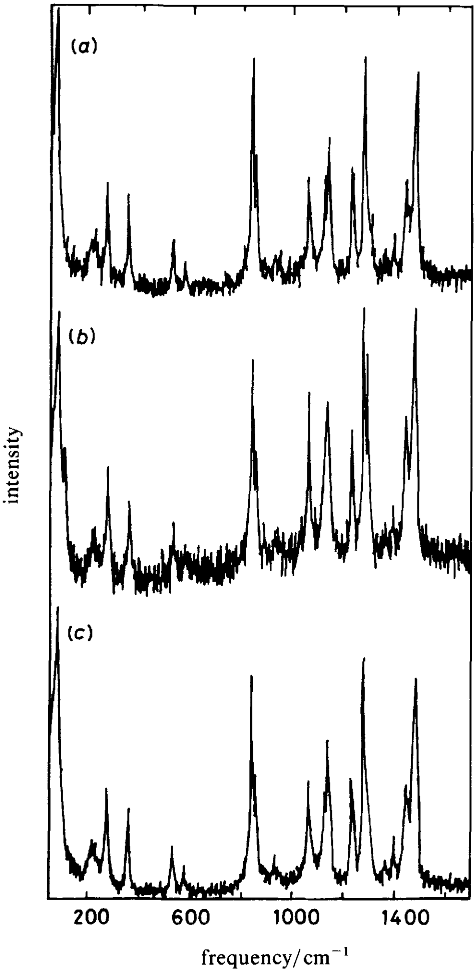

Fig. 1. Raman spectra of poly(oxyethylene) methyl-n-alkyl ethers at room temperature: samples (*a*) 1-53-16, (*b*) 1-27-21 and (*c*) 1-27-14, all crystallised at $T_c \approx 20\,°C$. The intensity scales and zeros are arbitrary.

weak scattering at 107–112 cm^{-1} apparent in the spectra of several samples, including that of sample 1-27-21 illustrated in fig. 1(*c*), is assignable to an internal mode of the oxyethylene helix.[18,21,22]

The prominent peak at *ca.* 80 cm^{-1} seen in all spectra (*e.g.* fig. 1) is a useful indicator of crystalline oxyethylene blocks, particularly since it lies in the low-frequency range. This scattering has been assigned to a local deformation of the poly(oxyethylene) helix[21] plus a lattice mode.[18]

Low-frequency Raman Spectra

Spectra were recorded over the range 5–40 cm^{-1}: examples are shown in fig. 2. Exceptionally the range was extended to 150 cm^{-1} in order to observe the characteristic scattering of oligo(oxyethylene)[17,18,21] at *ca.* 60 cm^{-1} (weak), 80 cm^{-1} (strong) and 105 cm^{-1} (weak). A weak scattering peak was consistently observed at *ca.* 45 cm^{-1}. These observations, together with the frequencies of the scattering peaks observed in

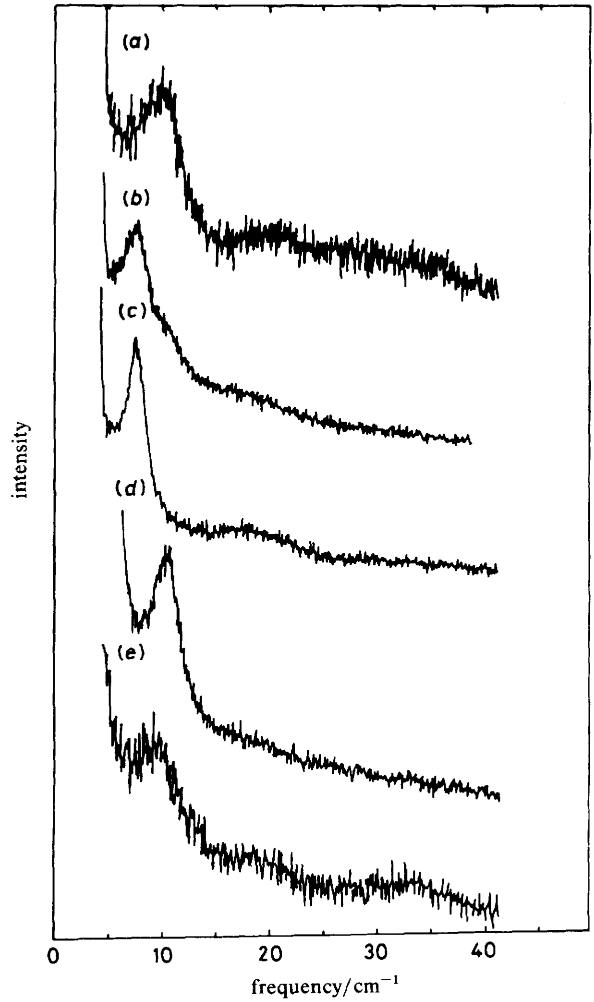

Fig. 2. Low-frequency Raman spectra of poly(oxyethylene) methyl-n-alkyl ethers at room temperature: samples (*a*) 1-27-12, $T_c \approx 20$ °C; (*b*) 1-40-14, $T_c \approx 20$ °C; (*c*) 1-40-14, $T_c \approx 45$ °C; (*d*) 1-53-21, $T_c \approx 20$ °C; (*e*) 1-53-21, $T_c \approx 45$ °C. The intensity scales and zeros are arbitrary.

the 5-40 cm^{-1} range, are recorded in table 2: other very weak peaks which were less reliably observed are omitted. Based on the assignments made earlier[17-20] the frequencies denoted (i), (ii) and (iii) in table 2 are assigned (as discussed later) to LAMs as follows: (i) LAM-1 of unfolded chains; (ii) LAM-1 of folded chains; (iii) LAM-3.

Discussion

Comparison with Previous Work

SAXD and low-frequency Raman measurements have been reported[11] for two of the ethers investigated in this work (1-53-12 and 1-53-18). The samples were prepared by Dr Al-Kafaji from the same starting materials. Those results, summarised in table 3 (and categorised as above), are in satisfactory agreement with the present work (see tables 1 and 2) bearing in mind differences in sample and crystallisation conditions.

Table 2. Observed peak frequencies in low-frequency spectra of poly(oxyethylene) methyl n-alkyl ethers[a]

		frequency/cm^{-1}						
		low T_c			high T_c			
sample	range/ cm^{-1}	(i)	(ii)	(iii)	(i)	(ii)	(iii)	other weak peaks[b]
1-13-16	<150	17.2	—	—	—	—	—	45, POE
1-13-18	<40	15.8	—	—	—	—	—	—
1-27-12	<150	9.8	—	20	10.5	—	17	35, 45, POE
1-27-14	<40	10.8	—	—	10.1	—	—	—
1-27-16	<40	9.9	—	—	10.1	—	—	—
1-27-18	<40	9.8	—	—	10.1	—	—	—
1-27-21	<40	10.4	—	—	9.9	—	—	—
1-40-12	<150	7.9	—	18	7.9	—	18	34, 45, POE
1-40-14	<40	7.9	11.2w	19	7.7	—	19	—
1-40-16	<40	8.1	—	19	7.9	—	19	—
1-40-18	<40	7.9	11.2w	19	7.5	—	20	34
1-53-12	<40	6.6w	10.1	17	6.8	—	16	5.1, 31
1-53-14	<40	6.2w	10.5	17	6.7	—	17	32
1-53-16	<40	—	10.6	—	6.6	9.5w	—	34
1-53-18	<40	—	10.3	—	6.4	9.4w	15	—
1-53-21	<40	—	10.4	—	6.0w	9.8	19	34

[a] Low $T_c \approx 20$ °C; high $T_c \approx 37$–38 °C for series 1-27-*n*, 44–45 °C for series 1-40-*n* and 1-53-*n*; w indicates weak scattering relative to that of the same mode in similar samples. Estimated errors: 0.3 cm^{-1} in (i) and (ii); 1 cm^{-1} in (iii) and other peaks. [b] POE indicates scattering peaks characteristic of the poly(oxyethylene) helix; *i.e.* *ca.* 60 cm^{-1} (weak), 80 cm^{-1} (strong,), 105 cm^{-1} (weak).

Table 3. Results for samples 1-53-12 and 1-53-18 reported in ref. (11)

			ν/cm^{-1}	
sample	$T_c/°\text{C}$	l_x/nm	(i)	(ii)
1-53-12	20	10.0	—	10.5
1-53-12	35	10.5, 15.1	6.5	10.5
1-53-18	20	9.6	—	11.0
1-53-18	35	9.8, 15.3	6.5	10.8

LAM-1 of Unfolded Chains

The frequencies denoted (i) in table 2 and assigned to LAM-1 of unfolded chains can be compared with those found[17,23] for unfolded dimethyl ethers of comparable chain length and polydispersity. This is done in fig. 3, where frequency is plotted against reciprocal oxyethylene block length, *i.e.* $1/l_{oe}$ where $l_{oe} = 0.0928(3m + 3)$ nm. The spread of frequencies between the various n-alkyl ethers of a given oligo(oxyethylene) is seen to be small compared with the large deviation from the behaviour of the dimethyl ethers.

Linear fits of LAM-1 frequency against reciprocal chain length are excellent evidence that the samples of a homologous series have the same chain conformation in their lamellar (or layer) crystals. The results presented elsewhere for poly- or oligo-(oxyethylene)s[17,18,23] show this to be the case from chain length 9 oxyethylene units (28

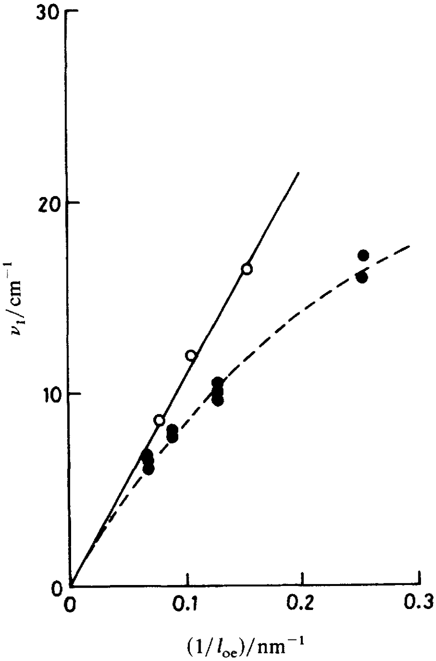

Fig. 3. LAM-1 frequency (ν_l) of unfolded chains *vs.* reciprocal oxyethylene-block length ($1/l_{oe}$): (○) poly(oxyethylene) dimethyl ethers; (●) poly(oxyethylene) methyl-n-alkyl ethers. The lines drawn are based only on the experimental data.

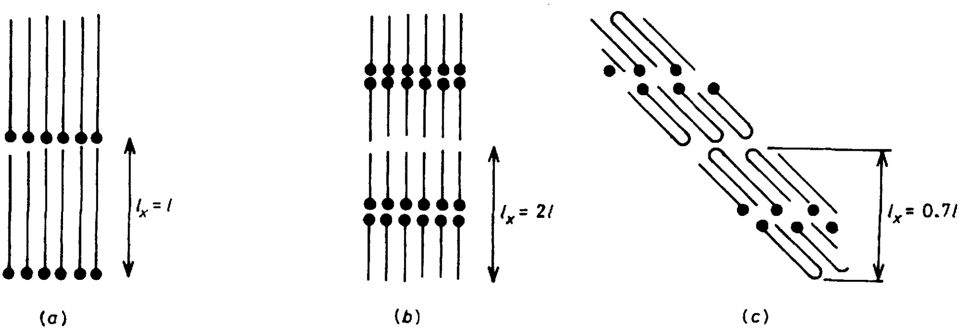

Fig. 4. Schematic diagrams of lamellar structures of poly(oxyethylene) methyl-n-alkyl ethers: (*a*) unfolded chains in monolayers, (*b*) unfolded chains in bilayers, (*c*) folded chains in bilayers. For simplicity the chains are depicted as uniform in chain length and crystallinity.

chain atoms) to 45 units (136 chain atoms). The conformation of these chains is undoubtedly the unfolded 7/2 helix. The curvature of the plot of LAM-1 frequency against $1/l_{oe}$ for the poly(oxyethylene) methyl-n-aklyl ethers (see fig. 3) is explicable in terms of damping of the longitudinal vibration of a helical oxyethylene block by the mass of the n-alkyl block. A detailed explanation of the effect is given in the following paper.[24]

The samples with LAM-1 frequencies assigned to unfolded chains also have values of l_x/l from SAXD of 1 or 2. Thus the structures of these crystalline samples is confirmed to be unfolded chains orientated normal to the end planes of monolayer ($l_x/l = 1$) or bilayer ($l_x/l = 2$) lamellae, as shown schematically in fig. 4.

LAM-1 of Folded Chains

LAM-1 frequencies corresponding to folded chains were found only for the longest chains examined, *i.e.* for the samples of series 1-53-*n* and for some of the samples of series 1-40-*n* (see table 2). Compared with the LAM-1 frequencies of the unfolded poly(oxyethylene) methyl-n-alkyl ethers (*i.e.* the dashed curve in fig. 3), those assigned to folded chains correspond to oxyethylene block lengths half as long. For example, from table 2, the average frequency found for folded chains of the samples of series 1-53-*n* of 10.3 cm^{-1} [frequency (ii), low T_c, high T_c sample 1-53-21] is almost identical to that found for unfolded chains of the samples of series 1-27-*n*, *i.e.* 10.1 cm^{-1} [frequency (i), low or high T_c]. This result is consistent with the chains being symmetrical once folded: the assumption that folded and unfolded chains of the present type behave similarly with regard to their LAM-1 vibrations is discussed in the following paper.[24]

From table 1 the values of l_x/l by SAXD for the folded-chain lamellae are 0.57–0.71, rather than 0.5 as required for once-folded chains orientated normal to lamellae end planes. This result is consistent with 'tilted' chains, the angle between the chain axis and the lamellar end plane being *ca.* $\sin^{-1}(0.65) = 40°$. Similar values of l_x/l have been found for other folded-chain lamellae of low molecular weight poly(oxyethylene)s with substantial end groups,[25] and has recently been observed[4] in homogeneous samples of oligo(oxyethylene) di-n-alkyl ethers *n*-45-*n*. Hitherto the structure of these once-folded-chain lamellae has been uncertain.[4,25] The present evidence from Raman spectroscopy combined with SAXD makes it probable that the structure is that indicated in fig. 4. As discussed earlier, the tilt corresponds to a regular displacement of adjacent chains by *ca.* 3 chain units (*i.e.* 9 chain atoms).

LAM-3

A peak in the frequency range 15–19 cm^{-1} is observed in the spectra of the samples of series 1-40-*n* and 1-53-*n*, but not (generally) in the spectra of samples of series 1-27-*n* and 1-13-*n* (see table 2). The ratio of frequencies of peak (iii) to peak (i) averages 2.4 for series 1-40-*n* and 2.6 for series 1-53-*n*. The frequency ratios LAM-3/LAM-1 found for poly(oxyethylene) dimethyl ethers (2.0 to 2.4)[17] and oligo(oxyethylene) di-n-alkyl ethers with $n = 12$ to 16 (2.6 to 3.0)[19] bracket the values found here and allow assignment of the peak (iii) to LAM-3 of the unfolded chain. A possible exception is peak (iii) observed for sample 1-53-21 (see table 2), which might be more comfortably assigned to LAM-3 of the folded chain.

Other Low-frequency Raman Peaks

The peak observed at 31–35 cm^{-1} (see table 2) was first reported by Rabolt *et al.*[21] (37 cm^{-1}) and assigned to an internal deformation of the oxyethylene helix. It has been confirmed as an optical mode by its independence of both chain length and temperature.[18] The other peak at 45 cm^{-1} (see table 2) has not been observed in the Raman spectra of poly(oxyethylene)s.

The peak observed at 5 cm^{-1} in sample 1-53-12 cannot be assigned at this time, but may be related to the transverse mode found[18] in oligo(oxyethylene)s and their di-n-alkyl ethers.[22]

Conclusions

In this work the longitudinal acoustic modes LAM-1 and LAM-3 have been observed for poly(oxyethylene) methyl-n-alkyl ethers crystallised with folded and unfolded chains. The LAM-1 frequencies measured have been compared with those previously published for poly(oxyethylene) dimethyl ethers.

The morphological structure revealed by SAXD is stacked lamellae. Most often the lamellae consist of unfolded chains in monolayers. Lamellae consisting of unfolded chains in bilayers predominate in the crystals of the samples of series 1-13-*n* ($l < 60$ chain atoms) and also the samples of series 1-27-*n* ($l < 105$ chain atoms) provided that they are crystallised slowly. This latter observation is consistent with the formation of monolayers being kinetically favoured.

Chain folding is important only in series 1-53-*n*, where it predominates in all samples (overall length $l > 170$ chain atoms) when crystallisation is rapid at low T_c, and in the longest sample (1-53-21, $l = 182$ chain atoms) even when crystallisation is slow. The lamellae probably consist of once-folded chains in bilayers.

The work confirms the nature and the extent of the information about the crystalline state of chain molecules which can be derived from a combination of Raman spectroscopy and small-angle X-ray diffraction. The low-frequency longitudinal acoustical modes are a valuable probe of the details of structures, including those formed from multicomponent chains.

We thank Mr P. Kobryn for help with the spectroscopic measurements. The British Council and the S.E.R.C. gave financial support.

References

1 D. L. Dorset, *J. Colloid Interface Sci.*, 1983, **96**, 172.
2 R. C. Domszy and C. Booth, *Makromol. Chem.*, 1981, **182**, 1051.
3 H. H. Teo, T. G. E. Swales, R. C. Domszy, F. Heatley and C. Booth, *Makromol. Chem.*, 1983, **184**, 861.
4 S. G. Yeates and C. Booth, *Makromol. Chem.*, 1985, **186**, 2663.
5 T. G. E. Swales, S. G. Yeates and C. Booth, *Br. Polym. J.*, 1985, **17**, 32.
6 T. G. E. Swales, R. L. Beddoes, C. Price and C. Booth, *Eur. Polym. J.*, 1985, **21**, 629.
7 T. G. E. Swales, R. C. Domszy, R. L. Beddoes, C. Price and C. Booth, *J. Polym. Sci., Polym. Phys. Ed.*, 1985, **23**, 1585.
8 M. Rösch, in *Nonionic Surfactants*, ed. M. J. Schick (Edward Arnold, London, 1967), p. 723.
9 D. R. Cooper, Y. K. Leung, F. Heatley and C. Booth, *Polymer*, 1978, **19**, 309.
10 R. C. Domszy, R. H. Mobbs, Y. K. Leung, F. Heatley and C. Booth, *Polymer*, 1979, **20**, 1204; 1980, **21**, 588.
11 J. K. H. Al-Kafaji and C. Booth, *Makromol. Chem.*, 1981, **182**, 3671.
12 H. H. Teo, S. G. Yeates, C. Price and C. Booth, *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**, 1787.
13 H. H. Teo, M. G. Styring, S. G. Yeates, C. Price and C. Booth, *J. Colloid Interface Sci.*, 1986, **114**, 416.
14 M. G. Styring, H. H. Teo, C. Price and C. Booth, *J. Chromatogr.*, accepted.
15 J. F. Rabolt, *CRC Crit. Rev., Solid State Mater. Sci.*, 1985, **12**, 165.
16 J. L. Koenig and A. C. Angood, *J. Polym. Sci., Part A2*, 1970, **8**, 1787.
17 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.
18 K. Viras, T. A. King and C. Booth, *J. Polym. Sci., Polym. Phys. Ed.*, 1985, **23**, 471.
19 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.
20 S. G. Yeates, H. H. Teo and C. Booth, *Makromol. Chem.*, 1984, **185**, 2475.
21 J. F. Rabolt, K. W. Johnson and R. N. Zitter, *J. Chem. Phys.*, 1974, **61**, 504.
22 K. Viras, T. A. King and C. Booth, *J. Chem. Soc., Faraday Trans. 2*, 1985, **81**, 491.
23 A. Marshall, R. C. Domszy, H. H. Teo, R. H. Mobbs and C. Booth, *Eur. Polym. J.*, 1981, **17**, 885.
24 F. Viras, K. Viras, C. Campbell, T. A. King and C. Booth, *J. Chem. Soc., Faraday Trans. 2*, 1987, **83**, 927.
25 C. Booth, R. C. Domszy and Y. K. Leung, *Makromol. Chem.*, 1979, **180**, 2765.

Paper 6/2316; *Received* 28*th July*, 1986