Crystallinity and fusion of low molecular weight α,ω-alkoxy-poly (ethylene oxide): octadecoxy to triacontanoxy end-groups

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Samples of α, ω-alkoxy-poly(ethylene oxide) with an average oxyethylene chain length of 45 units and with C_{18}, C_{21}, C_{26} and C_{30} end-groups have been prepared and characterized. Several experimental methods have been used to investigate the crystalline structure and the melting behaviour of the solids produced by crystallization in the range T_c = 25° to 45°C. The oxyethylene chains crystallize in folded-chain conformation in all samples. The methylene chains also crystallize in samples with C_{26} (low T_c) and C_{30} end-groups. The extent of crystallinity is low in the solids in which both types of chain crystallize. The melting points of the oxyethylene lamelae increase markedly as the methylene chain length is increased. This is explained by the high free energy change on mixing oxyethylene and methylene chains when the solid is transformed to a random melt, especially as unlike segments are more effectively segregated in the layer structure of the solid when the methylene chain is long.

INTRODUCTION

Low molecular weight α, ω-alkoxy-poly(ethylene oxide) with C_1 (methoxy) to C_{18} (octadecoxy) end-groups crystallizes into stacked layer structures in which crystalline and non-crystalline layers alternate.[1] The crystalline layers are formed exclusively from the oxyethylene inner block. The non-crystalline layers contain the methylene end-blocks together with a significiant part (about 20%) of the oxyethylene inner block. The extension of this series of polymers to include longer n-alkoxy end-groups permits a systematic approach to a system in which methylene block crystallization predominates over oxyethylene block crystallization. To this end we have prepared the C_{21}, C_{26} and C_{30} n-alkyl bromides and used them to prepare the corresponding α, ω-alkoxy-poly(ethylene oxides) by a modification of the Williamson ether synthesis due to Cooper.[2] These n-alkyl bromides are not available commercially: their preparation is described in Appendix A of this paper. For purposes of comparison with the earlier work[1] we have also prepared a new sample of α, ω-octadecoxy-poly(ethylene oxide).

EXPERIMENTAL AND RESULTS

Preparation

Samples of α, ω-alkoxy-poly(ethylene oxide) were prepared from α, ω-hydroxy-poly(ethylene oxide) of molecular weight $\bar{M}_n$ = 2000 g mol^{-1} (Fluka A.G.). Preparative details are given in Appendix B.

Notation

We denote samples by their number-average block lengths expressed in oxyethylene or methylene chain units as appropriate: thus α, ω-octadecoxy-poly(ethylene oxide) prepared from poly(ethylene oxide) 2000 is called 18-45-18.

Characterization

Infra-red spectroscopy (Perkin-Elmer Model 257 grating spectrometer) of dry films at room temperature was used as described earlier[2] to determine conversions of hydroxy to alkoxy of better than 95%. Proton magnetic resonance spectroscopy (Perkin-Elmer Model R12B spectrometer) of dilute solutions in tetrachloromethane was used to confirm these conversions: the predicted methylene/oxyethylene proton ratio exceeded that found experimentally by not more than 5%. No traces of bromide could be found by elemental analysis.

Gel permeation chromotography (g.p.c.) was used to determine the molecular weight distributions of the samples. The following conditions were used: tetrahydrofuran at 25°C flowing at 1 cm^3 min^{-1}, injection of 2 cm^3 of polymer solution of concentration 1.7 g dm^{-3}; six Styragel columns, each 1.2 m long, with nominal pore sizes 5-8, 10, 15-35, 20-50, 50-200 and 70-200 nm; detection by differential refractometry (Optilab Multiref 901). Calibration was by α, ω-hydroxy-poly(ethylene oxide) samples of known molecular weight.[1] The chromatograms were analysed by the method of Picket *et al.*[3] The results are given in *Table 1.* The values of $\bar{M}_n$ (± 100 g mol^{-1}) are in good agreement with those predicted (*Table 1*). The values of $\bar{M}_w/\bar{M}_n$ are essentially unchanged by alkoxylation.

Crystallization

The experiments described below were carried out with samples crystallized as completely as possible. Half an hour was allowed at 25°C. Crystallization of samples 21-45-21 and 26-45-26 was very slow at $T_c \geq 40$°C and several days were allowed (e.g. 5 days at T_c = 45°C) for completion of crystallization.

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Table 1 Molecular characteristics from g.p.c.

Sample	$\bar{M}_n$/g mol^{-1}		$\bar{M}_w/\bar{M}_n$
	Predicted	Found	
0–45–0	2000	2000	1.03
18–45–18	2504	2490	1.06
21–45–21	2586	2530	1.03
26–45–26	2726	2850	1.02
30–45–30	2840	3030	1.04

Small-angle X-ray scattering

A Rigaku-Denki slit-collimated camera was used with CuKα radiation to obtain small-angle X-ray scattering (SAXS) photographs. Thin films of the samples, supported on Melinex ployester film, were crystallized on a hot plate at temperatures in the range 25° to 45°C. All measurements were at room temperature. The scattering peaks for the samples were broader than observed[1] for the lower members of the series and, with the exception of sample 18–45–18, second order peaks were difficult to detect. (Under similar conditions of exposure 3 or more orders of scattering were observed for 0–45–0.) Lamella spacings (l_x, ± 0.2 nm) calculated by direct use of Bragg's Law are listed in *Table 2.* For comparison we list the lengths of the extended chains (l) calculated assuming the length of an oxyethylene unit in the 7 : 2 helix to be 0.28 nm and that of a methylene unit in the planar zig-zag to be 0.125 nm.

The results show that crystallization within the temperature range 25° to 45°C leads to folded-chain structures. Except for sample 26–45-26 the lamella spacings vary little with temperature.

Raman scattering

A Cary Model 82 spectrometer fitted with an argon ion laser (wavelength = 514.5 nm, power = 600 mW) was used to record Raman spectra over the frequency range 6 to 100 cm^{-1}. Samples were crystallized at the temperatures indicated in *Table 3,* and, to reduce fluorescent background were exposed to radiation for 1 h before recording the spectra. All measurements were at room temperature.

The low frequency Raman spectra of low molecular weight poly(ethylene oxide) show[1] two significant features. (a) Peaks at very low frequency corresponding to the longitudinal acoustic mode (*LAM*) fundamental ($\bar{\nu}_1$) and third overtone ($\bar{\nu}_3$). The frequencies of these peaks vary with chain length, extent of chain-folding and type of end-group.[1, 4] (b) A broad peak at about 80 cm^{-1}, independent of chain length, etc., associated with a torsional mode of crystalline poly(ethylene oxide). The Raman spectra of samples 18–45-18, 21–45-21 and 26–45-26, the latter when crystallized at 45°C, show all these features. The spectra of samples 26–45-26 (crystallized at 25°C) and 30–45-30 show none of these features. However, the spectrum of sample 30–45-30 shows a new peak centred on 72 cm^{-1} which we assign to the *LAM* fundamental of crystalline methylene lamellae.

Table 2 Small-angle X-ray scattering

Sample	Approximate chain length, l/nm	l_x/nm		
		T_c = 25°C	35°C	45°C
18–45–18	17.1	10.0	9.9	10.1
21–45–21	17.9	9.6	9.7	9.9
26–45–26	19.1	9.9	10.0	11.0
30–45–30	20.1	10.1	–	10.1

Table 3 Raman scattering

Sample	T_c/°C	*LAM* fundamental ($\bar{\nu}_1$/cm^{-1})
18–45–18	25	10.0
21–45–21	25	10.0
26–45–26	25	Not observed
26–45–26	45	10.0
30–45–30	25	72.0

In comparison with earlier results[1] the values of $\bar{\nu}_1$ found for samples 18–45-18 to 26–45-26 (*Table 3,* ± 0.5 cm^{-1}) show that the crystalline oxyethylene lamellae contain folded chains. Since the *LAM* frequencies are sensitive to changes in the non-crystalline layer[1, 4–6] and since the relationship between $\bar{\nu}_1$ and l_x is not straightforward,[6, 7] quantitative analysis of these data is not attempted here.

Wide-angle X-ray scattering

A Debye-Scherrer camera was used with CuKα radiation to obtain wide-angle X-ray scattering (WAXS) photographs and a Joyce-Loebl double beam microdensitometer was used to determine the film optical density as a function of scattering angle. Normally, molten samples were drawn into a borosilicate glass capillary and crystallized therein at or about 25°C. Films of samples 26–45-26 and 30–45-30 were crystallized on a hot plate at 45° and 55°C, respectively, and introduced into the capillary as a powder. For purposes of comparison a sample of high density polyethylene (Verstolen, Shell Chemical Co., density = 0.957 g cm^{-3}), crystallized from dilute solution in 1, 2, 4-trichlorobenzene as a fine powder, was also examined. All measurements were at room temperature.

The important features of the WAXS photographs, insofar as the present study is concerned, are between scattering angles 9° and 12°: these results are summarized in *Figure 1.* Attention is directed to the intense peaks at 9.6° (associated with the oxyethylene 7-2 helix) and 10.7° (associated with the methylene planar zig-zag). Samples 0–45-0 and 21–45-21 (*Figures 1a* and *1b*) contain only crystalline oxyethylene chains, as do the lower members of the α, ω-alkoxy series.[1] Samples 26–45-26 and 30–45-30 crystallized at 25°C (*Figures 1e* and *1f*) contain both crystalline oxyethylene and crystalline methylene chains. Sample 26–45-26 crystallized at 45°C (*Figure 1c*) contains no crystalline methylene chains: this is in contrast to sample 30–45-30 for which the WAXS results are practically unchanged even when crystallized at 55°C for many days.

The scattering from non-crystalline polymer (relative to crystalline) is noticeably high for the samples in which methylene chains crystallize. We have not attempted to quantify this observation since differential scanning calorimetry (see later) permits a more straightforward estimation of the fractional crystallinity.

Infra-red spectroscopy

The infra-red spectra of samples of α, ω-alkoxy-poly (ethylene oxide) with end-groups longer than C_2 exhibit low frequency (720-765 cm^{-1}) absorptions attributable to rocking modes of the methylene chains. This rocking mode is split into a doublet in samples 26–45-26 and 30–45-30 crystallized at 25°C and studied at room temperature. Such splitting is observed in crystalline polyethylene[8] as well as in most crystalline solid n-alkanes[9,10] and is absent in the molten samples.

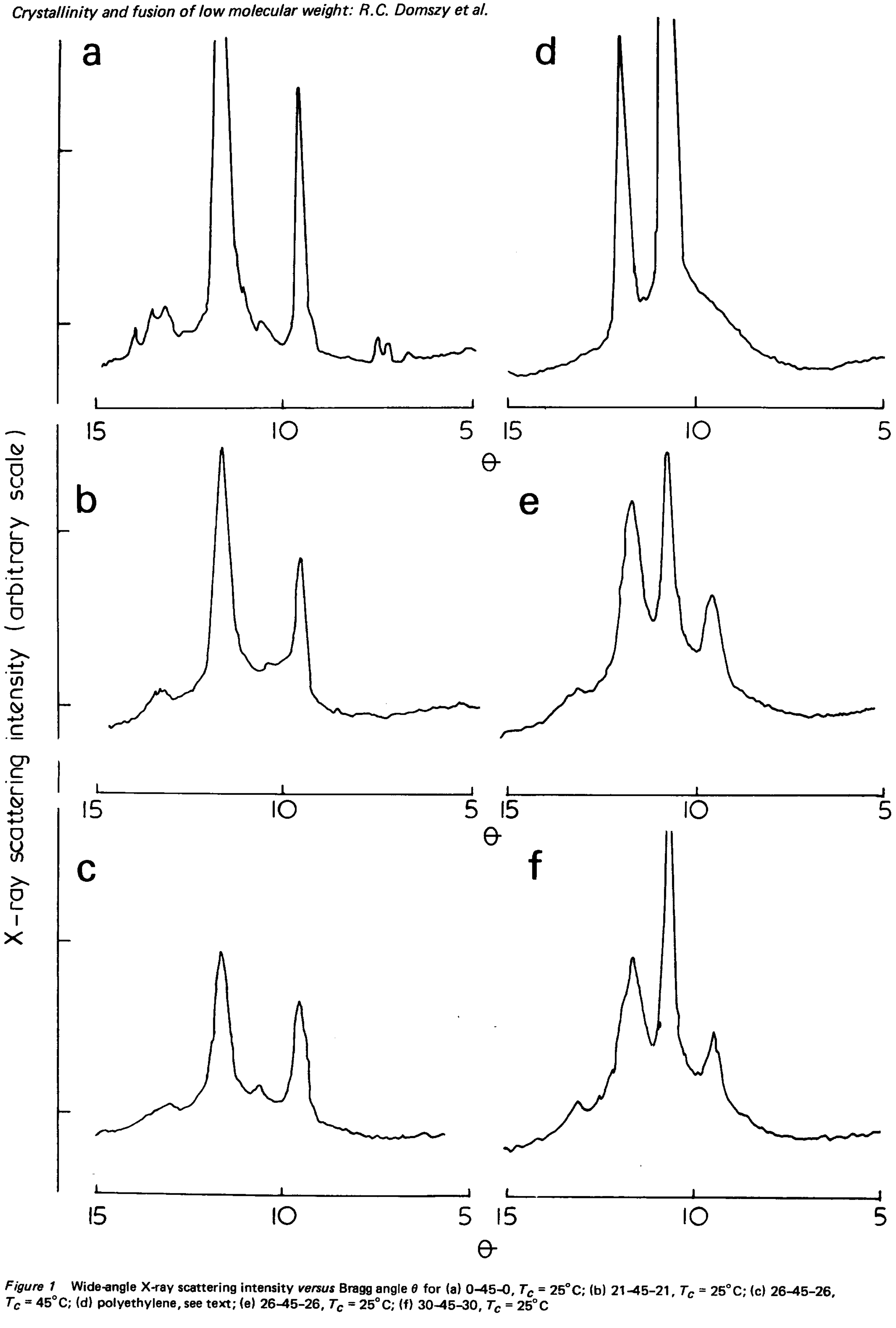

Figure 1 Wide-angle X-ray scattering intensity *versus* Bragg angle θ for (a) 0–45–0, T_c = 25°C; (b) 21–45–21, T_c = 25°C; (c) 26–45–26, T_c = 45°C; (d) polyethylene, see text; (e) 26–45–26, T_c = 25°C; (f) 30–45–30, T_c = 25°C

A Perkin-Elmer Model 577 infra-red spectrometer fitted with a vacuum temperature cell was used to investigate the infra-red spectra of samples 26–45-26 and 30–45-30 as a function of temperature. Samples were crystallized at 25°C and, for sample 26–45-26, at 40°C. The results for sample 30–45-30 are illustrated in *Figure 2,* the temperature of interest being about 49°C. These results serve to reinforce our findings from WAXS (and Raman scattering) that the methylene chains crystallize and serve to locate the melting transition of the crystalline methylene lamellae in sample 30–45-30 at or about 49°C. The splitting in sample 26–45-26 crystallized at 25°C disappears at approximately 35°C. No splitting was detected in the low temperature spectrum of sample 26–45-26 crystallized at 40°C; this observation is in keeping with the WAXS and Raman scattering results.

Dilatometry

Approximate melting points were determined on the hot stage of a Reichert polarizing microscope as described earlier.[1] More precise melting points were determined by dilatometry as described elsewhere:[11] the essential feature of the method is a rapid temperature rise to a temperature some 2°C or so lower than the melting temperature to be determined, so as to avoid annealing, followed by a slower rate of increase of temperature (6 K h^{-1}), so as to avoid superheating. Samples were crystallized at various temperatures as indicated in *Table 4.*

The melting points (± 0.2 K) obtained are listed in *Table 4.* Samples 18–45-18 and 21–45-21 have single melting transitions which are independent of T_c. Samples 26–45-26 (T_c = 25°C) and 30–45-30 (T_c = 25° or 45°C) have two very distinct melting points, illustrated in *Figure 3a,* which can be assigned to the melting of methylene chains (lower temperature) and of oxyethylene chains (higher transition) on the basis of the preceeding results of infra-red spectroscopy and WAXS. Sample 26–45-26 crystallized at 35°C has a single melting transition associated with the crystalline oxyethylene chains. Sample 26–45-26 crystallized at 45°C has two transitions, illustrated in *Figure 3b,* which we ascribe to melting of two types of crystalline oxyethylene lamellae differing with respect to chain-folding. This is consistent with the increase in lamella spacing found by SAXS (*Table 1*) and in keeping with other observations[12] of multiple melting in poly (ethylene oxide).

Table 4 Melting points (T_m/°C) determined by dilatometry and d.s.c.

Sample	T_c/°C				
	Dilatometry			d.s.c.	
	25	35	45	25	45
18–45-18	50.4	50.4	50.6	50.0	–
21–45-21	53.5	53.5	53.6	53.5	53.5
26–45-26	35.0, 56.3	56.4	55.3, 58.0	34.5, 55.5	58.0
30–45-30	49.5, 66.7	–	49.5, 66.8	49.5, 66.0	49.5, 66.0

Table 5 Heat of fusion, Δ*h*, determined by d.s.c.

Sample	Δ*h*/J g^{-1}	
	T_c = 25°C	45°C
18–45-18	112	–
21–45-21	108	120
26–45-26	50, 8	132
30–45-30	47, 11	46, 11

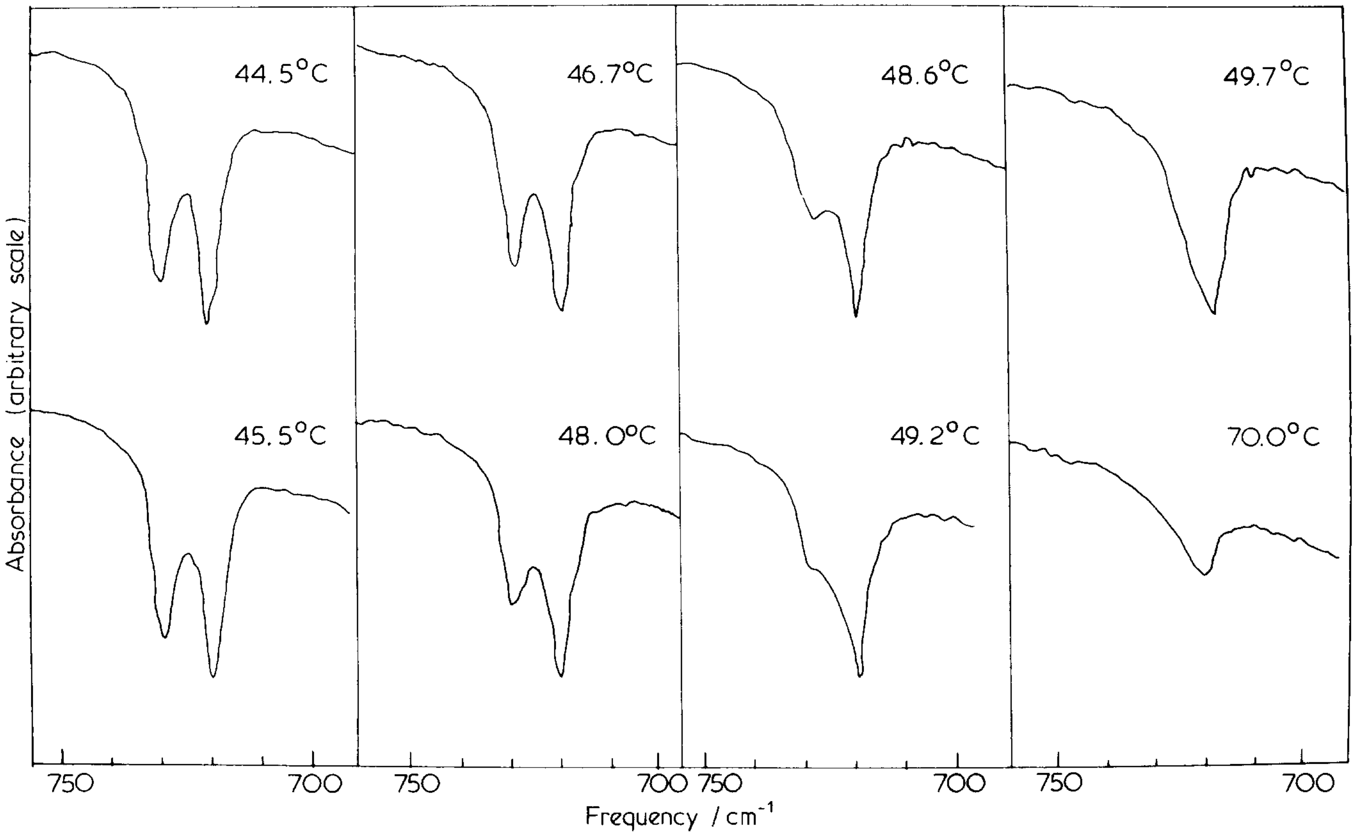

Figure 2 Low frequency infra-red spectra of 30–45-30 as a function of temperature between 44.5° and 70°C

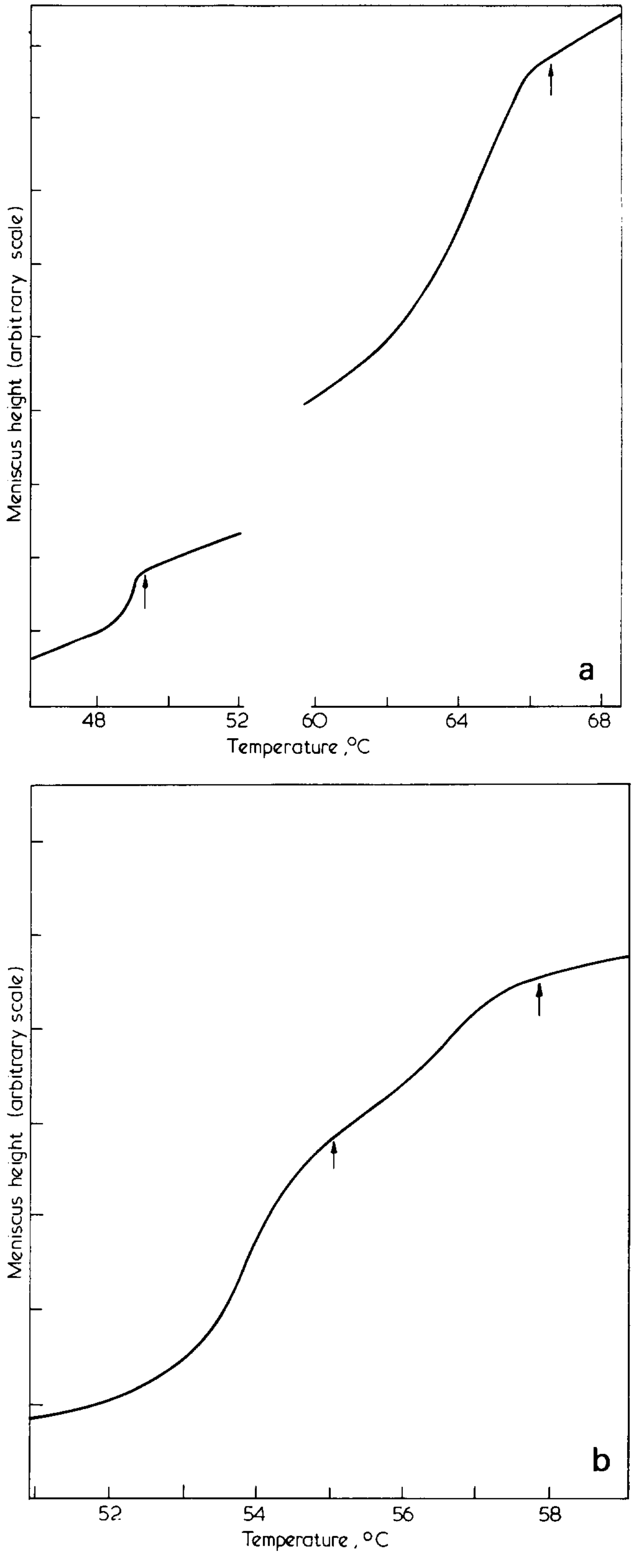

Figure 3 Dilatometer capillary height *versus* temperature (uncorrected) for (a) 30–45–30, T_c = 25°C; (b) 26–45–26, T_c = 45°C. The arrows indicate the tabulated melting points

Differential scanning calorimetry (d.s.c.)

A Perkin-Elmer Model 1B differential scanning calorimeter was used to determine melting temperatures and heats of fusion. Samples, sealed in aluminium pans, were melted at 70°C and crystallized on a hot plate at 25° or 45°C. The thermogram was measured from a point 20 K below the melting point; the heating rate was 2 K min^{-1}. Calibration of the heat of fusion was by melting indium. Calibration of the melting point was by melting point standards covering the temperature range of interest (30°-70°C). Allowance was made for thermal lag between sample and pan holder.[13]

The melting points (± 0.5 K) are listed in *Table 4*. Samples 18–45–18, 21–45–21 and 26–45–26 (T_c = 45°C) have single-peaked endotherms. (Sample 21–45–21 crystallized at 25°C showed slight premelting at about 47°C followed by recrystallization at 49°C. Premelting was not observed with any other sample.) Samples 26–45–26 (T_c = 25°C) and 30–45–30 (T_c = 25°C or 45°C) have two-peaked endotherms. These melting transitions have already been attributed to the melting of crystalline methylene chains (lower temperature) and of crystalline oxyethylene chains (higher temperature). Agreement between the two methods of determining T_m is good. (The lower melting transition at 55.3°C in sample 26–45–26 crystallized at 45°C could not be detected by d.s.c.)

The specific heats of fusion (± 5 J g^{-1}) measured at the melting point are listed in *Table 5*. The two values quoted for samples 26–45–26 (T_c = 25°C) and 30–45–30 (T_c = 25° and 45°C) refer to the melting of the crystalline oxyethylene chains (first number) and of the crystalline methylene chains (second number). The heat of fusion falls drastically when the methylene blocks crystallize, from values exceeding 100 J g^{-1} to values less than 60 J g^{-1}. The higher values of Δh found for samples 21–45–21 and 26–45–26 crystallized at 45°C may well be a result of very slow rate of crystallization of these samples at this temperature, i.e. a result of growing more perfect crystals.

Nuclear magnetic response

Proton and ^{13}C spin-lattice relaxation times (T_1) of molten samples 18–45–18, 26–45–26 and 30–45–30 were measured with a Varian Associates SC-300 spectrometer using the (π-τ-$\pi/2$) inversion recovery technique at frequencies of 300 MHz (^1H) and 75.5 MHz (^{13}C). The results for interior methylene nuclei are given in *Table 6*, where they are compared with T_1 found for a sample of 7–45–7 prepared previously. (The distinct ^{13}C resonances in the proton decoupled spectrum of 7–45–7 were used to extrapolate T_1 for an interior methylene carbon as described earlier.[1]) We have shown[1] that the values of T_1 found for molten 7–45–7 (and 18–45–18) are those expected for a homogeneous melt. The near identity of T_1 values illustrated in *Table 6* supports the view that all our samples have homogeneous melts.

DISCUSSION

The experimental results presented here for sample 18–45–18 can be compared with those reported earlier[1] for a similar sample. The samples do not differ appreciably in molecular weight, though the present sample has a

Table 6 N.m.r. spin-lattice relaxation times (T_1/s) at 70°C

Sample	^{13}C resonance		^{1}H resonance	
	Methylene	Oxy-ethylene	Methylene	Oxy-ethylene
7–45–7	0.7	1.09	1.2	0.82
18–45–18	0.77	1.15	–	–
26–45–26	0.76	1.05	–	–
30–45–30	0.74	1.05	0.8	0.92

narrower chain length distribution. Comparison of properties (l_x, $\bar{v}_1$, T_m, Δh) shows some differences. However, we feel justified in amalgamating the results for whole series, i.e. methylene chain length $n = 0$ to 30.

Crystallinity

The heats of fusion of the oxyethylene block per gram of oxyethylene in the sample (Δh_{oe}), and the corresponding quantities for the methylene block (Δh_{me}), are listed in *Table 7*. Opportunity is taken to present revised results for samples 0-45-0 to 18-45-18. The heat of fusion of perfectly crystalline poly(ethylene oxide) can be calculated from the work of Devoy and Roberts[14] to be:

$$\Delta h^0_{oe}/\mathrm{J\,g^{-1}} = 178.6 + 0.629(T/^\circ\mathrm{C}) - 2.83 \times 10^{-3}(T/^\circ\mathrm{C})^2$$

and a similar expression for perfectly crystalline poly (methylene) is given by Wunderlich and Dole:[15]

$$\Delta h^0_{me}/\mathrm{J\,g^{-1}} = 228.2 + 0.717(T/^\circ\mathrm{C}) - 2.66 \times 10^{-3}(T/^\circ\mathrm{C})^2$$

A simple model of perfect crystal plus perfect liquid with negligible excess surface enthalpy and with negligible effects due to segment mixing leads directly to the values of the fractional crystallinity ($X = \Delta h/\Delta h^\circ$) listed in *Table 7** ($\Delta h^\circ$ being calculated for the melting temperature indicated).

We find $X_{oe} \cong 0.85$ when the oxyethylene block crystallizes aone in extended-chain conformation ($n \leqslant 4$), $X_{oe} \cong 0.70$ when the oxyethylene block crystallizes alone in folded-chain conformation, and $X_{oe} \cong 0.33$ when both oxyethylene block and methylene block crystallize in overall folded-chain conformation. X_{me} calculated by this procedure is very low (0.12 to 0.14) and it may be that comparison might be better made with Δh measured for the *n*-alkanes,[16] i.e. about 170 J g^{-1} for $C_{30}H_{62}$ ($T_m = 66^\circ$C) or $C_{26}H_{54}$ ($T_m = 56^\circ$C). The assumptions made in calculating the values of X_{oe} and X_{me} mean that they represent lower limits of the fractional crystallinities of the blocks.

Table 7 Heat of fusion and fractional crystallinity for samples crystallized at 25°C

n	Δh_{oe}/J g^{-1}	T_m/°C	X_{oe}
0	171	54	0.84
1	174	53	0.85
2	176	54	0.86
3	170	53	0.83
4	173	53	0.85
7	164	47	0.81
10	148[a]	43	0.74
12	147	44	0.73
16	147	47	0.73
18	148	49	0.73
18	140	50	0.69
21	140	54	0.69
26[b]	68	56	0.33
30	67	66	0.32

n	Δh_{me}/ J g^{-1}	T_m/°C	X_{me}
26	30	35	0.12
30	37	50	0.14

[a] Δh misprinted in ref. 1: Δh = 130 J g^{-1}.

[b] $T_c = 45^\circ$C, $X_{oe} = 0.87$

Crystal structure ($T_c = 25^\circ$C)

The underlying crystalline structure of the polymers is stacked lamellae. Samples with $n < 7$ have lamella spacings which correspond to extended chains, whereas those with $n > 7$ have spacings consistent with folded chains.

Only the oxyethylene blocks crystallize when $n \leqslant 21$: the methylene blocks are in the non-crystalline layers, which alternate with the crystalline layers in the stacked structure. The fractional crystallinity of the oxyethylene block is high.

Both oxyethylene and methylene blocks crystallize in samples with $n \geqslant 26$ (at $T_c = 25^\circ$C). The fractional crystallinity of the blocks is low under these circumstances. We have no direct evidence to enable us to distinguish structures in which crystalline oxyethylene and crystalline methylene lamellae form a single stack from those in which they form separate stacks. The very low fractional crystallinities found for the dual crystals are consistent with the speculation that crystallization of the one component precludes crystallization of the other *within the same molecule*.

Variation of structure with crystallization temperature

Sample 26-45-26 is particularly interesting since rapid crystallization ($T_c \leqslant 35^\circ$C) leads to crystallization of oxyethylene and methylene blocks, whereas slow crystallization ($T_c \geqslant 40^\circ$C) leads to crystallization of the oxyethylene block alone. Provided that microphase separation is not a complicating factor (our n.m.r. measurements pertain to the melt at about 70°C, not to supercooled liquid at 25°C) it can be concluded that the formation of crystalline methylene lamellae, rather than more stable crystalline oxyethylene lamellae, is a consequence of a rate-determined process.

Melting points

In *Figure 4* we plot the melting points of the oxyethylene lamellae in our samples against the chain length of the methylene block (n). The drop in melting point found at $n = 7$ is due to the transition from extended-to-folded-chain conformation. (The second melting transition, $T_m \cong 47^\circ$C, observed[1] for sample 7-45-7, is not plotted.) The increase in melting point with increasing n found for the folded-chain crystals has been discussed earlier[1] and attributed to the effect of mixing unlike segments.

For our polymers the melting point of the oxyethylene block can be related to structural variables via the Flory-Vrij equation:[1, 17]

$$T_m = T^0_m\,[1 - 2\sigma_e/\Delta H^0 l_c]/[1 - RT^0_m \ln(\phi_{oe} I)/\Delta H^0 t l_c] \qquad (1)$$

in which T^0_m is the thermodynamic melting point of poly (ethylene oxide), ΔH^0 the thermodynamic enthalpy of fusion of poly(ethylene oxide) per mole of chain units, σ_e the end interfacial free energy of the crystalline lamellae, l_c the thickness of the crystalline lamellae, ϕ_{oe} the volume fraction of the oxyethylene block, t the extent of chain-folding in the crystal ($t = 1$ is extended) and I the combinatorial entropy parameter for the crystal. Here we assume that l_c and t (and consequently I) are constant for our folded-chain crystals, taking l_c to be 80% of the oxyethylene block length and t to be 2, and, since T^0_m and ΔH^0 are

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*The values calculated for $n = 0$ to $n = 18$ differ slightly from those given earlier[1] due in part to the different basis for temperature correction used here.

constants for poly(ethylene oxide), we assign the variation in T_m to variation in ϕ_{oe} and σ_e. In fact the effect of the variation of ϕ_{oe} on T_m is small[1] and can be ignored here.

The end interfacial free energy in equation (1) is the free energy of formation from the melt of the interface between non-crystalline and crystalline layers and includes the formation of the non-crystalline layer itself. The polymer in the non-crystalline layer will differ from that in the melt because of (a) a change in concentration of the methylene units and (b) a restriction in conformation due to the proximity of the crystalline lamellae. The surface free energy terms (J per mole of chains emerging) associated with these effects are denoted[1] σ_m (mixing) and σ_a (conformation). We assume that the term due to the imbalance of intermolecular forces (σ_0) is constant for a given type of crystal[1] and so assign the variation in T_m to variation in σ_m and σ_a.

An estimate of the effect of the restriction of conformation is available from Ashman's results[11] on block copolymers of ethylene oxide and propylene oxide, for which mixing effects are relatively small. We find,[1] with our assumptions, and for folded-chain crystals:

$$T_{m,n} \cong T_{m,o} - 20\log_{10}(1 + n/14) \qquad (2)$$

Given random mixing of oxyethylene and methylene units in the melt, the effect of mixing depends upon the model chosen to represent the stacked structure. Two extreme cases are *random mixing* of oxyethylene and methylene units in the non-crystalline layer,* for which:[1]

$$T_{m,n} \cong T_{m,o} + RT^2_{m,o}\chi(1-\phi_{oe})^2/\Delta H^0(1 - X_{oe}\phi_{oe}) \qquad (3)$$

and segregation of oxyethylene and methylene units in the non-crystalline layer, for which:

$$T_{m,n} \cong T_{m,o} + RT^2_{m,o}\chi(1-\phi_{oe})/\Delta H^0 X_{oe} \qquad (4)$$

We approximate χ by 0.7[1, 18] and, with sufficient accuracy for our purposes here, set $\Delta H^0 = 8.8$ kJ mol^{-1} and $v_{sp,me}/v_{sp,oe} = 1.32$ independently of temperature. We set $T_{m,o} = 43$°C: this brings the melting temperature calculated assuming random mixing in the melt into correspondence with the measured melting point at $n = 10$[1].

The calculated values of T_m are shown as broken curves in *Figure 4*; curve (a) being that calculated for segregation in the non-crystalline layer (via equations 2 and 4) and curve (b) being that calculated for random mixing in the non-crystalline layer (via equations 2 and 3). The measured melting points show a trend consistent with increasing segreagation of methylene and oxyethylene units in the non-crystalline layer, which is entirely consistent with the block structure of the polymer chains and our conclusions concerning the structure of the crystals.

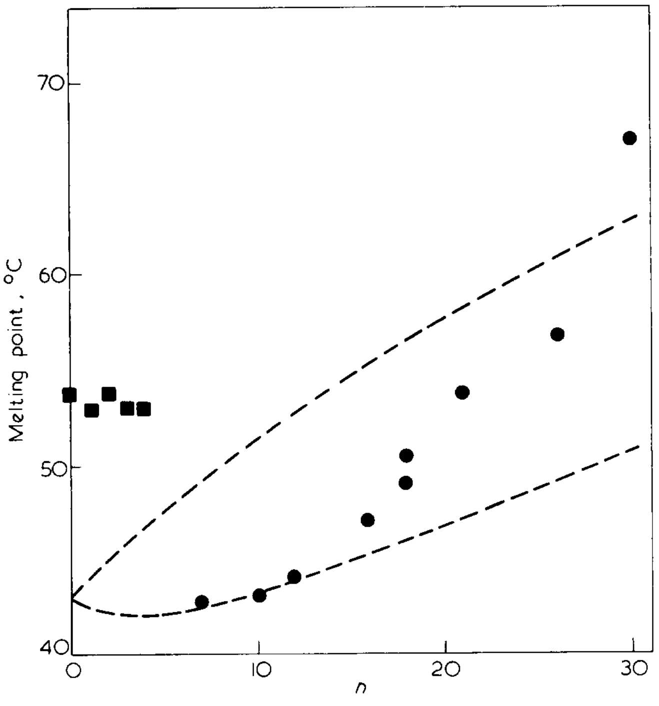

Figure 4 Melting point of the oxyethylene crystals *versus* methylene chain length *n*. Extended chain (■) and folded chain (●) crystals are included. Broken curves are calculated (a) from equations (2) and (4) and (b) from equations (2) and (3)

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APPENDIX A

n-Alkyl bromides are readily prepared by way of the *n*-alkanoic acids, since these can be converted to the bromo-compound by a single-stage modified Hunsdiecker reaction. We have used a modification by Cason and Walba[19] of a method first described by Cristol and Firth[20] in which the acid is degraded and brominated with mercuric oxide and bromine in tetrachloromethane. This reaction is known to proceed via the mercuric salt of the acid.[19, 21] In the case of the lower *n*-alkanoic acids, to which this reaction had hitherto been applied, these salts were quite soluble, but we have found that the higher acid salts are less so and in consequence have increased the volume of solvent in our preparations.

Also in the preparation of these higher *n*-alkyl bromides the removal of starting acid, which together with by-product ester contaminated the crude product, was not readily accomplished by the usual aqueous alkali wash, since the salts are only slightly water soluble. The best purification method, adopted in the case of *l*-bromohexacosane, was to vacuum distil the crude product before recrystallization. In addition, in the case of *l*-bromotriacontane it was found necessary to pass it into heptane solution through a magnesia-packed column to remove the last traces of carbonylic impurities.

Many methods of preparing the required higher *n*-alkanoic acids have been described.[22] Most suitable for our purpose was the addition of an acid chloride to a Grignard derived reagent.[22–27] We have combined a half-ester acid chloride of an *n*-alkanedioic acid with an alkyl zinc chloride, and then reduced and hydrolysed the keto-ester so produced to obtain the *n*-alkanoic acid. Special care was taken to establish the complete conversion of carbonyl to methylene since any non-methylene residues in the chain would affect its crystallization behaviour.

The reaction scheme for the preparation of *l*-bromoheneicosane(I) *l*-bromohexacosane(XIII) and *l*-bromotriacontane(VII) is given in *Figure A-1.* The numbering reflects the chronological order of preparation. Experimental details are given below.

Infra-red, proton magnetic resonance and mass spectra were recorded on Perkin-Elmer Model 257, Perkin-Elmer Model R12B and A.E.I. Model MS12 spectrometers, respectively.

Docosanioc acid (87%) was supplied by Price's Chemicals Ltd, as a mixture containing the C_{19} and C_{17} *n*-alkanoic acids as main impurities. Dimethyl decanedioate (Fluka) was used without further purification. Red mercuric oxide, zinc chloride (95%), magnesium turnings (Grignard quality), adipic acid (99%), hydrazine hydrate (98%), potassium hydroxide (85%), AR tetrachloromethane, and toluene were supplied by BDH and were used without further purification. AR methanol and benzene and laboratory reagent grade heptane (BDH) were dried and distilled from calcium hydride.

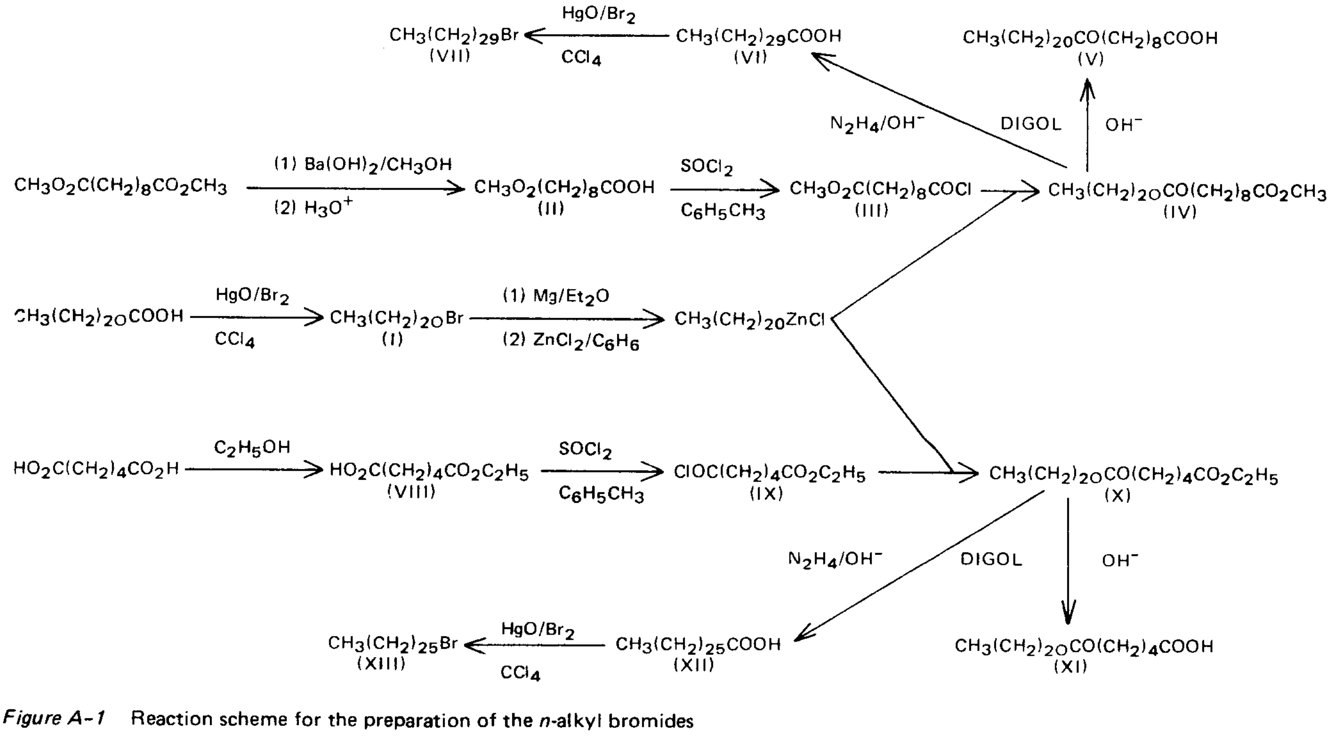

Figure A-1 Reaction scheme for the preparation of the *n*-alkyl bromides

Bromine and thionyl chloride were supplied by Hokin & Williams, the former used as received, the latter purified as described later. AR barium hydroxide octahydrate (BDH) was recrystallized (water) then dehydrated by heating at 100°C/13 Pa for 48 h.

Diethylene glycol (H. & W.) was redistilled, using a fraction of b.p. 157-159°C/4.3 x 10^3 Pa.

l-Bromoheneicosane(I)

A mixture of 87% docosanoic acid (100 g, 0.255 mol) and red mercuric oxide (40 g, 0.185 mol) was stirred and heated in AR tetrachloromethane (750 cm^3) until solvent was distilling from the top of an attached Vigreaux column (30 x 2 cm) at a rate of ~ 1 drop/sec.

With reduced heating a solution of bromine (59.5 g, 0.372 mol) in tetrachloromethane (175 cm^3) was added drop-wise over 3 h while solvent was distilled out at the same rate. More tetrachloromethane (150 cm^3) was then added similarly, excess bromine distilling out with the solvent.

The cold solution was filtered to remove mercuric bromide (62.8 g, 94% yield) and the filtrate washed with 1.25 m aqueous sodium hydroxide solution (200 cm^3). Filtration of the two-phase mixture removed a little gelatinous precipitate and the filtrate was washed with water (200 cm^3) and dried ($MgSO_4$). Removal of the solvent at reduced pressure then gave crude product (124.5 g) which was distilled through a Vigreaux column (30 x 2 cm) giving a main fraction (70.54 g, 74% yield) b.p. 176-184°C/ 13 Pa, m.p. 43°-46°C.

Recrystallization of a sample (1.7 g) from absolute ethanol (11 cm^3) gave white crystals of *l*-bromoheneicosane (1.61 g), m.p. 44.5°-45°C (literature[28] cites 44.5°-45°C) (Found: C, 67.6; H, 11.7; Br, 21.3%. Calculated for $C_{21}H_{43}Br$: C, 67.2; H, 11.5; Br, 21.3%). The infra-red and n.m.r. spectra were in accord with the expected structure.

A preparation on 2.5 times this scale gave a similar yield.

Methyl hydrogen decanedioate(II)

This was prepared following a method for methyl hydrogen hendecanedioate[29] by the addition of methanolic anhydrous barium hydroxide solution to molten dimethyl decanedioate. The precipitated barium salt of the half-ester acid was acidified and ether extraction followed by distallation gave a main fraction of (II) in 65% yield, b.p. 179°-183°C/500 Pa, m.p. 39.5°-41.5°C (literature[30] cites 40°-41°C) (Equivalent found 218.3, 217.9. Calculated for $C_{11}H_{20}O_4$, 216.3).

9-Methoxycarbonylnonoyl chloride[31](III)

Practical grade thionyl chloride was boiled with sublimed sulphur (3 h) then fractionally distilled. A centre-cut (b.p. 76°-77°C) was stirred over iron filings (4 h) and then fractionally distilled to give again a centre-cut, b.p. 76.5°-76.8°C.

From methyl hydrogen decadedioate (30.2 g, 0.139 mol), in refluxing toluene, was distilled 25 cm^3 of solvent to ensure an anhydrous system.

Thionyl chloride (47.5 g, 0.40 mol) was added and the solution was boiled for 5 h the internal temperature gradually rising to 108°C.

After removal of excess toluene and thionyl chloride at reduced pressure, the residue was fractionally distilled to give (III) (20.4 g, 63% yield), b.p. 137°C/5 x 10^2 Pa with a satisfactory elemental analysis and an infra-red spectrum consistent with the structure.

Methyl 10-oxohentriacontanoate(IV)

This was prepared following the procedure of Reinhard and Dixon[32] for methyl 20-oxotetracontanoate.

A solution of anhydrous zinc chloride (6.42 g, 0.045 mol since 95% purity) in dry diethyl ether (20 cm^3) was prepared and stored under dry nitrogen.

1-Bromoheneicosane (18.77 g, 0.05 mol) and magnesium turnings (1.34 g, 0.055 g atom) were stirred in refluxing diethyl ether (85 cm^3) for 4.5 h and the resulting cooled Grignard solution (96% yield, based upon magnesium consumed) was filtered under nitrogen through a glass wool plug. The filtrate was added drop-wise (5 min) to the prepared zonc chloride solution, heat being evolved and a creamy-white paste forming. Ether (~ 40 cm^3) was distilled slowly (2 h) from the stirred paste. A Gilman colour test[33] then showed absence of Grignard reagent indicating full conversion to heneicosyl zinc chloride.

9-Methoxycarbonylnonoyl chloride(III) (11.30 g, 0.05 mol) in anhydrous benzene (90 cm^3) was added drop-wise (10 min) to the stirred heneicosyl zinc chloride suspension, the solid disappearing and a clear brown solution forming. This solution was stirred and refluxed (2.75 h), allowed to stand overnight, then acidified with 3 N hydrochloric acid (42 cm^3). All the benzene and some water were removed by distillation in a bath which was gradually allowed to rise to 140°C. When cool, the solidified organic layer was crushed, water-washed and air-dried over several days. Crude IV (23.09 g, 93% yield) was obtained. Recrystallization (toluene) gave purer IV (16.87 g, 68% yield), m.p. 79.5°-81°C. Further recrystallization of a sample gave pure IV, m.p. 81-81.5°C, (Found: C, 77.5; H, 12.8%. Calculated for $C_{32}H_{62}O_3$: C, 77.7; H, 12.6%).

An infra-red spectrum (hexachlorobutadiene mull) with $\upsilon = 1740\ cm^{-1}$ (ester $> C = 0$) and 1710-1720 cm^{-1} (keto $> C = 0$) was in accord with the expected structure.

In a subsequent preparation on eight times the scale a 74% yield was obtained.

10-Oxohentriacontanoic acid(V)

Hydrolysis of IV (0.200 g, 0.0004 mol) with an excess of ethanolic potassium hydroxide gave, after acidification, a solid which was recrystallized (tetrachloromethane) to give V (0.133 g), m.p. 107°-108°C, (Found: C, 77.2; H, 12.8%. Calculated for $C_{31}H_{60}O_3$: C, 77.44; H, 12.58%). The mass spectrum showed only a small molecular ion at m/e 480 and a fragmentation pattern consistent with α-, β-, and α'-, β'-, fission around the 10-oxo group, as described by Raal *et al.*[34] for 18-oxo acids. Major fragments at m/e 200 [$-CH_2CO(CH_2)_8COOH+H$] and at m/e 182 ($-H_2O$ from m/e 200 fragment) were observed.

Hentriacontanoic acid(VI)

Methyl 10-oxohentriacontanoate (12.79 g, 0.026 mol), crushed 85% potassium hydroxide (11.1 g, 0.17 mol), redistilled diethylene glycol (110 cm^3) and 98% hydrazine hydrate (17.5 g, 0.35 mol) were heated at 140°C (internal temperature) for 1.5 h. Water and excess of hydrazone were then distilled off while the internal temperature rose to 200°C and the solution was held at this temperature for 4.5 h. The cooled solution was poured into 1.3 N hydrochloric acid (480 cm^3) and the resultant suspension was heated at 90°-95° for 3 h. The solid was filtered off, washed with hot water, and dried. Recrystallization (toluene) gave white crystals of VI (11.54 g, 95% yield), m.p. 94.8°-95.8°C. A second recrystallization did not alter the melting point appreciably. (Found: C, 79.4; H, 13.5%. Calculated for $C_{31}H_{62}O_2$: C, 79.8; H, 13.4%.)

An infra-red spectrum (thin solid film) showed υ = 1705 cm^{-1} (acid > C = 0) and 2500-3500 cm^{-1} (acid -OH) The sixteen equidistant progression bands in the 1180-1345 cm^{-1} region were difficult to distinguish because of interference from the broad band at 1310 cm^{-1} (> C = 0) but were distinct enough to provide support for the structure from the relationship: number of bands = ½(*n* +1) (ref 35).

The mass spectrum showed a large peak at $m/e = 466$ attributed to the molecular ion and lesser peaks at $m/e = 448$ ($M\text{-}H_2O$) and at $m/e = 423$ ($M\text{-}C_3H_7$). Between $m/e = 185$ and 422 peaks were < 5% of the base peak and the spectrum was very similar to that of the longer chain *n*-alkanoic acids described by Raal*et al.*[34] The absence of 10-oxohentriacontanoic acid was shown by complete absence of peaks at $m/e = 200$ and 182.

1-Bromotriacontane(VII)

This was preapred from hentriacontanoic acid (14 g, 0.03 mol), red mercuric oxide (4.07 g, 0.019 mol) and bromine (6.08 g, 0.038 mol) in tetrachloromethane (650 cm^3) essentially as described for 1-bromoheneicosane (I) but using a much larger volume of solvent, and adding the bromine in tetrachloromethane solution rapidly (20 min), in an attempt to minimize ester formation. Crude VII (14.56 g) containing carbonylic impurities (υ, 1740, 1720 cm^{-1}) was recrystallized once from ethanol (200 cm^3) and again from 9 : 1 V/V ethanol; heptane (110 cm^3) giving (VII) (9.57g), m.p. 63.5°C – 65.5°C containing lesser amounts of carbonylic impurities.

G.p.c. analysis showed the presence of a small amount of impurity (thought likely to be *n*-triacontyl hentriacontanoate) with a smaller retention volume than the main peak.

A solution of the recrystallized material (2.25 g) in dry heptane (300 cm^3) was passed through a 50 × 2.8 cm column of BDH 'heavy' grade magnesium oxide (160 g) which had previously been heated at 210°C/5 h. Passage of more heptane (750 cm^3) completed the elution of the bulk of pure product (1.72 g).

The whole quantity was treated in this way to give 1-bromotriacontane(VII) (6.76 g, 45% yield), m.p. 63°-64.5°C free from any carbonylic contaminants.

Recrystallization of a sample (1.1 g) from heptane gave pure VII (0.96 g), m.p. 65°-65.2°C (literature[36] cites 66.4°C) (Found: C, 72.1; H, 12.4; Br, 15.5. Calculated for $C_{30}H_{61}Br$: C, 71.82; H, 12.25; Br, 15.93%.)

The infra-red spectrum (solid film) was very similar to that of l-bromo-octadecane and l-bromoheneicosane with υ, 650 cm^{-1} (> C-Br), except in the progression band region (1180-1345 cm^{-1}) where narrower spacing of the bands was evident.

The n.m.r. spectrum was consistent with the expected structure.

In another similar preparation the crude product, after one recrystallization, was distilled under vacuum to give material b.p. approximately 230°C/2.6 Pa from which the ester had been virtually all removed. However, since acidic material was still present the column purification was carried out giving a lower yield overall (35%) of pure VII.

Ethyl hydrogen adipate (VIII)

This was prepared according to the method of Swann *et al.*[37] in 68% yield from adipic acid.

5-Ethoxycarbonylpentanoyl chloride[38](IX)

This was prepared from VIII in 84% yield by the method used by Durham *et al*[39] to prepare 5-methoxycarbonylpentanoyl chloride.

Ethyl 6-oxoheptacosanoate (X)

This was prepared from 1-bromoheneicosane (40.6 g, 0.108 mol) and (IX) (18.89 g, 0.098 mol) via the Grignard and subsequently-formed alkyl zinc chloride reagent, essentially as described for methyl 10-oxohentriacontanoate (IV).

Two recrystallizations of the crude product (42.30 g) from ethanol (220, 175 cm^3) gave pearly white plates (36 g, 83% yield based upon zinc chloride) of ethyl 6-oxoheptacosanoate(X), m.p. 65.5°-66°C.

The infra-red spectrum (solid film) had υ, 1710 cm^{-1} (ketone > C = 0) and 1740 cm^{-1} (ester > C = 0) and was very similar to that of methyl 10-oxohentriacontanoate (Found: C, 76.9; H, 12.7%. Calculated for $C_{29}H_{56}O_3$: C, 76.93; H, 12.47%.)

6-Oxoheptacosanoic acid(XI)

Hydrolysis of X (0.327 g, 0.00072 mol) with an excess of ethanolic potassium hydroxide gave after acidification, a solid which was recrystallized (tetrachloromethane) to give XI (0.125 g, 41% yield), m.p. 103°-104°C, (Found: C, 76.7, H, 12.6%. Calculated for $C_{27}H_{52}O_3$: C, 76.36; H, 12.34%.)

The mass spectrum showed only a small molecular ion at $m/e = 424$ and a fragmentation pattern consistent with α-, β-, and α'-, β'-, fission around the 6-oxo group. The two major fragments occurred at $m/e = 144(\text{-}CH_2CO(CH_2)_4COOH\text{+}H)$ and at $m/e = 126$ ($\text{-}H_2O$ from the $m/e = 144$ fragment).

Heptacosanoic acid (XII)

Huang-Minlon[40] reduction of X (35 g, 0.077 mol) essentially as described for the reduction of IV gave a product, which after two recrystallizations (ethanol, 125 cm^3, then toluene, 75 cm^3) afforded white crystals of heptacosanoic acid (25.37 g, 80% yield) m.p. 85.5°-87.0°C (literature[41] cites 86°-87°C) (Found: C, 78.6; H, 13.2%. Calculated for $C_{27}H_{54}O_2$: C, 78.96; H, 13.25%.)

The infra-red spectrum (solid film) υ = 1705 cm^{-1} (> C = 0) was very similar to that of hentriacontanoic acid the main difference being in the progression band region (1180-1345 cm^{-1}) where 14 equidistant bands were observed giving a 27 carbon chain as expected.[35]

The mass spectrum exhibited the molecular ion $m/e = 410$ as a major peak, the remaining peaks largely occurring at the low end of the spectrum up to $m/e = 130$, as described for longer chain normal acids. Only a negligible peak at $m/e = 144$ was observed indicating the virtual absence of 6-oxoheptacosanoic acid.

1-Bromohexacosane (XIII)

This was prepared from bromine (12.4 g, 0.077 mol), red mercuric oxide (8.19 g, 0.038 mol) and XII (24.7 g, 0.060 mol) in tetrachloromethane (850 cm^3) using essentially the procedure as for 1-bromotriacontane. A similar work-up gave crude product (22.75 g, 84% yield), containing a suspected ester impurity (υ, 1730-1740 cm^{-1} displayed in the infra-red spectrum). Vacuum distillation gave a cream solid (18.84 g), b.p. 205°C/2.6 Pa, which was recrystallized from acetone (40 cm^3) affording pure 1-bromohexacosane (17.45 g, 65% yield), m.p.55.5°-56.0°C (literature[42] cites 55.3-55.5°C) (Found: C, 69.9; H, 12.1; Br, 17.6%. Calculated for $C_{26}H_{53}Br$: C, 70.08; H, 11.99; Br, 17.93%.)

The infra-red spectrum (thin solid film) was similar to the analogous C_{21}- and C_{30}- compounds with $\upsilon = 650$ cm^{-1} (> C-Br).

APPENDIX B

A modified[1, 2] Williamson ether synthesis was used to prepare α, ω-alkoxy-poly(ethylene oxide). The basis of the method is the irreversible reaction between an alkoxide ion, formed by addition of potassium hydroxide to poly(ethylene glycol), and an alkyl halide, e.g.:

$$RO^- + R'Br \rightarrow ROR' + Br^-$$

For alkyl halides with β-hydrogen atoms the nucleophilic substitution reaction is accompanied by an elimination reaction:

$$RO^- + R''CH_2CH_2Br \rightarrow ROH + R''CH = CH_2 + Br^-$$

A large molar excess of alkyl halide (8-fold) compensates for losses in this way while an even larger excess of potassium hydroxide (50-fold) ensures that the reaction proceeds at a reasonable rate.

The general procedure is illustrated by the following preparation of sample 30-45-30.

Poly(ethylene glycol) 2000 (5 g, 0.0025 mol) was dissolved in warm laboratory reagent grade chlorobenzene (40 cm^3) and the solution was cooled to room temperature. Meanwhile to a slurry of powdered 85% potassium hydroxide (16 g, 0.25 mol) in chlorobenzene (20 cm^3) was added a solution of 1-bromotriacontane (20 g, 0.04 mol) in chlorobenzene (40 cm^3), and the flask was purged with dry nitrogen, then cooled in an ice bath. Stirring was commenced and the polymer solution was added drop-wise over a period of 15 minutes. Chlorobenzene was then added to fill the flask and stirring was continued for 8 h.

Residual potassium hydroxide was filtered off through a glass sinter and washed with chlorobenzene (2 x 50 cm^3). The fltrate was reduced to a small volume by rotary evaporation at 50°C and dissolved in warm toluene (20 cm^3) before adding hot iso-octane (200 cm^3, 60°C). When cool the precipitated polymer was filtered off using a glass sinter. This precipitation from toluene/iso-octane was repeated eight times, i.e. until alkyl bromide could not be detected by heating a portion of the precipitate with silver nitrate in acidified methanol.

The product was dissolved in dichloromethane (100 cm^3) and washed with distilled water (5 x 10 cm^3) until the solution was neutral. Rotary evaporation of the solution gave a residue which was freeze-dried from distilled benzene (50 cm^3) then melt evacuated (70°C/0.13 Pa) to give product (6.4 g, 90% yield).

Sample 26-45-26 was prepared by the same procedure while samples 21-45-21 and 18-45-18 were prepared by the slightly different procedure described earlier.[1]