the dimensionless time, X, for different values of R. *Figure 1* gives the results. The plot for $R = 1$ has been obtained by integrating equation (3):

$$\frac{1}{Y} = \frac{[P]_0}{[P]} = 1 + \frac{1}{2}k_p[P]_0t = \left(1 + \frac{X}{2}\right) \qquad (16)$$

According to equation (8), the slope of the $1/Y$ *versus* X curve for $X \to 0$ is equal to $R/2$. For small values of X, there is a curvature and as X approaches large values, $1/Y$ (= $\overline{DP}$) *versus* X becomes linear with a slope of 0.5, independent of the value of R. The curvature increases as R increases and the smaller the value of R, the larger is the time taken to reach the linear region. In the linear region, (*Figure 1*) there is a set of parallel lines corresponding to different values of R. This is expected physically because the larger the value of R, the faster is the monomer consumed and the linear region starts from the values of X when the monomer is almost completely consumed. For curves for $R = 25$ and above, only small differences in the behaviour are observed.

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Crystallinity and fusion of low molecular weight poly(ethylene oxide): effect of end-group

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Many interesting observations have been made on low molecular weight fractions of α,ω-hydroxy-poly(ethylene oxide), notably by Kovacs, Skoulios, Spegt and coworkers at Strasbourg[1–4]. Fractions of $\bar{M}_n < 3000$ when crystallized from the melt at (say) 25°C typically form stacked lamella structures[2–5] in which the polymer chains are unfolded[3–5]. In these extended chain crystals the end-groups of the poly(ethylene oxide) chains are concentrated in the surface layers of the lamella crystals. It has been argued[1,6] that the formation of hydroxy–hydroxy hydrogen bonds in the surface layers of the crystalline lamellae is an important factor in determining the mode of crystallization and the stability of the crystals. Our experiments with poly(ethylene oxide) fractions having a variety of end-groups (e.g. alkoxy[7,8], acetoxy[9]) lead us to the view that the experimental results obtained with hydroxy-ended fractions are not unique. (We note a similar viewpoint expressed in ref 2.) Our intention here is to promote this view by the presentation of further experimental results obtained with α,ω-methoxy- and α,ω-ethoxy-poly(ethylene oxide) fractions.

Samples of α,ω-hydroxy-poly(ethylene oxide) were obtained from commercial sources: Shell Chemical Co. Ltd (1000, 1500), Hoechst Chemicals Ltd (2000) and Fluka AG (3000). Before use samples were precipitated from dilute solution in benzene by addition of iso-octane and thoroughly dried. The α,ω-methoxy- and α,ω-ethoxy-poly(ethylene oxide) fractions were prepared by the method described elsewhere[10]. Infra-red spectroscopy, elemental analysis and end-group analysis were used to confirm conversions of hydroxy to alkoxy end-groups exceeding 99%. The molecular weights and molecular weight distributions of the fractions were checked against standard samples by gel permeation chromatography (g.p.c.). We denote the samples by their nominal molecular weights and by a suffix H (hydroxy), M (methoxy) or E (ethoxy). The g.p.c. data listed in *Table 1* show that the chain length distributions are essentially unchanged by the alkoxylation process.

Melting points (T_m, *Table 1*) were measured by dilatometry[11] for fractions crystallized at several temperatures (T_c, *Table 1*) and were found to be independent of T_c. Only single melting transitions were observed. Specific volumes (ν_{sp}, *Table 1*) were measured at 25°C by picnometry[11] for the 1500 fractions crystallized at 25°C. Lamella spacings (l, *Table 1*) were measured by small-angle X-ray scattering[11] at room temperature (~20°C) for samples crystallized at 25° and 35°C and were found to be independent of T_c. Double maxima were observed for 1000H (T_c = 35°C) and 1000M (T_c = 25° and 35°C): this effect is attributable[4] to fractionation during the crystallization process. Because of this complication, and also because of possible fractionation during the preparative processes (*Table 1*), the following remarks are restricted to fractions with $\bar{M}_n > 1500$.

The evidence of the lamella spacings and the specific volumes is that the stacked lamella structure of these fractions is not affected by the end-groups. Comparison of l with the extended-chain lengths of the fractions [calculated assuming 64×10^{-3} nm/g as for the 7:2 helical poly(ethylene oxide) chain[12]] listed in *Table 1* shows that the lamellae contain extended chains. Comparison of ν_{sp} with that of perfectly crystalline poly(ethylene oxide), i.e. 0.813 cm^3/g at 25°C[12], shows that the stacked lamella structures contain a significant amount of non-crystalline material.

In *Table 1* the melting points for a given molecular weight are practically identical. The stability of a stacked lamella polycrystal is measured by its free energy of formation from the

Table 1 Molecular weights, melting points, specific volumes and lamella spacings of poly(ethylene oxide) fractions

	Gel permeation chromatography		Dilatometry				
Sample	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	T_c(°C)	T_m(°C)	Picnometry V_{sp}(cm^3/g)	X-ray scattering l(nm)	Extended chain length (nm)
1000H	1010	1.06	25–35	38.4	–	6.6, 7.6	6.5
1000M	1070	1.04	25–32	37.4	–	6.7, 7.7	6.8
1000E	1200	1.02	25–36	40.0	–	7.6	7.7
1500H	1490	1.03	35–42	47.8	0.826	9.6	9.5
1500M	1460	1.05	35–44	47.5	0.841	10.1	9.3
1500E	1510	1.04	35–44	47.9	0.835	10.1	9.7
2000H	1920	1.04	35–42	53.6	–	13.0	12.3
2000M	1950	1.04	35–44	53.2	–	13.4	12.5
2000E	2040	1.04	35–40	53.8	–	13.8	13.1
3000H	2750	1.06	35–49	58.8	–	20.8	17.6
3000E	2890	1.04	35–42	59.4	–	20.8	18.5

Table 2 Melting points (°C) of poly(ethylene oxide) fractions

	End-group					
$\bar{M}_n$	–OH	–OCH$_3$	–OC$_2$H$_5$	–OCOCH$_3$	–OC$_6$H$_5$	–Cl
1000 ± 100	38.4	37.4	–	–	31*	30*
1500 ± 100	47.8	47.5	47.9	45.1	43*	43.6
2000 ± 100	53.6	53.2	53.8	51.9	–	–

* Measured by polarizing microscope to ±1 K

melt, and the melting point is the temperature at which this free energy change becomes zero. Hence the melting point is an adequate indicator of the stability of the polycrystal *relative to its melt.* Our results indicate that there are no significant differences in relative stability between hydroxy and methoxy or ethoxy ended poly(ethylene oxide) fractions of the same molecular length.

In *Table 2* we summarize the melting point data obtained here and heretofore[9,13] for well-characterized fractions of poly(ethylene oxide) with a variety of end-groups: chloro, phenoxy and acetoxy in addition to those presented in *Table 1.* It is evident that the stability of crystalline poly(ethylene oxide) relative to its melt can be substantially affected by the nature of the end-group. It is also evident that the stabilizing effect of the hydroxy-end-group is not unique.

A contribution to the free energy of formation of the stacked lamella polycrystal from the melt is the free energy of segregation ($-\Delta G_{\text{mixing}}$) of the end- and chain-groups due to the concentration of end-groups into the surface layers of the crystalline lamellae. Given certain simplifying assumptions this contribution can be estimated. Assuming random mixing of end-groups and chain segments in the non-crystalline layer, conventional solution theory leads to:

$$-\Delta G_{\text{mixing}} = \frac{nRT\chi(1-\phi_e)^2 X}{(1-X\phi_e)} \qquad (1)$$

per mole of polymer chains, where n is the number of crystallizable segments in each chain; ϕ_e is the volume fraction of crystallizable segments; X is the fraction of the crystallizable segments to have entered the crystalline lamellae; χ is the Flory–Huggins interaction parameter for crystallizable and end-group segments.

For complete crystallization of the chain segments, or equally for complete segregation of unlike segments in the non-crystalline layers, this equation must be modified to:

$$-\Delta G_{\text{mixing}} = nRT\chi(1-\phi_e) \qquad (2)$$

which provides an upper limit to the magnitude of the mixing term.

In our calculations we have selected a poly(ethylene oxide) repeat unit in the melt to define the volume of a segment. We have then derived the corresponding values of the χ-parameters by examination of results for mixtures of poly(ethylene oxide) and low molecular weight liquids. The thermodynamic data in the literature usually pertain to polymer–liquid mixtures in which important contributions to χ arise from large differences in the liquid properties of the two components[14]. If the equations of state of end and chain groups are similar then the contributions to χ from this source are small, and its value can be assessed from the contact interchange parameter, X_{12}, in the Flory formulation[14]. The results:

Poly(ethylene oxide)–benzene[15]:
$X_{12} = -15$ J/cm^3

Poly(ethylene oxide)–alkane[16]:
$X_{12} = +55$ J/cm^3

lead to estimates of χ, based on a segment equal in volume to a poly(ethylene oxide) chain unit in the melt, of about:

Phenyl-group: $\chi = -0.2$
Alkyl-group: $\chi = +0.7$

The additional assumption that volume fractions can be approximated by weight fractions allows the following free energy changes to be calculated by equation (2):

Phenyl-group: $-\Delta G_{\text{mixing}} = +1.7$ kJ/mol
Methyl-group: $-\Delta G_{\text{mixing}} = -1.3$ kJ/mol
Ethyl-group: $-\Delta G_{\text{mixing}} = -2.4$ kJ/mol

If, as has been suggested[11], the non-crystalline layers contribute 30% by volume to the polycrystal and if the end and chain groups are randomly mixed therein then the values of the free energy change calculated by equation (1) are:

Phenyl-group: $-\Delta G_{\text{mixing}} = +0.3$ kJ/mol
Methyl-group: $-\Delta G_{\text{mixing}} = -0.1$ kJ/mol
Ethyl-group: $-\Delta G_{\text{mixing}} = -0.2$ kJ/mol

Given our present knowledge of the constitution of the surface layers we conclude that actual values of $-\Delta G_{\text{mixing}}$ will lie somewhere within the ranges defined by the limiting cases above.

The Flory–Vrij theory of melting can be used, in the manner described elsewhere[11], to show that an increase in $-\Delta G_{\text{mixing}}$ of about 2.0 kJ/(mol of chains) is sufficient to produce a depression in melting point of a 1500 fraction of about 4K. This value (2.0 kJ/mol) lies centrally within the range we estimate for the increase in $-\Delta G_{\text{mixing}}$ due to exchange of phenoxy for alkoxy ends (and, for that matter, phenoxy for hydroxy ends). This result lends credance to the view that a proper treatment of mixing effects will eventually provide an explanation of the differences in relative stability exemplified by the results of *Table 2.*

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Poly(*S*-alkyl-L-cysteines) containing long aliphatic side chains

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INTRODUCTION

Conformational studies of branched polymers containing long aliphatic side chains have been investigated.

It has been reported that the *S*-lower alkyl derivatives of poly(L-cysteine), such as *S*-methyl, *S*-benzyl, and *S*-benzyloxycarbonyl, are hardly soluble in most of the common organic solvents, and form a stable *β*-structure: in coil-promoting solvents, such as dichloroacetic acid (DCA) and trifluoroacetic acid (TFA), they are in a random coil[1–4].

In a previous paper, we have reported that poly(*S*-menthyloxycarbonylmethyl-L-cysteine)[5] and poly(*S*-benzyl-L-penicillamine)[6] which are soluble in many organic solvents, are in the *α*-helical or the *ω*-helical conformation. It seems interesting to study the synthesis and conformational analysis of poly(*S*-alkyl-L-cysteines) which are easily soluble in many organic solvents.

In the present paper, we report the results of structural investigations in solution and in the solid state on polypeptides with long alkyl side chains, such as poly(*S*-lauryl-L-cysteine) (I), poly(*S*-myristyl-L-cysteine) (II), and poly(*S*-stearyl-L-cysteine) (III). These higher side-chain homologues of *S*-alkyl-L-cysteine were prepared by a reaction of L-cysteine and the corresponding higher alkyl bromides. The cysteine derivatives were then polymerized to the above polymers by the *N*-carboxyanhydride (NCA) method. These polymers were soluble in chloroform, hot monochlorobenzene, DCA, and TFA. In order to investigate the effect of the side-chain lengths on the polypeptide structure, the conformation of the polymers were studied by means of the infra-red (i.r.) spectra, X-ray diffraction, and optical rotatory dispersions (o.r.d.) in the solid state and in solution.

EXPERIMENTAL

Materials

The physical and analytical data of the materials are shown in *Tables 1* and *2*.

Table 1 The physical properties and elemental analyses of monomers

Sample	Yield (%)	M_p* (°C)	$[\alpha]_D$†	Molecular formula	Calculated C (%)	Calculated H (%)	Calculated N (%)	Found C (%)	Found H (%)	Found N (%)
S-lauryl-L-cys	69.2	209	–2.09	$C_{15}H_{31}O_2NS$	62.24	10.79	4.84	62.35	10.56	4.83
S-myristyl-L-cys	46.0	201	–0.36	$C_{17}H_{35}O_2NS$	64.30	11.11	4.41	64.61	10.94	4.36
S-stearyl-L-cys	36.4	196	–0.62	$C_{21}H_{43}O_2NS$	67.51	11.60	3.75	67.16	11.60	3.67
S-lauryl-L-cys NCA	68.8	70		$C_{16}H_{29}O_3NS$	60.92	9.27	4.44	60.94	9.31	4.37
S-myristyl-L-cys NCA	78.6	77		$C_{18}H_{33}O_3NS$	62.70	9.65	4.06	62.41	9.65	4.06
S-stearyl-*L*-cys NCA	58.5	83		$C_{22}H_{41}O_3NS$	66.11	10.34	3.50	66.09	10.56	3.54

* All melting points were determined on a Yamato MP-1 melting-point apparatus.
† Optical rotation: all samples were measured at 20°–25°C in DCA

Table 2 The physical properties and elemental analyses of polymers

Polymer	Yield (%)	D_p*	$[\eta]$† (dl/g)	Molecular formula	Calculated C (%)	Calculated H (%)	Calculated N (%)	Found C (%)	Found H (%)	Found N (%)
Poly(*S*-lauryl-L-cys)	58.1	20	0.140	$(C_{15}H_{29}ONS)_n$	66.37	10.77	5.16	66.53	10.71	5.13
Poly(*S*-myristyl-L-cys)	79.6	22	0.152	$(C_{17}H_{33}ONS)_n$	68.40	10.81	4.69	68.29	10.58	4.60
Poly(*S*-stearyl-L-cys)	56.2	15	0.138	$(C_{21}H_{41}ONS)_n$	70.93	11.62	3.94	70.60	11.35	3.94

* Degree of polymerization (D_p): all samples were determined from the amino end-group titration using crystal violet as an indicator
† Intrinsic viscosity: all samples were measured at 25°C in DCA using an Ubbelohde viscometer