Conformation of liquid short chain polyethers from flow birefringence*

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The stress-optical coefficient (∇) has been determined from flow birefringence measurements for the short chain polymers poly(ethylene glycol) (PEG) and poly(propylene glycol) (PPG) over a range of temperatures and molecular weights (*DP* from 1 to 200 for PEG, 1 to 40 for PPG). By using samples blended from monodisperse material of known M_n, it is shown that it is the *z*-average molecular weight that characterizes the stress-optical coefficient. Hence in making comparisons between various samples of the same material due to different authors, it is necessary to have a knowledge of the *z*-average molecular weight of the sample. A critical comparison is made of the number of monomer units per statistical segment (the parameter describing chain conformation) as derived from the theories of Lodge, Gotlib and Svetlov, and Noda and Hearst.

INTRODUCTION

The problem of describing and determining the conformation of short chain polymers in the liquid state has interested many authors in recent years[1,2]. A series of oligomers that exist as liquids provides a useful basis for experiment, and it is mainly for this reason we have chosen to investigate the poly(ethylene glycol) (PEG) and poly(propylene glycol) (PPG) series using the technique of flow birefringence. The only other comparable data in the literature[3] is limited in the range of molecular weights investigated and the samples used are insufficiently characterized to permit analysis in terms of the conformational behaviour. The aim of the work presented here is to investigate the applicability of flow birefringence methods to determine the flexibility of short chain polymers, using the number of monomer units per statistical segment (*S*) as the parameter to describe the conformational behaviour of the polymer. To this end we have determined: (a) the flow birefringence behaviour of two fully characterized series of oligomers of PEG and PPG; (b) which average molecular weight characterizes the stress-optical coefficient and hence the parameter *S*, and (c) we have analysed the data in terms of the current theories of flow birefringence to evaluate the parameter *S*.

EXPERIMENTAL

Materials

Poly(propylene glycol), $HO(CH_2CHMeO)_nH$. The poly(propylene glycols) investigated were linear atactic chains having M_n in the range 76 to 2840. The monomer and dimer were obtained from Koch–Light and had purity grades of puriss and pure, respectively. The samples (PPG, 425, 1025 and 2025) were supplied by BDH and had a specified maximum water content of 0.3%. The samples (PPG 400, 1200, 1800 and 4000) were provided by Dr Weibull (of MoDoKemi AB), their synthesis being carried out at ~120°C with KOH as a catalyst. All the samples (with the exception of PPG 4000) were clear and colourless, the PPG 4000 samples contained ~0.1 → 0.01% wt/vol of colloidal impurity and had a hazy blue appearance. The impurity in PPG 4000 could be removed by filtering solutions using chloroform as solvent through 0.1 μm Millipore filters.

The values of the average molecular weights, refractive index (*n*) at 546 nm and density (ρ) at 25°C of the samples are shown in *Table 1*.

The number-average molecular weights were determined using a Hitachi–Perkin–Elmer osmometer (model 15) with benzene as solvent, the accuracy of determination was ±2%. The polydispersity factors M_w/M_n were determined from computer analysis of gel permeation chromatograms, using tetrahydrofuran as the solvent. One sample, PPG 2025 had M_w determined by light scattering (using a Sofica photodiffusometer), the Zimm plot gave a value of intercept corresponding to an M_w of 2150 ± 100.

Poly(ethylene glycols), $HO(CH_2CH_2O)_nH$. Polyethylene glycols investigated were linear chains, with M_n in the range 62 to 10 000. The monomer, dimer, trimer and tetramer were obtained from Fluorochem Ltd and had purity grades of puriss; the 230 mer was also supplied by Fluorochem hav-

Table 1 Characterization of poly(propylene glycol)

Sample	M_n	M_w	M_w/M_n	n_{25} (at 546 nm)	ρ_{25} (kg/m^3)
Propylene glycol	76	–	–	1.4328	1033
Dipropylene glycol	134	–	–	1.4408	1019
PPG 425	400	440	1.1	1.4471	1003
PPG 400	420	483	1.15	1.4472	
PPG 1025	995	1055	1.06	1.4496	1001
PPG 1200	1191	1286	1.08	1.4502	
PPG 1800	1694	1762	1.04	1.4505	
PPG 2025	1960	2156	1.1	1.4505	1001
PPG 4000	2840	3124	1.1	1.4509*	

* Unfiltered

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Table 2 Characterization of poly(ethylene glycol)

Sample	M_n	M_w	M_w/M_n	n_{25} (at 546 nm)	ρ_{25} (kg/m^3)
Ethylene glycol	62		–	1.4321	1111
Diethylene glycol	106	–	–	1.4477	1114
Triethylene glycol	150	–	–	1.4564	1120
PEG 200	200	212	1.06	1.4602	1121
PEG 400	403	455	1.13	1.4673	1121
PEG 600	595	678	1.13	1.4696	1122
PEG 1000	995	1095	1.10	–	–
PEG 4000	2526	2728	1.08	–	–
PEG 6000	5280	5755	1.09	–	–
PEG 20 000	10 000	13 000	1.30	–	–

ing a purity grade of pract. The other samples were supplied by Hopkin and Williams, and were of laboratory reagent grade.

The values of molecular weight, refractive index at 546 nm and density are shown in *Table 2.*

EXPERIMENTAL METHODS

The flow birefringence measurements were carried out using apparatus described previously[4], and involve the determination of the phase difference δ induced by the sheared liquid and the angle of isocline χ. δ is related to the birefringence (Δn) by:

$$\Delta n = \frac{\lambda_0 \delta}{2\pi L}$$

where λ_0 is the wavelength in vacuum (546 nm) and L is the path length. δ was determined using a quarter-wave plate and an analyser as a Senarmont compensator, the end point being determined visually.

To measure the angle of isocline, χ, the quarter-wave plate was removed and the analyser set for extinction. For sheared liquids exhibiting flow birefringence in excess of 2×10^{-8} a visible cross of isocline was produced in the telescope focused on the bottom of the intercylinder gap. A pair of adjustable double cross hairs mounted on a setting circle ~2 cm beneath the bottom of the intercylinder gap, were used to determine the angular position of the arms of the cross of isocline. Tests with liquids for which χ was known to be 45° (such as oleic acid)[5] served to establish the 45° position with the cross hairs; by reversing the direction of rotor rotation another determination of position was made which differed from the original determination by less than 0.1°. In the velocity gradient range of 10^3 to 1.6×10^4 sec^{-1} a value of $\chi = 44.95 \pm 0.1$ was obtained for oleic acid. Using a rigidly coupled analyser and polarizer unit (set for extinction), angular positions of the cross could be determined to an accuracy of ±0.03° for birefringence in excess of 10^{-7}. In all the flow birefringence and χ measurements the duration of the flow field, i.e. the time of shearing was always less than 10 sec in order to minimize the perturbing effects of viscous heating.

RESULTS

Flow birefringence and χ measurements

For all the polymer samples at the various temperatures the variation of birefringence, Δn, with velocity gradient G was investigated. All the samples displayed a linear relationship between birefringence and velocity gradient, including the clarified PPG 4000 sample. Consequently the Maxwell constants $M = \Delta n/G$ were independent of velocity gradient. Each Maxwell constant was obtained from the least squares fitted slope of a Δn *versus* G plot. *Figure 1* shows the variation of the Maxwell constant with temperature for the six PPG samples investigated as a function of temperature. *Table 3* shows the separate determinations of Maxwell constant (M) for the nine PPG samples at 25° ± 0.2°C, together with values of the viscosity and stress-optical coefficient, $\nabla = \Delta n/\eta G$.

The values of χ as a function of velocity for PPG 2025 at 25°C are shown in *Figure 2.* Each point shown is the average of approximately eight separate readings of angular position. The results of the χ determination using the rotable polarizer and analyser unit are also shown in *Figure 2* for PPG 2025 at 25°C, four readings being used for each point shown. Measurements of χ for PPG 1025 over a velo-

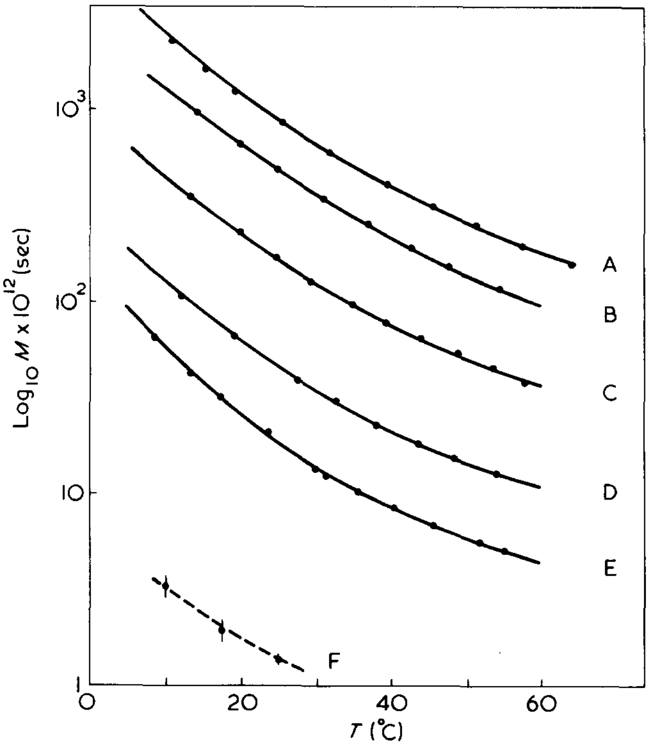

Figure 1 Maxwell constant M as a function of temperature T for six poly(propylene glycol) samples: A, PPG 4000; B, PPG 2025; C, PPG 1025; D, PPG 425; E, dipropylene glycol; F, propylene glycol

Table 3 Variation of ∇ with molecular weight at 25°C for PPG

Sample	M_n	$M \times 10^{12}$ (sec)	η(cP)	$\nabla \times 10^{10}$ (cm^2/dyne)
PG	76	1.37	38.5	0.036
DPC	134	18.7	72	0.26
425	400	45.4	64	0.71
400	420	54.0	67	0.80
1025	995	164.0	139	1.18
1200	1191	234	177	1.32
1800	1694	381	259	1.47
2025	1960	485	315	1.54
4000	2840	860	518	1.66

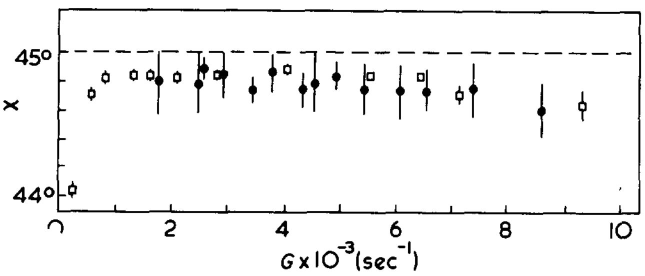

Figure 2 Variation of χ with velocity gradient *G* of PPG 2025 at 25°C, determined using crosshairs (●), and using the rotatable crossed polarizer analyser unit (□)

city gradient range between 5000 sec^{-1} and 13 200 sec^{-1} give $\chi = 44.93 \pm 0.1$.

The decrease in χ at low velocity gradients shown in *Figure 2* is attributable to the presence of the radially strained quartz annulus used as the top window in the apparatus. The effect is most pronounced at low velocity gradient due to the reduction of polymer birefringence and the strain birefringence becoming appreciable. The values of χ obtained experimentally are very sensitive to small parasitic birefringences (from slightly strained windows or reflections), and consideration of Sadron's rule[5] indicates the origin of this sensitivity. The loss of accuracy occurring at high velocity gradients, is due to the effects of viscous heating (proportional to ηG^2) and the consequent distortion of the light beam and subsequent loss of contrast. Correcting for the effect of window strain on the χ measurements, however, still indicates a small (~0.1°) deviation from 45° of χ at high *G*. A concentrated solution ($c = 0.9385$ g/cm^3) of PPG 2025 in cyclohexanone yielded uncorrected values of $\chi = 44.91 \pm 0.08$, between $G = 2000$ and 8500 sec^{-1}, i.e. at smaller values of shear stress, a measurable deviation from 45° was observed, but smaller than the deviation of the bulk polymer. However by reducing the temperature of PPG 2025 to 5°C no increase in the deviation of χ was observed ($\chi = 44.89 \pm 12$) at ~3000 sec^{-1}. Consequently if the deviations of χ from 45° are attributable to molecular behaviour, rather than parasitic effects, an upper limit of ~0.07° at a shear stress of 3.2×10^3 N/m^2 may be set for PPG 2025. For the lower molecular weight polymers investigated $(45° - \chi) \leqslant 0.05°$ after allowance for window strain.

The behaviour of χ is important in three respects: (1) impurity detection; (2) molecular behaviour; (3) theoretical considerations, in that the theories used in the analysis of the experimental results in this work were derived in the limit of $\chi = 45°$. The constancy of $\chi = 45° \pm 0.1°$ with velocity gradient shows that there is no high molecular weight impurity (e.g. colloidal impurity) making any measurable contribution to the observed birefringence. The colloidal impurity present in PPG 4000 was first detected by the rapid decrease in χ from 45° at low velocity gradients (~0.05 sec^{-1}). Many observations have been made of the departure from 45° of χ of solutions of high molecular weight polymers, the deviation being a function of the shear stress. For the pure liquid polymers investigated in this work, although high shear stresses were used (~3×10^3 N/M^2) no deviation from 45° greater than 0.07° was observed.

Similar results for the variation of angle of isocline with velocity gradient were found for the poly(ethylene glycols); for this homologous series the Maxwell constants were determined at 25° and 65°C.

Viscosity

The viscosities of the five poly(propylene glycol) samples investigated in the flow birefringence section and the monomer were measured as a function of temperature (between 10° and 60°C) and velocity gradient (1–10^4 sec^{-1}). A Ferranti–Shirley viscometer was used for the measurements. After applying corrections to account for viscous heating, the viscosities of all the polymers were found to be independent of velocity gradient over the temperature range investigated. The variation of viscosity with temperature is shown in *Figure 3*. The viscosities of the PEG samples were determined at 25° and 65°C, and were found to be independent of velocity gradient (1–10^4 sec^{-1}).

Stress optical coefficients, ∇

Poly(propylene glycol). The stress optical coefficients $\nabla = \Delta n/\eta G$ of all the poly(propylene glycol) samples at 25°C are shown in *Table 3*, the values of Maxwell constant and viscosity are also included.

The variation of ∇ with number-average degree of polymerization is shown in *Figure 4*. The increase in ∇ with molecular weight is determined by the chain's conformational flexibility (see Discussion section), and we quantify flexibility by the number of monomer units per statistical segment, *S*. The quantity *S* for a particular polymer system should be independent of molecular weight. For a polydisperse system the value of *S* determined from the increase of ∇ with molecular weight is dependent on the particular average of molecular weight used in the analysis. Consequently to compare the results of this work with other investigations concerning the flexibility of polymers, it is important to ascertain which average molecular weight best characterizes ∇ and hence *S*. To investigate the dependence of polydispersity on ∇ in this low molecular weight region several samples of the narrow molecular weight fractions $M_w/M_n < 1.1$ were

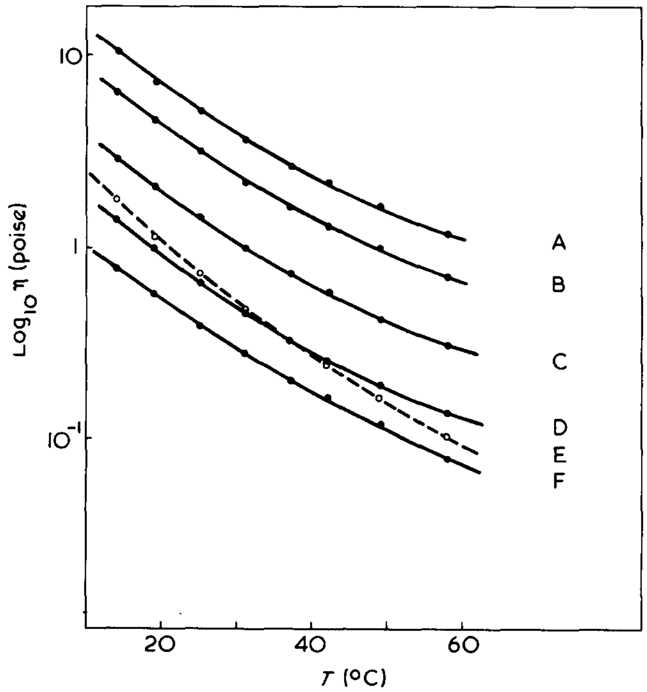

Figure 3 Variation of viscosity, η, with temperature *T* for polypropylene glycols: A, PPG 4000; B, PPG 2025; C, PPG 1025; D, PPG 425; E, dipropylene glycol; F, propylene glycol

blended to produce samples having identical values of M_w but polydispersity factors of M_w/M_n = 1.18, 1 36 and 1.47 and M_z/M_n = 1.35, 1.75 and 2.03. These factors were calculated using the number average molecular weights of the original samples forming the blends. The calculated values of M_n of the blended samples were 676, 732 and 842, all ± 3%. To check the accuracy of the calculated M_n values, the number-average molecular weights were determined by vapour pressure osmometry, the values being shown in *Table 4*. The values of viscosities of the three blended samples, and the original sample (M_n = 995) were within 9% of one another. The following empirical relation predicted the blended samples with viscosity to within 1.5%:

$$\log \eta_{\text{mixture}} = \sum_i c_i \log \eta_i$$

and the measured and calculated values of the viscosity are shown in *Table 4*, and where c_i is the mass/unit volume of the *i*th species.

The symbols $(M_w)_n$ and $(M_z)_n$ refer to the weight- and *z*-average molecular weights, calculated by assuming the blended samples consisted purely of monodisperse components whose molecular weight were equivalent to the M_n of the pure sample. The values of viscosity are, as expected, seen to follow the changes in the weight-average molecular weight.

The stress-optical coefficient, ∇, of the blended samples were determined and are also shown in *Table 4*. It may be seen that as $(M_n)_n$ decreases, $(M_w)_n$ remains constant and $(M_z)_n$ increases, the stress-optical coefficient increases. The values of ∇ for the blended samples fit on the experimental curve of ∇ *versus* molecular weight for the pure polymer provided values of $(M_z)_n$ are used, indicating that it is the *z*-average molecular weight which characterizes the stress-optical coefficient. The consequences of this behaviour are discussed later.

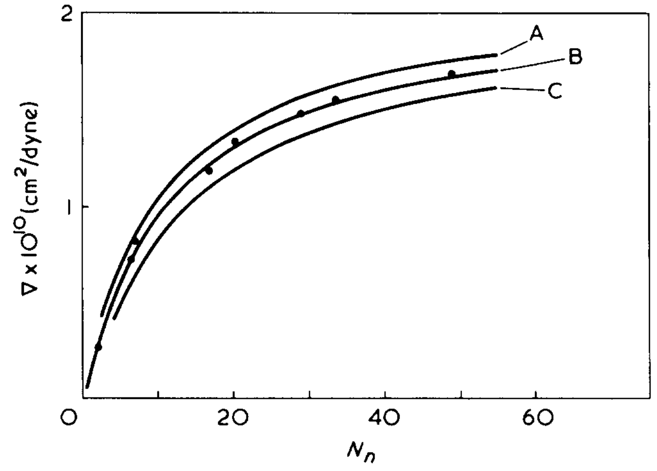

Figure 4 Stress-optical coefficient, ∇, *versus* the number-average degree of polymerization N_n of polypropylene glycol at 25°C ——, Calculated from the theory of Gotlib and Svetlov for: A, 5.5; B, 6.5; C, 7.5; monomer units per persistence length (*S*/2).

Poly(ethylene glycol)

The values of stress optical coefficient are shown in *Table 5*, the measurements being made at 25°C and 65°C. At 25°C only six samples were liquid limiting the measurement to sample PEG 600 and below. However by increasing the temperature to 65°C the samples of molecular weight up to 20 000 are viscous liquids. The PEG 4000 sample had a slight cloudy appearance when liquid which could be reduced but not eliminated by filtration, this resulted in a lack of contrast in the flow birefringence determination hence the error bar shown in *Figure 6*.

DISCUSSION

To interpret the measured values of the stress-optical coefficient, it is necessary to review the applicability of the solution theories of flow birefringence to pure liquid samples. In solution flow birefringence an expression for the reduced stress-optical coefficient given by:

$$\nabla' = \lim_{\substack{c \to 0 \\ G \to 0}} \frac{\Delta n - \Delta n_0}{(\eta - \eta_0)G}$$

has been developed by Peterlin and Lodge[6] for long chains:

$$\nabla' = \frac{4\pi}{45kT} \frac{(n^2+2)^2}{n} \langle \Delta a \rangle = K\langle a \rangle \tag{1}$$

where n is the refractive index of the liquid and $\langle \Delta a \rangle$ the Kuhn statistical segmental optical anisotropy.

Since the polypropylene and poly(ethylene glycol) samples investigated here do not contain sufficient monomer units for long chain statistics to be applied, equation (1) is not strictly valid; ∇′ is not constant but tends to an asymptotic value ∇'_∞. The variation of ∇′ with molecular weight has been theoretically calculated by Tsvetkov[7], Gotlib and Svetlov[5] and Noda and Hearst[9], using the persistence chain model. Gotlib and Svetlov's theory[8] of flow birefringence of short polymer chains gives an expression for ∇′ in terms of $\langle \Delta a \rangle$ and a parameter $x = L/a$, a being the persistence length of a wormlike chain and L the polymer contour length, giving:

$$\nabla' = K\langle \Delta a \rangle F(x) \tag{2}$$

Table 4

Sample	$(M_n)_n$	$(M_w)_n$	$(M_z)_n$	η_{meas} (cP)	η_{calc} (cP)	n (at 546 nm)	$M_{n,\text{vap}}$	$M \times 10^{12}$ (sec)	$\nabla \times 10^{10}$ (cm^2/dyne)
PPG 1025	995	995	995	139	139	1.44960	995	171	1.23
1	842	995	1120	134	133	1.44926	797	171	1.28
2	732	995	1267	128	128	1.44895	694	168	1.31
3	676	995	1370	127	125	1.44877	640	170	1 34

Table 5

Sample	n	Temperature (°C)	η (cP)	$M \times 10^{12}$ (sec)	$\nabla \times 10^{10}$ (cm²/dyne)	$\langle \Delta a \rangle$ (Å³)
EG	1	25.0	15.0	1.74	0.11 (6)	0.15
DEG	2	25.0	25.5	5.22	0.20 (5)	0.26
TEG	3	25.0	33.5	11.8	35 (2)	0.44
PEG 200	4	25.0	46.3	23.5	0.50 (8)	0.64
PEG 400	8.7	25.0	84.0	80.0	0.95 (2)	1.19
PEG 600	13.1	25.0	120	135	1.13	1.41
PEG 200	4	65.0	9.7	5.9	0.61	0.88
PEG 400	8.7	65.0	16.8	16.1	0.96	1.38
PEG 600	13.1	65.0	24.8	27.5	1.11	1.54
PEG 1000	22	65.0	44.2	575	1.30	1.86
PEG 4000	57	65.0	175	265	1.51	2.16
PEG 6000	118	65.0	1150	2000	1.74	2.49
PEG 20 000	~230	65.0	18 600	33 000	1.77	2.54

where $F(x)$ is a complex numerical function of x only. For long chains $x \to \infty$ and $F(x) \to 1$ giving equation (1). Noda and Hearst[9] obtained a similar result, but their theory was presented in terms of ∇'/∇'_∞ and x.

Peterlin[6] has shown that equation (1) is valid for finite concentrations, and extending his approach to successively higher concentrations leads to equation (1) with ∇ replacing ∇'. Peterlin's approach is supported by the fact that it is the rotational motion of the macromolecules which determines both the viscosity and the flow birefringence. The experimentally observed flow birefringence behaviour of the polymers investigated here, i.e. birefringence being linearly proportional to velocity gradient and $\chi = 45°$ is characteristic of simple liquids such as benzene, where the birefringence is solely due to orientation. This fulfils the requirement of $G \to 0$, as the stress-optical coefficient is velocity gradient invariant in the velocity gradient range experimentally used, and also is compatible with the physical basis (molecular orientation) of the short chain theories.

Poly(propylene glycol)

Figure 4 shows the variation of ∇ with molecular weight of the nine poly(propylene glycols) investigated at 25°C. The solid line shown is that predicted by the Gotlib and Svetlov[8] theory for $\langle \Delta a \rangle = 2.7$ Å³ and 6.5 monomer units per persistence length ($S/2$). The line was obtained by varying both $\langle \Delta a \rangle$ and the number of monomers per persistence length; the result for $\langle \Delta a \rangle = 2.7$ Å³ and $S/2$ equal to 5.5 and 7.5 is also shown. As the segment length is twice the persistence length this result corresponds to 13 monomer units per statistical segment. By using the Noda and Hearst theory[9] a value of 7.5 monomer units per segment has been calculated using an asymptotic value $\langle \Delta a \rangle = 2.7$ Å. However by using Tsvetkov's theory, then ~5 monomer units per segment appear to fit the high molecular weight samples best (where the theory should be valid).

Another method of determining the number of monomer units per segment, is to evaluate the segment anisotropy of polarizability of the monomer unit along an all *trans* chain axis[10]. In general, the components of the monomer unit polarizability tensor are given by:

$$\alpha_{ij} = \sum_{n=1} \{\alpha_{n_1}\cos(j,n_1)\cos(i,n_1) + \alpha_{n_2}\cos(j,n_2)\cos(i,n_2) + \alpha_{n_3}\cos(j,n_3)\cos(i,n_3)\}$$

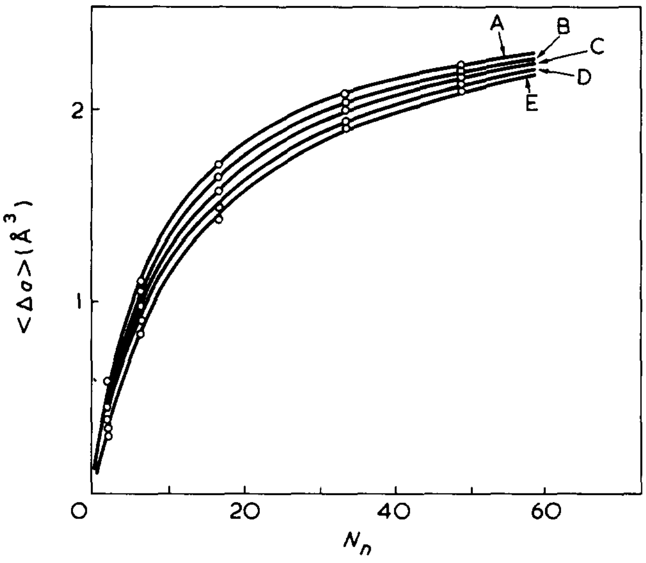

Figure 5 Variation of Δa with number-average degree of polymerization N_n of poly(propylene glycol), at 15°C, 25°C, 35°C, 45°C and 55°C. ———, Calculated from the theory of Gotlib and Svetlov using the values of $S/2$ given in the text for: A, 55°C; B, 45°C; C, 35°C; D, 25°C; E, 15°C

where $i,j = x, y, z$. $\alpha_{n_1}, \alpha_{n_2}, \alpha_{n_3}$ being the principal polarizabilities of the nth bond of an N bond molecule, and (j,n_1), (j,n_2) and (j,n_3) being the angles between the principle bond directions and the x,y,z coordinate axes. Using this scheme the anisotropy of polarizability of the monomer unit along the chain direction may be calculated[10]. The anisotropy of the poly(propylene glycol) monomer unit was found to be 0.43 Å³, using the following values of polarizability parallel and perpendicular to the bond axis[11]:

	$\alpha_\parallel$ (Å³)	$\alpha_\perp$ (Å³)
C–C	0.99	0.27
C–H	0.64	0.64
C–O	0.89	0.46

With the flow birefringence value of $\langle \Delta a \rangle = 2.7$ Å³, this gives 6.3 monomer units per statistical segment.

In *Figure 5* the variation of $\langle \Delta a \rangle$ calculated from equation (1) is shown as a function of the number of monomer units in the chain at five temperatures between 15° and 55°C.

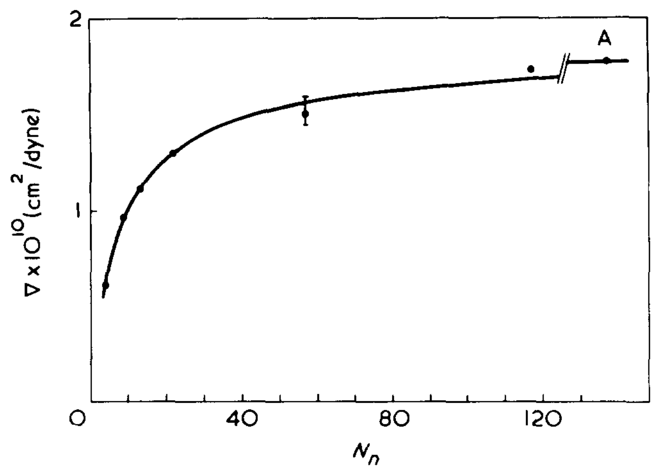

Figure 6 Stress-optical coefficient *versus* the number-average degree of polymerization N_n of poly(ethylene glycol) at 65°C. ——, Calculated from the theory of Gotlib and Svetlov for 4 monomer units per persistence length ($S/2$). A, N_n = 230

The solid lines shown are the Gotlib and Svetlov theory[8], the variation of S with temperature being:

T(°C)	$S/2$
15	7.3
25	6.6
35	5.9
45	5.5
55	4.8

with the value of $\langle\Delta a\rangle$ in the high molecular weight limit found to be temperature independent to within experimental error (±5%). The increase in S with decreasing temperature may be associated with an increase in chain stiffness i.e. a decrease in the *gauche* to *trans* ratio. However, the asymptotic value of $\langle\Delta a\rangle$ in the high molecular weight limit implies that the number of monomer units per statistical segment is independent of temperature. Remembering that $\langle\Delta a\rangle = a\delta a$, where δa is the anisotropy per unit length of the wormlike chain, then δa must decrease if the persistence length increases with decreasing tempeature (as indicated by the short chain polymer theories). A similar apparent discrepancy between the variation of S obtained by the Gotlib and Svetlov theory and the assymptotic value of ∇ was noted by Noordermeer[12] for solutions of cellulose tricarbonate. A possible explanation of the difference in the change of S with temperature is that of angular correlation. Frisman and Dadivanyn[13] have shown the large effect of anisotropic solvents on the measured anisotropy of polymers. The temperature dependence of the viscosity of dipropylene glycol (the viscosity of the dimer being higher than that of the heptamer at room temperature) is a clear indication that not just single molecules are being observed. For rigid molecules, the stress-optical coefficient varies with T^{-1}, however for many small rigid molecules in the pure liquid state experimental determination of $\nabla . T$ shows a variation with temperature (e.g. benzene)[14]. The variation of $\nabla . T$ with temperature in this case is attributable to the effect of angular correlations, and their reduction with increasing temperature. The value of $\nabla . T$ for dipropylene glycol increases with increasing temperature, which indicates that in the more strongly correlated situation, i.e. at low temperatures, the dipropylene glycol system appears less optically anisotropic. The change of angular correlation with molecular weight may in part explain the apparent decrease in δa with decreasing temperature. Infra-red absorption measurements of poly(propylene glycols) show two peaks attributable to the O–H stretching vibration. One of them at the normal position of an O–H bond, 3650 cm^{-1} is due to the vibration of free (non-hydrogen bonded) O–H groups. The ratio of the intensity of the non-bonded to the bonded is observed to increase with molecular weight. Solution measurements indicate that both inter- and intramolecular hydrogen bonding is present. These results indicate a large change in intermolecular interactions with increasing molecular weight. For this type of system the short chain theories would indicate that the PPG chain was stiffer, i.e. had a larger value of S, than the isolated chain value.

Tsvetkov *et al.* have measured the variation of ∇ with molecular weight of some poly(propylene glycols) at 21°C. Their measurements were made on poorly characterized samples which were slightly discoloured, over a smaller molecular weight than used in this work. Using the Gotlib and Svetlov theory to interpret the Tsvetkov *et al.* data, a value of S_n equal to 8 ± 2 was found. If the discrepancy between the values of S, determined in this and Tsvetkov's work is due to differing values of polydispersity, then this approach indicates the average M_w/M_n of Tsetkov's samples was 1.35. This value is not unlikely when considering their description of the samples – unfractionated polymers with pronounced molecular weight polydispersity.

Poly(ethylene glycol)

The variation of ∇ with the number-average degree of polymerization at 65°C is shown in *Figure 6*, the solid line being the Gotlib and Svetlov theory. For the measurements at 65°C, a value of $\langle\Delta a\rangle$ = 2.6 (±0.2) Å^3 and 8 (±1) monomers per segment (~4.6 monomers using Noda and Hearst) gives the best fit. At 25°C the best fit corresponds to $\langle\Delta a\rangle$ = 2.4 (±0.3) Å^3 and 10 ± 3 monomer units per segment (~5.8 monomers per segment using Noda and Hearst). The fit is primarily based on the 9 mer and 13 mer (all the oligomers above DP = 13 were solid at 25°C) because problems in the applicability of the wormlike chain arise when x (the ratio of the contour to the persistence length) is less than 2, due to the fact that the wormlike chain forms an infinitely thin rod as the contour length approaches the persistence length. Using the bond polarizability scheme outlined in the previous section, the anisotropy of the monomer unit along the chain axis was calculated to be ~0.8 Å^3 corresponding to 3 (±0.4) monomer units at 25°C and 3.2 (±0.2) monomers per segment at 65°C. Consequently within the experimental error both $\langle\Delta a\rangle$ and S are independent of temperature and the values of S given by the short chain and long chain theories vary consistently with temperature within the experimental accuracy of determination.

It is important to note that in both the long chain and short chain theories, poly(ethylene glycol) has fewer monomer units per segment than the poly(propylene glycol). The difference in stiffness is to be expected when the structure of PPG is studied using space filling molecular models. We may tentatively infer that the lowest energy conformation of the PPG chain is that of an all *trans* chain, but the independence of S from temperature of the PEG indicates that a *gauche* bond in the monomer unit would be the lowest energy configuration. The conclusions for PEG agree with the studies of Mark and Flory who conclude that the C–O bonds lowest energy state is *trans* but the C–C lowest energy state is *gauche*.

CONCLUSIONS

To summarize, the variation of stress-optical coefficient with chain length has been used to calculate the numbers of monomer units per statistical segment S, of poly(ethylene glycol) and poly(propylene glycol). The parameter S was also calculated using the anisotropy of polarizability of the statistical segment (calculated from ∇_∞) and of the monomer unit (calculated using the bond polarizability additivity scheme). The results may be summarized as follows.

Values of S were determined using (a) Gotlib and Svetlov theory; (b) Noda and Hearst theory; (c) the asymptotic value of ∇.

Sample	(a)	(b)	(c)
PPG (25°C)	13 ± 1	7.5 ± 1	6.3 ± 0.3
PPG (55°C)	9.6 ± 1	5.6 ± 1	6.3 ± 0.3
PEG (25°C)	10 ± 3	5.8 ± 2	3 ± 0.4
PEG (55°C)	8 ± 1	4.6 ± 1	3.2 ± 0.2

The temperature variation of S calculated using the short chain theories indicates an increase in chain flexibility with temperature for the PPG. However, from the asymtotic value of ∇ (within the experimental error) S was independent of the temperature for both the PEG and PPG. The values of S calculated from the theories of Gotlib and Svetlov, and Noda and Hearst when both use the short free draining worm-like chain model are different by a constant factor, i.e., the value of S in column (a)/value of S in column (b) = 1.72 ± 0.02. It was noted by Noda and Hearst that a factor of 2 occurs in a direct numerical comparison of the two theories at the coil limit, and suggest that this is due to the different averaging procedures used in determining the chain optical anisotropy. It would appear that this is also true away from the coil limit although the numerical factor may be different.

Measurements of the flow birefringence and viscosity of blended PPG samples indicate that M_z best characterizes the stress-optical coefficient, and consequently the value of S calculated using the short chain flow birefringence theories should be the z-average value.

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