Crystallization of block poly(ethylene oxide)

A. Friday and C. Booth
Department of Chemistry, University of Manchester, Manchester M13 9PL, UK
(Received 8 March 1978)

Urethane linked block polymers of poly(ethylene oxide) have been prepared and fractionated. Samples having 1 to 20 blocks per molecule, with molecular weights ranging from 1500 to 67 000 g/mol, have been examined by a number of techniques (small-angle X-ray scattering, differential scanning calorimetry, dilatometry, optical microscopy) in order to determine their crystallinities, melting points and spherulite growth rates. For a series of fractions having an average block length of 34 oxyethylene units with a range of 3 to 20 blocks per molecule, we find that equilibrium melting points are practically independent of molecular weight ($6000 < \bar{M}_w < 40\,000$). Analysis of the temperature dependence of the spherulite growth rates of these fractions leads to the conclusion that the pre-exponential factor (G_0) is practically independent of molecular weight and that the end interfacial free energy (σ_e) increases with molecular weight. Analysis of the experimental results for series of fractions having average block lengths of 45 or of 90 oxyethylene units is complicated by chain folding in the crystalline lamellae.

INTRODUCTION

The crystallization and crystallinity of poly(ethylene oxide) has been studied over a wide molecular weight range[1–20]. The results obtained with low molecular weight poly(ethylene oxide) reveal effects due to chain folding[1–10], polydispersity[11–13] and end groups[7–10,14]. Consequently interpretation of the variation of properties with molecular weight is not straightforward. It is of course only when $M < 10^5$ g/mol that molecular weight becomes an important variable.

It is possible to prepare block polymers by condensing low molecular weight poly(ethylene oxide) into longer chains. Such chains have the same crystallizing block irrespective of their length. Samples of differing molecular weight within the range of interest ($M < 10^5$ g/mol) might well have similar melting points. The work described herein was undertaken with this possibility in mind and was directed principally towards the effect of molecular weight on crystal growth rate.

EXPERIMENTAL AND RESULTS

Preparation

Galin *et al.*[21] have condensed α,ω-hydroxy-poly(ethylene oxide) with 2,4-diisocyanatotoluene to form chains containing up to 4 oxyethylene blocks. Since we had good reason[8] to suppose that changes in melting point would be smaller if alkylene rather than phenylene groups were incorporated into the chain we have used 1,6-diisocyanatohexane to effect the condensation. Our preparative methods lead to block polymers (I) in which m is 34, 45 or 90 and n is 2 to 20. The end groups are randomly –OH and $-CO.NH(CH_2)_6NH_2$.

$$HO[(CH_2CH_2O)_mCO.NH(CH_2)_6NH.CO.O]_{n-1}(CH_2CH_2O)_mCO.NH(CH_2)_6NH_2 \qquad (I)$$

For the purposes of comparison with the block polymers we also prepared samples of α,ω-propyliminocarbonyloxy- and (II), α,ω-hexyliminocarbonyloxy-poly(ethylene oxide).

$$CH_3(CH_2)_5NH.CO.O(CH_2CH_2O)_mCO.NH(CH_2)_5CH_3 \qquad (II)$$

Commercial samples of α,ω-hydroxy-poly(ethylene oxide) (Hoechst Chemicals) were purified by recrystallization from a mixture of toluene and 2,2,4-trimethylpentane and freeze-dried from solution in benzene.

Poly(ethylene oxide) of molecular weight 1500 was dried by evacuation of the melt (<1 Pa, 50°C, 2 h). This polymer (11.21 g) was dissolved in dry benzene (250 cm^3, dried over and distilled from calcium hydride) and catalyst (stannous octoate, 0.10 g) was added. A solution of 1,6-diisocyanatohexane (freshly distilled under reduced pressure; 1.26 g) in dry benzene (10 cm^3) was added to the vigorously stirred polymer solution over a period of 15 min. The mixture was then refluxed (80°C, 10 h; calcium chloride moisture trap). The resulting block polymer was recovered by freeze-drying the mixture. Similar recipes were used to form block copolymers from poly(ethylene oxide) 2000 and 4000.

The essential features of the procedure were (a) that moisture was rigorously excluded, (b) that the reaction mixture was equimolar in isocyanato and hydroxy groups, (c) that the reactants were dilute and (d) that the temperature was kept well below 100°C. Under these conditions chain termination and crosslinking reactions were minimized. At the end of the reaction terminal isocyanato groups reacted with moisture to form amino groups.

1-Isocyanatopropane was prepared by the method of Ulrich and Sayigh[22]. Dry poly(ethylene oxide) of molecular weight 1500 (1.74 g) in dry benzene (30 cm^3) was added slowly to a vigorously stirred solution of 1-isocyanatopropane (freshly distilled, 0.20 g) and stannous octoate (0.01 g) in dry benzene (30 cm^3). Stirring was continued for 5 h. The resulting α,ω-propyliminocarbonyloxy-ended polymer was

0032–3861/78/1909–1035$02.00

Table 1 Molecular characteristics of the samples

Sample	$\bar{M}_n$ (g/mol)				
	V.p.o.	E.g.a.	G.p.c.	n	$\bar{M}_w/\bar{M}_n$
$(34\text{–}0)_1$	1 550	1 550	1 500	1	1.05
$(34\text{–}3)_1$			1 600	1	1.04
$(34\text{–}6)_1$			1 700	1	1.04
$(34\text{–}6)_3$			5 100	3.1	1.21
$(34\text{–}6)_5$			8 200	4.9	1.12
$(34\text{–}6)_8$			12 800	7.7	1.12
$(34\text{–}6)_{11}$			19 100	11.4	1.20
$(34\text{–}6)_{16}$			26 400	15.8	1.14
$(34\text{–}6)_{20}$			33 500	20.1	1.20
$(45\text{–}0)_1$	2 050	2 300	2 000	1	1.03
$(45\text{–}3)_1$			2 100	1	1.03
$(45\text{–}6)_1$			2 100	1	1.03
$(45\text{–}6)_2$			3 980	1.8	1.16
$(45\text{–}6)_5$			9 900	4.6	1.09
$(45\text{–}6)_6$			13 900	6.4	1.16
$(45\text{–}6)_9$			18 600	8.6	1.17
$(45\text{–}6)_{10}$			21 300	9.8	1.20
$(45\text{–}6)_{12}$			26 000	12.0	1.19
$(45\text{–}6)_{15}$			32 700	15.1	1.28
$(90\text{–}0)_1$	4 100	4 200	3 800	1	1.06
$(90\text{–}3)_1$			3 900	1	1.06
$(90\text{–}6)_1$			3 900	1	1.06
$(90\text{–}6)_2$			8 900	2.1	1.27
$(90\text{–}6)_5$			19 300	4.6	1.29
$(90\text{–}6)_6$			24 200	5.8	1.50
$(90\text{–}6)_8$			32 700	7.8	1.36
$(90\text{–}6)_{12}$			51 200	12.3	1.40
$(90\text{–}6)_{16}$			67 100	16.1	1.28

recovered by freeze-drying the mixture. Similar recipes were used to form the other propyliminocarbonyloxy- and hexyliminocarbonyloxy-ended polymers.

Fractionation of block polymers

The condensation reaction leads to block polymers of moderate molecular weight ($\bar{M}_w$ from g.p.c. in the range 20 000 to 50 000) with wide molecular weight distributions ($\bar{M}_w/\bar{M}_n$ from g.p.c. in the range 2.0 to 2.3). Samples suitable for our experiments were obtained by fractionating the polymers by an adaptation of the procedure used earlier for poly(ethylene oxide) homopolymers[18,23]. Some refractionation of fractions was necessary in order to obtain samples of suitably narrow molecular weight distribution.

Nomenclature

Samples are denoted by the average length of the oxyethylene block (in oxyethylene units) and the length of the methylene chain of the end or linking group. For example, the polymers formed from α,ω-hydroxy-poly(ethylene oxide) of $\bar{M}_n$ = 1500 g/mol are denoted $(34\text{–}X)_n$ where $X = 0$ (OH), $X = 3$ [$CH_3(CH_2)_2NH.CO.O$] or $X = 6$ [$CH_3(CH_2)_5NH.CO.O$ or $O.CO.NH(CH_2)_6NH.CO.O$], and n is the average number of oxyethylene blocks in the polymer.

Characterization

Infra-red spectroscopy was used to determine residual hydroxy end groups in the alkyliminocarbonyloxy-ended polymers. Estimated conversions were >95%.

Vapour pressure osmometry (v.p.o., Mechrolab Model 301A, benzene at 25°C) and end group analysis (phthaloylation in pyridine) were used to measure the number-average molecular weights ($\bar{M}_n$) of the hydroxy-ended polymers. All other molecular weights were measured by gel permeation chromatography, and compared with poly(ethylene oxide) fractions of known molecular weight. Solvents were either tetrahydrofuran at 25°C ($n = 1$) or *N,N*-dimethylacetamide at 80°C ($n > 1$): details of the method have been given elsewhere[18,24]. All chromatograms were corrected for instrumental spreading.

Results are given in *Table 1*. The molecular weight distributions of the low polymers ($n = 1$) are practically unchanged by the preparative methods we have used. Average molecular weights (known to ± 100 g/mol) are increased slightly when the hydroxy end groups are replaced by the heavier alkyliminocarbonyloxy end groups. The values of $\bar{M}_n$ found for the hydroxy-ended polymers are close to those quoted by the manufacturers; accordingly the numbers of oxyethylene blocks (n) in the fractions were calculated assuming average oxyethylene block weights of 1500, 2000 or 4000 g/mol as appropriate.

Small-angle X-ray scattering

Lamella spacings (l_x) were determined by small-angle X-ray scattering (SAXS). The method has been described elsewhere[13]. Lamella spacings calculated via Bragg's Law are listed in *Table 2*. Scattering peaks of the block polymers ($n > 1$) were diffuse: peak widths corresponded to ±2 nm compared with less than ±0.5 nm for the polymers with n = 1. Consequently lamella spacings are known to ±1 nm (n > 1) and ±0.2 nm (n = 1).

Table 2 Lamella spacings (l_x/nm) by SAXS

Sample	T_c (°C)	
	23	33
$(34\text{–}0)_1$	10.0	9.7
$(34\text{–}3)_1$	11.0	11.0
$(34\text{–}6)_1$	11.3	11.3
$(34\text{–}6)_3$	14.8	13.2
$(34\text{–}6)_5$	15.4	14.8
$(34\text{–}6)_8$	16.0	15.6
$(34\text{–}6)_{11}$	16.8	15.7
$(34\text{–}6)_{16}$	17.9	19.3
$(34\text{–}6)_{20}$	18.8	19.3
$(45\text{–}0)_1$	13.1	13.1
$(45\text{–}3)_1$	13.9	13.8
$(45\text{–}6)_1$	11.1	13.5
$(45\text{–}6)_2$	11.1	–
$(45\text{–}6)_9$	12.5	17.5
$(45\text{–}6)_{10}$	12.7	18.1
$(45\text{–}6)_{12}$	13.3	20.0
$(45\text{–}6)_{15}$	13.9	19.7
	T_c (°C)	
	40	45
$(90\text{–}0)_1$	15.4	15.4
$(90\text{–}3)_1$	16.0	–
$(90\text{–}6)_1$	16.4	16.2
$(90\text{–}6)_2$	17.4	18.8
$(90\text{–}6)_5$	18.0	21.7
$(90\text{–}6)_6$	19.6	–
$(90\text{–}6)_8$	19.6	20.0
$(90\text{–}6)_{12}$	20.1	23.1
$(90\text{–}6)_{16}$	19.8	20.5

Table 3 Heats of fusion (Δh) and crystallinity of the oxytheylene component (X_{oe}) from d.s.c.

Sample	$\Delta h(T_m)$ (J/g)	X_{oe}
T_c = 25°C:		
$(34-0)_1$	175	0.90
$(34-3)_1$	134	0.79
$(34-6)_1$	125	0.80
$(34-6)_3$	105	0.62
$(34-6)_5$	100	0.59
$(34-6)_8$	92	0.55
$(34-6)_{11}$	88	0.53
$(35-6)_{16}$	75	0.46
$(34-6)_{20}$	54	0.34
T_c = 25°C:		
$(45-0)_1$	172	0.86
$(45-3)_1$	153	0.84
$(45-6)_1$	126	0.72
$(45-6)_2$	120	0.67
$(45-6)_5$	118	0.66
$(45-6)_6$	99	0.56
$(45-6)_9$	99	0.56
$(45-6)_{10}$	93	0.53
$(45-6)_{12}$	85	0.48
$(45-6)_{15}$	71	0.41
T_c = 40°C:		
$(90-0)_1$	173	0.85
$(90-3)_1$	164	0.84
$(90-6)_1$	140	0.73
$(90-6)_2$	142	0.73
$(90-6)_5$	128	0.66
$(90-6)_6$	115	0.59
$(90-6)_8$	103	0.53
$(90-6)_{12}$	103	0.53
$(90-6)_{16}$	99	0.51

Differential scanning calorimetry

Heats of fusion of the solid polymers were determined by differential scanning calorimetry (d.s.c., Perkin–Elmer DSC-2, details elsewhere[10]). Samples $(45-6)_1$ (T_c = 25°C) and $(90-6)_1$ (T_c = 40°C) showed double melting peaks characteristic of poly(ethylene oxide) samples containing two kinds of lamellae. The temperature scale of the calorimeter was not calibrated and consequently melting temperatures are not recorded; the changes in melting point within a series of samples confirmed those found by dilatometry (see later). Values of the heat of fusion at the melting point, $\Delta h(T_m)$, are listed in *Table 3*. These values were reproduced to ±5 J/g. Values of the heat of fusion per g of oxyethylene at 54°C [Δh_{oe}(54°C)], calculated as described elsewhere[10], were divided by the heat of fusion of perfectly crystalline poly(ethylene oxide) at 54°C[10] to obtain the fractional crystallinity of the oxyethylene component [$X_{oe} = \Delta h_{oe}$ (54°C)/200] of the samples (*Table 3*).

Dilatometry

Melting points were determined by dilatometry as described elsewhere[13]. Values are listed in *Table 4*. Melting points of the low molecular weight polymers (n = 1) were independent of T_c (reproducibility of determination was ±0.2°C); those of the block polymers ($n > 1$) increased as T_c was increased. The effect was most marked at the highest values of n. Reproducibility of T_m for the block polymers was ±0.5°C.

We were concerned about the possible effect of annealing upon T_m of a block polymer. Accordingly the melting programme (heating rate 6°C/h) was started at various temperatures in the range 2 to 5°C below T_m. This had no effect upon T_m in series $(34-6)_n$ and $(45-6)_n$. Series $(90-6)_n$ was not studied in this way.

The volume change on crystallization, Δv, was determined by dilatometry as described elsewhere[19]. In order to correctly assess the height of mercury in the capillary of the dilatometer at the start of the crystallization the rate of crystallization must be low. At a given T_c the crystallization rate varies greatly within a series: by a factor of 10–20 within a series of block polymers ($n > 1$) and by a much larger factor if the low polymers (n = 1) are included. Consequently the values of Δv for the block polymers listed in *Table 5* are subject to considerable uncertainty (perhaps ±25%) particularly when n is small. Values of the volume change on crys tallization per g oxyethylene (Δv_{oe}) were divided by the volume changes on perfect crystallization (Δv^0), calculated as described elsewhere[19], to obtain the fractional crystallinities of the oxyethylene component ($X_{oe} = \Delta v_{oe}/\Delta v^0$) listed in *Table 5*.

Optical microscopy

Radial growth rates of spherulites were measured on the hot stage of a polarizing microscope as described earlier[18]. At the lower temperatures used for series $(34-6)_n$ and $(45-6)_n$ the stage was modified to allow temperature control (to ±0.05°C) by water circulated from a thermostat. Only the block polymers ($n > 1$) were studied. Comparable results for poly(ethylene oxide) homopolymers can be found elsewhere[4,7,15–20].

Table 4 Melting points T_m (°C) by dilatometry

Sample	T_c(°C)			
	20	25	29	33
$(34-0)_1$	48.4	48.6	48.7	48.6
$(34-3)_1$	47.3	47.3	47.4	47.1
$(34-6)_1$	46.7	46.8	–	47.2
$(34-6)_3$	48.6	48.9	49.6	50.3
$(34-6)_5$	–	48.8	49.7	–
$(34-6)_8$	47.1	47.6	48.4	49.8
$(34-6)_{11}$	46.4	47.9	47.6	49.0
$(34-6)_{20}$	45.7	46.6	47.4	48.7
$(45-0)_1$	53.5	53.6	53.7	53.8
$(45-3)_1$	53.4	53.0	52.9	58.2
$(45-6)_1$	51.2	51.2	50.8	51.2
$(45-6)_2$	49.4	51.5	52.5	53.0
$(45-6)_6$	48.6	49.0	51.2	51.9
$(45-6)_{12}$	47.2	48.5	50.3	51.5
$(45-6)_{15}$	46.2	48.5	50.1	51.0

	T_c (°C)		
	35	40	45
$(90-0)_1$	61.9	–	62.2
$(90-3)_1$	59.0	–	59.0
$(90-6)_1$	57.6	58.4	57.8
$(90-6)_2$	58.1	58.5	59.2
$(90-6)_5$	56.6	57.3	58.4
$(90-6)_6$	56.2	56.9	58.8
$(90-6)_8$	55.7	56.6	58.4
$(90-6)_{12}$	55.4	56.5	58.4
$(90-6)_{16}$	55.5	56.5	58.4

Spherulites were initiated sporadically with time over the initial part of the crystallization. Impinged spherulites eventually filled the field of view. The spherulite number density (ν) increased as n increased; the melting temperature (normally 100°C) was decreased to 80°C in order to increase ν when n was low. All spherulites had a close-textured appearance: the Maltese cross extinction pattern was not apparent in the block polymers of low n. Spherulite radii increased linearly with time up to the point of impingement. Variation of melting temperature (80° to 100°C), melting time (2 to 20 min) and film thickness (0.1 to 1 mm) had no effect on the growth rate.

Table 5 Volume contracton and crystallinity of the oxyethylene component (X_{oe}) from dilatometry

Sample	T_c (°C)					
	25	29	33	25	29	33
	Δv_{sp} (10^{-2} cm^3/g)			X_{oe}		
(34–6)$_3$	3.6	3.9	4.7	0.51	0.54	0.64
(34–6)$_5$	3.3	3.6	–	0.47	0.50	–
(34–8)$_8$	3.3	3.7	4.2	0.47	0.52	0.57
(34–6)$_{11}$	2.7	2.9	–	0.39	0.40	–
(34–6)$_{20}$	3.3	3.4	3.5	0.47	0.47	0.48
(45–6)$_2$	3.3	2.5	3.5	0.46	0.34	0.46
(45–6)$_6$	4.0	4.3	4.8	0.56	0.58	0.64
(45–6)$_{12}$	3.6	3.2	3.8	0.50	0.43	0.50
(45–6)$_{15}$	2.9	3.5	3.9	0.40	0.48	0.52
	T_c (°C)					
	35	40	45	35	40	45
	Δv_{sp} (10^{-2} cm^3/g)			X_{oe}		
(90–6)$_2$	4.3	4.2	4.5	0.53	0.51	0.53
(90–6)$_6$	4.0	4.0	4.0	0.50	0.49	0.47
(90–6)$_8$	4.7	4.5	4.7	0.58	0.55	0.55
(90–6)$_{12}$	4.5	4.2	3.9	0.56	0.51	0.46

Radial growth rates (G_s) were measured for 3 spherulites in each film and 3 films were studied for each sample. Films were crystallized only once in order to avoid possible degradation. Reproducibility was ±10%. Values of G_s are listed in *Table 6* together with (for convenience) the weight-average molecular weights ($\bar{M}_w$) of the polymers.

DISCUSSION

Crystal structure

The SAXS photographs show that the stacked lamella structure characteristic of low molecular weight poly(ethylene oxide)[1,2] is present in all our polymers, although the width of the scattering peaks for $n > 1$ indicates greater irregularity in the structure of the block polymers. The lamella spacings of *Table 2*, in conjunction with the calorimetric and dilatometric results of *Tables 3* and *5*, can be used to illuminate interesting features of the lamella structure.

Series 34. There is no dependence of l_x on T_c within the range T_c = 23° to 33°C. The extended chain length of the oxyethylene block of 34 units is 9.5 nm* so it seems likely that all samples have the crystalline oxyethylene blocks in

Table 6 Spherulite growth rates (G_s/μm/min) from optical microscopy

Sample	$\bar{M}_w$	T_c (°C)									
		18.1	20.1	21.1	23.1	25.0	25.9	27.0	28.1	29.3	31.3
(34–6)$_3$	6 200	–	–	190	125	98	84	69	51	27	8.1
(34–6)$_5$	9 200	–	–	120	82	62	50	35	32	17	5.8
(34–6)$_8$	14 300	–	120	77	52	38	26	23	12	7.2	–
(34–6)$_{11}$	22 900	91	63	52	33	21	19	12	6.6	1.9	–
(34–6)$_{16}$	30 200	65	46	38	26	16	11	8.0	4.6	–	–
(34–6)$_{20}$	40 200	71	50	40	27	17	12	6.5	3.1	–	–
		T_c(°)									
		25.1	26.2	28.0	28.9	30.1	31.9	33.0	34.0	35.2	36.2
(45–6)$_5$	10 800	–	160	120	106	87	53	32	18	8.3	6.4
(45–6)$_6$	16 100	–	110	82	67	54	36	17	12	6.8	3.8
(45–6)$_9$	21 800	110	87	63	51	37	26	12	5.3	–	–
(45–6)$_{10}$	25 600	96	77	58	45	27	18	6.8	4.0	–	–
(45–6)$_{12}$	30 900	84	66	45	33	22	13	5.1	3.2	–	–
(45–6)$_{15}$	42 000	81	60	36	25	18	6.9	4.0	1.8	–	–
		T_c (°C)									
		41.0	42.0	42.5	43.0	43.5	44.0	44.4	45.1	45.5	46.1
(90–6)$_2$	11 300	–	–	–	180	120	72	59	30	16	7.8
(90–6)$_5$	24 900	–	–	–	100	57	35	26	15	7.1	2.9
(90–6)$_6$	36 300	–	–	86	56	39	22	11	4.2	–	–
(90–6)$_8$	44 500	140	91	77	44	28	11	6.4	–	–	–
(90–6)$_{12}$	71 700	76	60	54	23	15	7.8	–	–	–	–
(90–6)$_{16}$	85 900	52	37	31	16	9.5	3.1	–	–	–	–

---

* Calculated for [25] a 7.2 helix with a length of 0.28 nm/unit. Note that the alkyliminocarbonyloxy groups will increase the extended chain length by 0.5 to 0.75 nm/group.

Table 7 Crystallinity of the oxyethylene component (X_{oe})

	T_c(°C)		
	23	25	25
Sample	SAXS	D.s.c.	Dilatometry
$(34\text{–}0)_1$	0.80[a]	0.90	–
$(34\text{–}3)_1$	0.81	0.79	–
$(34\text{–}6)_1$	0.83	0.80	–
$(34\text{–}6)_3$	0.60	0.62	0.55
$(34\text{–}6)_5$	0.58	0.59	0.50
$(34\text{–}6)_8$	0.56	0.55	0.51
$(34\text{–}6)_{11}$	0.53	0.53	0.40
$(34\text{–}6)_{16}$	0.50	0.46	–
$(34\text{–}6)_{20}$	0.47	0.34	0.48

[a] Assumed

extended chain conformation (i.e. unfolded). The increase of l_x with n within the series is consistent with an increase in the proportion of oxyethylene blocks entering non-crystalline layers in the stack. With this model, and assuming that the thickness of a crystalline layer is not changed by changes in the non-crystalline layers, we can calculate a fractional crystallinity of the oxyethylene component of the samples from the equation

$$X_{oe} = 0.8 l_{x,0}/w_e l_x$$

where we further assume that samples $(34\text{–}0)_1$, with spacing $l_{x,0}$, is 80% crystalline[10] and where w_e, the weight fraction of oxyethylene in the sample, is used to approximate the corresponding volume fraction. A comparison of the values of X_{oe} derived from SAXS, d.s.c. and dilatometry is made in *Table 7*. The agreement is satisfactory. The simple model in which the proportion of oxyethylene blocks in the non-crystalline layers increases with n seems justified for series 34. The width of the scattering peak when $n > 1$ is possibly due to variation in thickness of the non-crystalline layers.

Series 45. Except for samples $(45\text{–}0)_1$ and $(45\text{–}3)_1$ there is a marked difference between l_x for T_c = 23°C and that for T_c = 33°C (*Table 2*). The extended chain length of the oxyethylene block of 45 units is 12.6 nm. We conclude that at T_c = 33°C all samples have the crystalline oxyethylene blocks in extended chain conformation, whereas at T_c = 23°C [excepting samples $(45\text{–}0)_1$ and $(45\text{–}3)_1$] the oxyethylene blocks may fold in the crystalline layers. An earlier study[10] of an homologous series of α,ω-alkoxy-poly(ethylene oxide) samples based on a central oxyethylene block of 45 units showed that, at T_c = 25°C, folded chain crystals formed in the α,ω-heptoxy and higher homologues. Consequently our present finding of a transition in behaviour between sample $(45\text{–}3)_1$ and $(45\text{–}6)_1$ is not surprising. The values of X_{oe} of 0.85 for samples $(45\text{–}0)_1$ and $(45\text{–}3)_1$ and 0.72 for samples $(45\text{–}6)_1$ are also in keeping with those found earlier[10] for extended (0.85) and folded (0.70) chain crystals of α,ω-alkoxy-poly(ethylene oxide). Another parallel between the alkoxy- and the alkyliminocarbonyloxy-ended polymers is the finding by d.s.c. of a double peaked endotherm for sample $(45\text{–}6)_1$ as for the α,ω-heptoxy-polymer[10], i.e. an endotherm characteristic of a solid containing both extended and folded chain crystals. Calculation of the crystallinity from SAXS is not sensible for systems in which the extent of chain folding may change in response to changes in composition. Nevertheless the values of X_{oe} obtained by d.s.c. and dilatometry, considered together with the SAXS results, *qualitatively* confirm the conclusion drawn from consideration of the results for series 34 (in which chain folding is not a problem) that the proportion of oxyethylene blocks entering the non-crystalline layers is increased as n is increased.

Series 90. There is no dependence of l_x on T_c within the range T_c = 40° to 45°C. The extended chain length of the oxyethylene block of 90 units is 25.2 nm and we conclude that all samples have the oxyethylene blocks in the crystalline layers in folded chain conformation. The SAXS results for sample $(45\text{–}6)_1$, l_x = 11.1 nm, and for sample $(90\text{–}6)_1$, l_x = 16.4 nm, are consistent with a greater extent of chain folding in the sample with the longer oxyethylene block. As before our results (*Tables 2, 3* and *5*) *qualitatively* indicate that the proportion of the oxyethylene blocks entering the non-crystalline layers is increased as n is increased.

Melting points

The changes in melting point resulting from end group modification and condensation are illustrated for series 34 in *Figure 1*. Similar changes are apparent in the melting of series 45 and 90 (*Table 4*) although these results are complicated by chain folding.

When n = 1, in all three series, the introduction of alkyliminocarbonyloxy end groups depresses the melting point by 2° to 4°C (*Table 4*). This effect differs from that found[10] for alkyloxy end groups where. within the homologous series 45, the melting points were roughly constant (extended-chain crystals) or increased with an increase in the methylene chain length (folded-chain crystals). We suppose that endothermic mixing of methylene and oxyethylene segments, which acts to increase the stability of the crystals relative to the melt, is offset by exothermic mixing of iminocarbonyloxy and oxyethylene segments.

There are three obvious effects of condensation in series 34 (see *Figure 1*): (a) an initial increase in T_m compared with that of sample $(34\text{–}6)_1$; (b) a fall in T_m as n is increased; (c) a sensitivity of T_m to T_c which is particularly marked when n is large. Similar trends can be discerned in the results for series 45 and 90 if allowance is made for the probable effects of chain folding.

The sensitivity of T_m to T_c (absent when n = 1) is an indication of the importance of kinetic factors during the crystallization of the block polymers. The equilibrium melting point (T_m^e) of a polymer is that of a sample crystallized (and

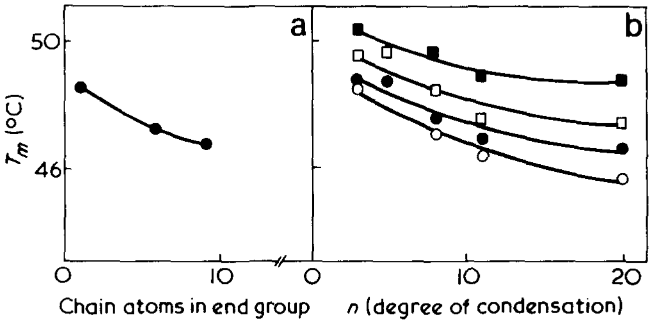

Figure 1 Melting points of the samples of series 34 plotted against: (a) number of chain atoms in end group when n = 1; (b) average degree of condensation when n > 1. Values of T_c are ○, 20; ●, 25; □, 29; ■, 33°C. Values of T_m for n = 1 are practically independent of T_c

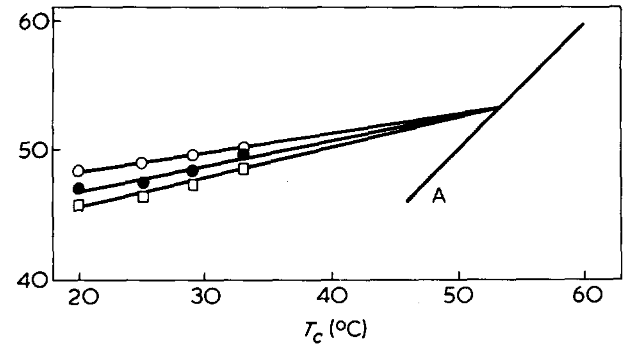

Figure 2 Melting points of samples plotted against T_c: ○, $(34–6)_3$; ●, $(34–6)_8$; □, $(34–6)_{20}$. A, $T_m = T_c$

melted) whilst maintaining equilibrium between solid and liquid phases at all times. This is the case when G_s approaches zero, i.e. when T_c is near to T_m. Extrapolation of T_m *versus* T_c to $T_m = T_c$ has been used to estimate T_m^e [26–28]: such an extrapolation is shown in *Figure 2*. The extrapolation is unguided by theory, especially for block polymers, and must be interpreted with caution[27]. The simplest interpretation is that T_m^e is identical for all the block polymers of series 34.

We have not examined the results for series 45 and 90 in this way since we are wary of changes in chain folding in the solids.

We have shown elsewhere[29] that the coupling of two poly(ethylene oxide) blocks of length 36 oxyethylene units leads to an increase in melting point of about 4°C. This can be explained if both blocks enter the crystal successively (adjacent entry) so that the entropy decrease per block on crystallization from the melt is reduced compared to the entropy decrease per block on independent entry of blocks from two molecules. The Flory–Vrij[30] theory of melting can be used[29] to quantify this effect. We have also shown[31] that the theory can be used to predict T_m^e for a series of block polymers differing only in degree of condensation n. For *constant end interfacial free energy* of the lamellae (σ_e), T_m^e increases with n for adjacent entry of successive blocks (as pointed out above) and T_m^e is constant for random entry of successive blocks. We find no evidence (*Table 4, Figure 1*) of an increase in T_m beyond that found between $n = 1$ and $n = 2$ or 3. A possible interpretation of our results is that entry is adjacent for 2 (or 3) successive blocks in the chain but that over a longer range entry becomes more random. This is in keeping with the disordered structures found for the solid block polymers. Adopting this view allows us to fix T_m^e for the block polymers of series 34 at a constant value just above 50°C. The linear extrapolation of *Figure 2* is to $T_m^e = 53$°C. This will be an upper limit to T_m^e since downward curvature in the plot is likely[27]. We are aware that our results would accommodate a variation of T_m^e within series 34 of ±2°C.

Spherulite growth rates

The effect of molecular weight on spherulite growth rate is illustrated in *Figure 3*. Radial growth rates (G_s) for given values of T_c chosen centrally within the ranges studied are compared with similar rates obtained[18] for poly(ethylene oxide) homopolymers. Not only is the molecular weight dependence of crystallization rate opposite in sign for the two types of polymer, but also the crystallization temperatures at which the rates are similar are very different (*Figure 3*: $T_c = 54$°C for the poly(ethylene oxide) homopolymers compared with, for example, 25°C for the series 34 block polymers).

Assuming that crystallization is by a single mechanism the crystal growth rate (G) can be written[32,33] with sufficient accuracy for a small undercooling:

$$G = G_0 \exp(-\Delta F^a/RT_c)\exp(-\Delta F^*/RT_c) \quad (1)$$

The product $G_0 \exp(-\Delta F^a/RT_c)$ represents the elementary rate of transport of chain segments across the melt/crystal interface, ΔF^a being the activation free energy for that process. Forms of the equation other than the Arrhenius may be more appropriate[4,32]. The elementary rate is modified by the nucleation rate and the term $\exp(-\Delta F^*/RT_c)$ incorporates the free energy of formation from the melt of a growth nucleus of critical size. For growth of lamella crystals via monolayer nucleation, given that one nucleus leads uniquely to one monolayer[34], ΔF^* can be written:

$$\Delta F^* = \frac{4\sigma_u \sigma_e T_m^e}{\Delta h^0 (T_m^e - T_c)} = \frac{4\sigma_u \sigma_e T_m^e}{\Delta h^0 \Delta T} \quad (2)$$

where σ_u and σ_e are the free energies of formation from the melt of the lateral (σ_u) and end (σ_e) interfaces of the lamella crystal, T_m^e is the equilibrium melting point (already defined) and Δh^0 is the enthalpy of fusion of perfectly crystalline polymer. The temperature difference $\Delta T = T_m^e - T_c$ is the undercooling. In equation (2) all the free energies and the enthalpy are expressed in J/mol. *For practical purposes over a limited temperature range* the parameters, σ_u, σ_e and Δh^0 can be treated as temperature independent.

For a homopolymer, provided that chain ends are not cocrystallized, T_m^e depends upon molecular weight. Theory[30,35] predicts a rapid increase in T_m^e with M at molecular weights less than 10^5 g/mol. Experiment shows that the melting points of poly(ethylene oxide) vary from 39°C ($M \sim 10^3$) to 68°C ($M \sim 10^5$). The increase of T_m^e with M serves to increase ΔT with M and, through equations (1) and (2), to increase G with M. Thus, in a qualitative way, the difference in behaviour of the homopolymer and the block polymers (T_m^e constant) can be partly explained.

Analysis of growth rates: series 34

We avoid complication due to chain folding by considering only the results for *series 34*.

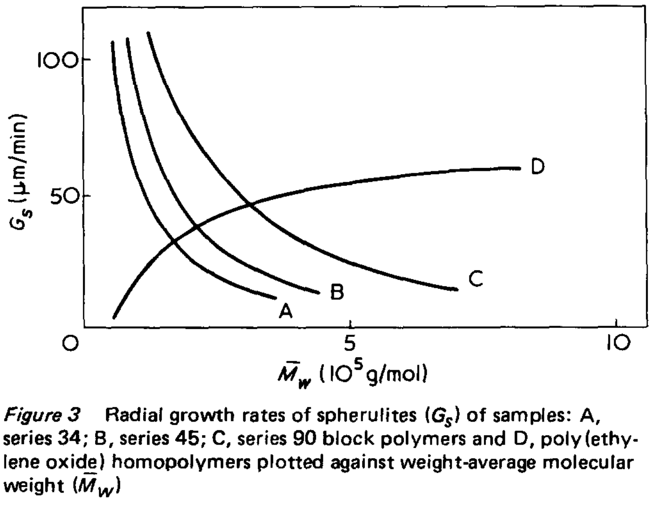

Figure 3 Radial growth rates of spherulites (G_s) of samples: A, series 34; B, series 45; C, series 90 block polymers and D, poly(ethylene oxide) homopolymers plotted against weight-average molecular weight ($\bar{M}_w$)

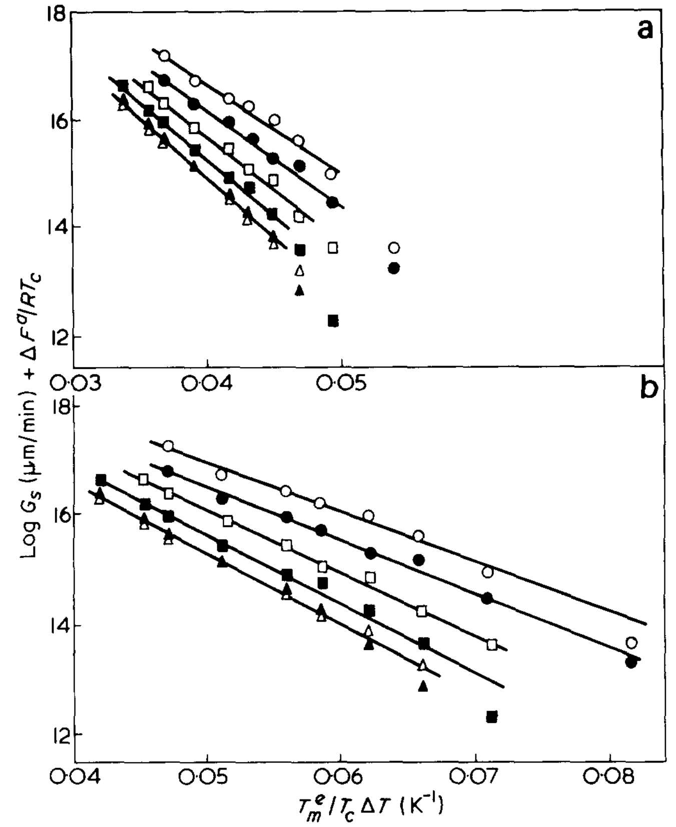

Figure 4 The effect of temperature on spherulite growth rates: ○, $(34\text{–}6)_3$; ●, $(34\text{–}6)_5$; □, $(34\text{–}6)_8$; ■, $(34\text{–}6)_{11}$; △, $(34\text{–}6)_{16}$; ▲, $(34\text{–}6)_{20}$. T_m^e is taken to be (a) 51°C and (b) 44°C

Kovacs and Gonthier[4] and others[7] have shown that spherulite growth rates (G_s) of poly(ethylene oxide) bear a one to one correspondence to crystal growth rates wherever the two have been measured. Accordingly we substitute G_s for G in equation (1).

A proper analysis of the temperature dependence and molecular weight dependence of the growth rates requires correct identification of both ΔF^a and T_m^e.

We have used an Arrhenius approximation for the transport term and have equated ΔF^a, following Kovacs and Gonthier, with the activation energy for viscous flow, i.e. 29.3 kJ/mol. Our analysis depends somewhat on this assumption. However, we have carried through the calculation using the universal WLF approximation with $T_g = -67$°C. The results are similar; the conclusions are unchanged.

The problem of identifying T_m^e from our results has already been discussed. In the absence of unequivocal values we have examined several possibilities; results are presented for (a) $T_m^e = 51$°C for all samples and (b) T_m^e decreasing with n from 51°C ($n = 3$) to 49°C ($n = 20$).

Conventional plots of $\log G_s + \Delta F^a/RT_c$ against $T_m^e/T_c\Delta T$, as required by equations (1) and (2), are illustrated in *Figure 4(a)* for the case $T_m^e = 51$°C. Deviation from linearity is apparent at high T_c. To allow for this we ignore the last point and compute the best straight line through the remainder (least squares). Values of K_s (the negative of the slope) and $\log(G_0)$ (the intercept) are listed in *Table 8*. Because of the limited range of the plots and the long extrapolation to the intercept we determine K_s to no better than ±10°C and $\log(G_0)$ to no better than ±0.5. The values of K_s are higher than those found[4] for poly(ethylene oxide) homopolymers by a similar procedure. We also detect a slight increase in K_s with n. According to equations (1) and (2):

$$K_s = 4\sigma_u\sigma_e/R\Delta h^0$$

We take for granted that σ_u and Δh^0 are independent of n, so that the increase in K_s presumably reflects an increase in σ_e†. The pre-exponential factor G_0 is practically independent of n. The trend in the results obtained with constant T_m^e is towards an increase in $\log(G_0)$ with n but this is not outside the error of the experiment. We note that varying T_m^e in the range 51° ($n = 3$) to 53°C ($n = 20$) does not change this conclusion.

The stable solids of the block polymers of series 34 have their oxyethylene blocks in extended chain conformation. However, as Kovacs and Gonthier have pointed out[4], it is likely that the growth nuclei have folded chains. We have shown[7] that transitions in growth rate due to chain folding are not confined to hydroxy ended polymers. If the oxyethylene blocks are once-folded on crystallization then it is appropriate[4] to calculate the undercooling from the equilibrium melting point of the metastable once-folded chain crystal. We have taken this point of view in other publications[16,18] where we have implicitly used equilibrium melting points of folded chain crystals in our calculations.

We have observed[10] a difference of about 6°C between the melting points of folded and extended chain crystals of α,ω-octadecoxy-poly(ethylene oxide) with an oxyethylene block of length 34 chain units. The double peaks observed by d.s.c. for samples $(45\text{–}6)_1$ and $(90\text{–}6)_1$ were separated by 8° and 5°C, respectively. We suppose that the equilibrium melting points of once-folded crystals of series 34 would lie some 5° to 10°C below the melting points of the extended chain crystals. A conventional plot of the growth rate data for $T_m^e = 44$°C is illustrated in *Figure 4(b)*. The plots are linear over the temperature range. Values of K_s and $\log(G_0)$ calculated (least squares) using all the points are listed in *Table 8*. The trends in the results are similar to those calculated earlier using other estimates of T_m^e: in particular K_s increases slightly with n and $\log(G_0)$ is independent of n. The values of K_s are higher than that, of about 10°C, found by Kovacs and Gonthier for poly(ethylene oxide) 6000 by calculating the undercooling from 55.7°C (once-folded chain) rather than 59.3°C (extended chain).

Our analysis of the temperature and molecular weight dependence of the block polymers of *series 34* leads us to the following conclusions. (a) The uncertainty regarding the exact values of T_m^e for the series of block polymers is not a serious problem since several sensible assumptions lead to similar results. (b) The pre-exponential factor G_0 is practically independent of molecular weight for the block co-

Table 8 K_s and $\log(G_0)$ for series 34 assuming (a) $T_m^e = 51$°C, (b) $T_m^e = 51$° to 49°C in equal decrements, and (c) $T_m^e = 44$°C*

Sample	$\bar{M}_w$ (g/mol)	K_s (K) (a)	K_s (K) (b)	K_s (K) (c)	Log G_0 (μm/min) (a)	Log G_0 (μm/min) (b)	Log G_0 (μm/min) (c)
$(34\text{–}6)_3$	6 200	167	167	98	23.4	23.4	21.9
$(34\text{–}6)_5$	9 200	173	167	96	23.1	23.0	21.3
$(34\text{–}6)_8$	14 300	204	192	112	23.9	23.7	21.7
$(34\text{–}6)_{11}$	22 900	219	200	135	24.0	23.6	22.4
$(34\text{–}6)_{16}$	30 200	219	194	124	23.3	23.1	21.4
$(34\text{–}6)_{20}$	40 200	235	202	140	24.3	23.6	22.3

* See text for details

---

† There is no inconsistency in setting T_m^e constant and finding σ_e to vary with n: an increase in σ_e may well compensate a decrease in the entropy of crystallization caused by statistical factors (see earlier discussion).

polymers ($6000 < \bar{M}_w < 40\,000$). (c) The end interfacial free energy (σ_e) increases as the molecular weight increases. (This increase is probably a consequence of the increase in the thickness of the non-crystalline layers in the stacked lamella structures.)

Analysis of growth rates: series 45 and 90

We have examined the temperature dependence of the growth rates of series 45 and 90 assuming values for T_m^e of 54° and 60°C respectively. The plots of $\log G_s + \Delta F^a/RT_c$ against $T_m^e/T_c\Delta T$ are pronouncedly non-linear: presumably this is a consequence of a change in the mechanism of crystallization. Hoffman *et al.*[36] working with polyethylene have associated changes in the temperature dependence of growth rate with changes in morphology. We do not have a detailed record of observation which would enable us to detect any subtle change in morphology. Because of this complication, and because we are also aware of changes in chain folding in these samples, we have not pursued the analysis further.

CONCLUSIONS

In the region of small undercooling the analysis of the temperature dependence of spherulite growth rate depends on knowing the equilibrium melting temperature as a function of molecular weight with reasonable accuracy. A recent study of polyethylene fractions by Hoffman *et al.*[36] makes use of a theoretically justified[30] extrapolation of Broadhurst's results[37] for the orthorhombic n-alkanes to obtain T_m^e as a function of M. Magill[38] measured melting points of poly(tetra-methyl-*p*-silphenylene)-siloxane fractions directly using a very slow heating rate, while van Antwerpen and van Krevelen[39] considered T_m^e an adjustable parameter and fitted their growth rates of poly(ethylene terephthalate) fractions with a single value of T_m^e. Others have followed Mandelkern *et al.*[40] in using the theory of Flory[35] to calculate T_m^e from T_m^0 (the thermodynamic melting point of the polymer of infinite molecular weight), for example Mandelkern and Devoy[41], Lovering[42] and Booth *et al.*[16,18]. Our strategy (i.e. the synthesis of polymers with differing molecular weights but, because of their constitution, with similar equilibrium melting points) has the merit of partly curcumventing the difficulty. Our result that G_0 is roughly constant over the molecular weight range (6000 to 40 000) of the *series 34* block polymers differs from that found earlier[18] from analysis of the growth rates of spherulites of homopoly(ethylene oxide). It is, however, in keeping with the findings of Hoffman *et al.*[36] for polyethylene.

ACKNOWLEDGEMENTS

We wish to thank Mr D. J. Roy, Mr A. Redfern and Mr J. J. Smith for technical assistance, Dr P. Egerton for advice and the SRC for financial support.

REFERENCES

1 Arlie, J. P., Spegt, P. A. and Skoulios, A. E. *Makromol. Chem.* 1966, **99**, 160; 1967, **104**, 212
2 Spegt, P. A. *Makromol. Chem.* 1970, **140**, 167
3 Ashman, P. C. and Booth, C. *Polymer* 1972, **13**, 459
4 Kovacs, A. J. and Gonthier, A. *Kolloid Z.* 1972, **250**, 530
5 Kovacs, A. J., Gonthier, A. and Straupe, C. *J. Polym. Sci. (Polym. Symp.)* 1975, **50**, 283
6 Buckley, C. P. and Kovacs, A. J. *Prog. Colloid Polym. Sci.* 1975, **58**, 44; *Colloid Polym. Sci.* 1976, **254**, 695
7 Fraser, M. J., Marshall, A. and Booth, C. *Polymer* 1977, **18**, 93
8 Fraser, M. J., Cooper, D. R. and Booth, C. *Polymer* 1977, **18**, 852
9 Thierry, A. and Skoulios, A. *Eur. Polym. J.* 1977, **13**, 169; *Colloid Polym. Sci.* 1977, **255**, 334
10 Cooper, D. R., Leung, Y-K., Heatley, F. and Booth, C. *Polymer* 1978, **19**, 309
11 Gilg, B., Spegt, P., Terrisse, J. and Skoulios, A. *Makromol. Chem.* 1967, **107**, 39
12 Gilg, B. and Skoulios, A. *Makromol. Chem.* 1970, **140**, 149
13 Ashman, P. C. and Booth, C. *Polymer* 1975, **16**, 889
14 Mathis, A., Thierry, A., Terrise, J. and Skoulios, A. *Makromol. Chem.* 1972, **158**, 205
15 Barnes, W. J., Luetzel, W. G. and Price, F. P. *J. Phys. Chem.* 1961, **65**, 1742
16 Beech, D. R., Booth, C., Hillier, I. H. and Pickles, C. J. *Eur. Polym. J.* 1972, **8**, 799
17 Godovsky, Y. K., Slonimsky, G. L. and Garbar, N. M. *J. Polym. Sci. (C)* 1972, **38**, 1
18 Maclaine, J. Q. G. and Booth, C. *Polymer* 1975, **16**, 191
19 Maclaine, J. Q. C. and Booth, C. *Polymer* 1975, **16**. 680
20 Martuscelli, E. and Scafora, E. *Chim. Ind.* 1976, **58**. 601
21 Galin, J-C., Spegt, P., Suzuki, S. and Skoulios, A. *Makromol. Chem.* 1974, **175**, 991
22 Ulrich, H. and Sayigh, A. A. R. *Angew. Chem. Int. Edn* 1966, **5**, 724
23 Booth, C. and Price, C. *Polymer* 1966, **7**, 85
24 Friday, A., Cooper, D. R. and Booth, C. *Polymer* 1977, **18**, 171
25 'Polymer Handbook' (Eds J. Brandrup and E. H. Immergut) Interscience, New York, 1975, p. III–40
26 Lauritzen, J. I. and Hoffman, J. D. *J. Res. Nat. Bur. Stand. (A)* 1960, **64**, 73
27 Gopalan, M. and Mandelkern, L. *J. Phys. Chem.* 1967, **71**, 3833
28 Beech, D. R. and Booth, C. *J. Polym. Sci. (B)* 1970, **8**, 731
29 Maclaine, J. Q. C., Ashman, P. C. and Booth, C. *Polymer* 1976, **17**, 109
30 Flory, P. J. and Vrij, A. *J. Am. Chem. Soc.* 1963, **85**, 3548
31 Ashman, P. C. and Booth, C. *Polymer* 1976, **17**, 105
32 Hoffman, J. D. *SPE Trans.* 1964, **p 315**
33 Mandlekern, L. 'Crystallisation of Polymers' McGraw–Hill, New York, 1964
34 Lauritzen, J. I. *J. Appl. Phys.* 1973, **44**, 4353
35 Flory, P. J. *J. Chem. Phys.* 1949, **17**, 223
36 Hoffman, J. D., Frolen, L. J., Ross, G. S. and Lauritzen, J. I. *J. Res. Nat. Bur. Stand. (A)* 1975, **79**, 671
37 Broadhurst, M. G. *J. Res. Nat. Bur. Stand. (A)* 1966, **70**, 481
38 Magill, J. H. *J. Appl. Phys.* 1964, **35**, 3249; *J. Polym. Sci. (A-2)* 1967, **5**, 89; 1969, **7**, 1187
39 van Antwerpen, F. and van Krevelen, D. W. *J. Polym. Sci. (Polym. Phys. Edn)* 1972, **10**, 2423
40 Mandelkern, L., Fatou, J. G. and Howard C. *J. Phys. Chem.* 1964, **68**, 3386; 1965, **69**, 956
41 Devoy, C. J. and Mandelkern, L. *J. Polym. Sci. (A-2)* 1969, **7**, 1883
42 Lovering, E. G. *J. Polym. Sci. (C)* 1970, **30**, 329; *J. Polym. Sci. (A-2)* 1970, **8**, 747