

# Characterization of oligo-poly(dimethylsiloxanes) and their solutions in toluene

Malcolm B. Huglin and Maimunah B. Sokro†

Department of Chemistry and Applied Chemistry, University of Salford, Salford, M5 4WT, UK  
(Received 26 November 1979; revised 18 February 1980)

A commercial sample of poly(dimethylsiloxane) [PDMS] has been subjected to vacuum distillation, yielding five fractions of  $\bar{M}_n$  ranging from 481 to 1132 g mol<sup>-1</sup>. These have been characterized at different temperatures with respect to density, refractive index, coefficient of isothermal compressibility, light scattering depolarization ratio and Rayleigh ratio. Similar measurements were made on pure toluene and PDMS/toluene mixtures over the whole composition range for each fraction. For these solutions, linearity in light scattering plots held up to PDMS concentrations of  $\sim 0.2$  g cm<sup>-3</sup>, yielding  $\bar{M}_w$  (500–1176 g mol<sup>-1</sup>) and large positive values of the second virial coefficient,  $A_2$ . In contrast to the findings of others, there was no evidence for association. Data recast in a form in which toluene was regarded as solute and PDMS as solvent gave negative values of  $A_2$ . The Mark-Houwink constants for oligomeric PDMS in toluene at 25°C have also been determined. The properties of oligo-PDMS and solutions in toluene are discussed in relation to those of high molecular weight PDMS.

## INTRODUCTION

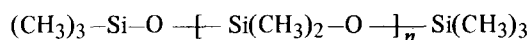
Light scattering techniques are among the methods available for investigating polymer compatibility<sup>1</sup>. We are currently using one of these techniques<sup>2</sup> to study compatibility in simple model systems, viz: oligo-poly(dimethylsiloxanes) [PDMS]/oligo(polyethylenes). The former are liquid, whilst the latter, which are actually long chain alkanes, are liquids at not too elevated temperature.

As a preliminary requisite, it was necessary to characterize the PDMS, since the properties of oligomers are known to differ in value from those of normal high molecular weight polymer. In addition to this characterization, we also report here light scattering studies on solutions comprising oligo-PDMS dissolved in a simple low molecular weight solvent, toluene. These systems display miscibility over the whole composition range, even at room temperature. It is intended that the findings may provide a basis of comparison with results obtained when toluene is replaced by oligo-poly(ethylene).

## EXPERIMENTAL

### Materials

The samples originated from Dow Corning poly(dimethylsiloxane) fluid DC 200/5 of nominal bulk viscosity 5 centistokes, which possesses trimethylsilyl end-groups, viz:



Separation into five fractions (A, B, C, D, E) was effected by

† Present address: Jabatan Kimia, Universiti Kebangsaan Malaysia Jalan Pantai Baru, Kuala Lumpur, Malaysia

vacuum distillation (1–1.5 mm Hg), the distillate within discrete temperature intervals being collected at  $\sim 1$  cm<sup>3</sup> min<sup>-1</sup>. For two of the fractions, D and E, the light scattering depolarisation ratio  $\sigma_u$  (denoted thus rather than by the more customary  $\rho_u$  to avoid confusion with density  $\rho$ ) was abnormally high, viz. 0.28 and 0.50 respectively at 25°C. The presence of an impurity was suspected and purification was attempted by dissolving 1 volume silicone in 3 volumes of distilled, filtered, methanol followed by vigorous shaking. After separation and removal of residual methanol in a vacuum oven at 30°C, the resultant purified samples D<sub>1</sub> and E<sub>1</sub> had  $\sigma_u$  values of 0.086 and 0.41 respectively. These values were unchanged after samples D<sub>1</sub> and E<sub>1</sub> had been subjected to a further purification procedure to yield samples D<sub>2</sub> and E<sub>2</sub>. Hence, it was concluded that no further reduction in  $\sigma_u$  would be effected by additional extractions and the value of  $\sigma_u$  for D<sub>1</sub> (and D<sub>2</sub>) was considered satisfactorily low. However, for E<sub>1</sub> (and E<sub>2</sub>) we have been unable to account for the large value of  $\sigma_u = 0.41$  and, indeed, chromatographic analysis (courtesy of Dr. J. A. Semlyen, University of York, UK) indicated only pure linear oligomer and absence of cyclic species.

Toluene was dried with anhydrous MgSO<sub>4</sub> and distilled at atmospheric pressure. The b.p., refractive index (25°C,  $\lambda_0 = 436$  nm) and density (25°C) were 110°C, 1.5152 and 0.8623 g cm<sup>-3</sup>, respectively.

### Density

Densities of samples A–E were measured at 9 temperatures within the interval 30°C–110°C, the dilatometer used being calibrated with mercury. No difference was observed between the densities of D and D<sub>1</sub> or between those of E and E<sub>1</sub>.

**Table 1** Fractionation data, molecular weights and intrinsic viscosities for PDMS fraction

Fraction	b.p. at 1 mm Hg pressure (°C)	Yield (% volume of original)	$\bar{M}_w$	$\bar{M}_n$	$[\eta]^*$ (cm <sup>3</sup> g <sup>-1</sup> )
A	60–120	20.0	500	481	0.723
B	120–140	22.5	606	598	0.871
C	140–170	25.0	714	677	1.02
D	170–200	17.0	952	850	1.38
D <sub>1</sub>	170–200	—	930	893	1.40
E	200–270	15.0	1176	1004	1.70
E <sub>1</sub>	200–270	—	1176	1132	1.66

\* In toluene at 25°C

### Refractive index

Refractive indices of all samples were measured with a Pulfrich refractometer at  $\lambda_0 = 436$  nm and with an Abbé refractometer at  $\lambda_0 = 589$  nm. Nine temperatures within the interval 20°C–60°C were taken. For toluene,  $\lambda_0 = 436$  nm was used and the temperatures were 25°C, 35°C and 50°C.

**Refractive index increments.** A differential refractometer accommodates a pair of liquids differing in refractive index by not more than  $\sim 0.01$ . Consequently, it is suitable for a solvent/dilute solution pair in order to obtain  $(d\tilde{n}/dc)_{c \rightarrow 0}$ . However, we are concerned here and in future work on these systems with the whole composition range. Moreover, the refractive index of PDMS is much smaller than that of toluene. Hence, it proved much more convenient to derive  $d\tilde{n}/dc$  from directly measured refractive indices of solutions (as in the preceding section) covering the whole range of composition.  $\lambda_0 = 436$  nm and temperatures of 25°C, 35°C and 50°C were used. For a particular composition, linearity between refractive index and temperature allowed interpolation to an additional temperature of 70°C. At a fixed temperature, the best fit of experimental data was one of the second degree invoking concentration  $c$  (mass/volume), thus enabling  $d\tilde{n}/dc$  to be calculated at any value of  $c$ .

### Intrinsic viscosity ( $[\eta]$ )

Values of  $[\eta]$  for A, B, C, D, D<sub>1</sub>, E and E<sub>1</sub> were determined in toluene at 25°C in an Ubbelohde suspended level viscometer. Because of the low molecular weights, the concentrations used were rather high, viz.  $\sim 0.08$  g cm<sup>-3</sup>– $0.20$  g cm<sup>-3</sup>. Good agreement was obtained by extrapolations according to the Huggins and Kraemer equations.

### Vapour pressure osmometry

For samples A, B, C, D, D<sub>1</sub>, E and E<sub>1</sub> values of  $\bar{M}_n$  were determined in toluene at 55°C with a Hitachi–Perkin Elmer vapour pressure osmometer using concentrations up to  $\sim 26$  g (kg solvent)<sup>-1</sup>. Calibration was made with solutions of benzil in toluene. This calibration subsequently yielded  $\bar{M}_n = 254.0$  (theoretical value = 254.5) for octadecane in the same solvent.

### Light scattering

Light scattering experiments were performed with a Sofica photometer (Model 42000) calibrated with the makers' glass standard in conjunction with the total Rayleigh ratio  $R_B$  of benzene at different temperature  $T$ (K). The following dependence of  $R_B$  on  $T$  was employed<sup>3</sup>:

$$R_B(\text{cm}^{-1}) = 10^{-6} [45.4 + 0.109(T - 273)]$$

Scattering at an angle of 90° was measured with unpolarized incident light ( $\lambda_0 = 436$  nm).  $\sigma_u$  was determined from the ratio horizontal: vertical components of the incident light. Because of the low intensity of horizontal components (especially for pure PDMS and very concentrated solutions), accuracy was enhanced by registering all light scattering outputs on a digital voltmeter.

Temperatures up to 50°C were controlled by circulating water from an external thermostat. At 70°C, the internal thermostat of the instrument was used. Solutions and solvent were clarified by filtrations (usually three) at room temperature through a very fine porosity glass sinter.

## RESULTS

First, we report characteristics of the PDMS fractions themselves, then some properties of PDMS/toluene mixtures. Where essential to clarify, subscript-1 will relate to toluene and subscript-2 to PDMS.

### Properties of pure components

Table 1 gives the b.p. range over which the fractions were collected, the intrinsic viscosities,  $\bar{M}_n$  and  $\bar{M}_w$  (via light scattering). The values of  $\bar{M}_n$  and  $[\eta]$  for the original, unfractionated sample were 667 and 1.175 cm<sup>3</sup> g<sup>-1</sup> respectively.

Table 2 gives the coefficients in the observed linear dependence of density on temperature. Similarly, coefficients relating to the variation of refractive index with temperature appear in Table 3.

Appropriate coefficients derived for the thermal dependence of  $\sigma_u$  for all the PDMS fractions and toluene are listed in Table 4.

With regard to the total Rayleigh ratio  $R_T$ , values were obtained via:

$$R_T = (R_B \times 1.19/I_G)(\tilde{n}/\tilde{n}_B)^2$$

**Table 2** Density  $\rho_2$  (g cm<sup>-3</sup>) as a function of temperature  $T$ (K) for PDMS fractions in accord with  $\rho_2 = a + bT$ 

Fraction	$a$ (g cm <sup>-3</sup> )	$-b \times 10^4$ (g cm <sup>-3</sup> K <sup>-1</sup> )
A	1.1718	9.571
B	1.1881	9.599
C	1.1859	9.158
D <sub>1</sub>	1.1952	8.984
E <sub>1</sub>	1.1979	8.839

**Table 3** Refractive index  $\tilde{n}_2$  as a function of temperature  $T$ (K) for PDMS fractions in accord with  $n_2 = a + bT$ 

Fraction	$a$		$-b \times 10^4$ (K <sup>-1</sup> )	
	$\lambda_0 = 436$ nm	$\lambda_0 = 589$ nm	$\lambda_0 = 436$ nm	$\lambda_0 = 589$ nm
A	1.5011	1.5123	3.321	4.013
B	1.4992	1.5141	3.185	4.004
C	1.5003	1.5129	3.160	3.988
D	1.5007	1.5147	3.133	3.999
D <sub>1</sub>	1.4944	1.5208	2.909	4.128
E	1.4853	1.5154	2.578	3.980
E <sub>1</sub>	1.4920	1.5177	2.793	3.980
Original sample	—	1.5124	—	3.918

where  $I$  and  $I_G$  are the digital voltmeter readings for the substance and glass standard, respectively,  $\tilde{n}$  and  $\tilde{n}_B$  are the refractive indices of substance and benzene respectively, and the factor 1.19 is the glass standard calibration factor with respect to benzene.

The isotropic Rayleigh ratio  $R_{iso}$  is given by:

$$R_{iso} = R_T(6 - 7\sigma_u)/(6 + 6\sigma_u) \quad (1)$$

For the pure PDMS fractions and toluene, values of both Rayleigh ratios varied with temperature as indicated in Table 5. Using the coefficients of the derived polynomial, the values of  $R_T$  (or  $R_{iso}$ ) at any temperature differed by a maximum of 1% from the measured ones.

Einstein<sup>4</sup> has shown that the density fluctuation scattering  $R_d$  in a pure liquid as well as in a mixture is given by:

$$R_d = (\pi^2/2\lambda_0^4)kT\beta[\rho(\partial\epsilon/\partial\rho)_T]^2 \quad (2)$$

where  $\lambda_0$  is the wavelength in vacuo,  $k$  is the Boltzmann constant,  $\epsilon$  is the optical dielectric constant ( $=\tilde{n}^2$ ) and  $\beta$  is the coefficient of isothermal compressibility. With regard to the factor  $\rho(\partial\epsilon/\partial\rho)_T$  in equation (2), we have used the following Eykmann expression:

$$\rho(\partial\epsilon/\partial\rho)_T = 2\tilde{n}(\tilde{n}^2 - 1)(\tilde{n} - 0.8)/(\tilde{n}^2 + 0.4\tilde{n} + 1) \quad (3)$$

For a pure liquid  $R_d \equiv R_{iso}$  and combination of equations (2) and (3) yields  $\beta$ . Values thereby derived for  $\beta$  were found to vary with temperature as indicated in Table 6.

#### Properties of mixtures

*Refractive index and refractive index increment.* As mentioned previously, the refractive index of a mixture could be

Table 4 Depolarization ratios  $\sigma_u$  (at  $\lambda_0 = 436$  nm) for PDMS fractions and toluene as a function of temperature in accord with  $\sigma_u = a + bT + eT^2$

Fraction	$a$	$-b \times 10^2$ (K <sup>-1</sup> )	$e \times 10^4$ (K <sup>-2</sup> )
A	1.721	0.8824	0.1184
B	1.717	0.8753	0.1171
C	1.622	0.8143	0.1080
D	1.232	0.5329	0.0719
D <sub>1</sub>	0.674	0.3339	0.0458
E	1.814	0.7608	0.1071
E <sub>1</sub>	1.326	0.5107	0.0679
Toluene	2.729	1.3132	0.1882

Table 5 Total and isotropic Rayleigh ratios at  $\lambda_0 = 436$  nm for PDMS fractions and toluene as a function of temperature in accord with  $R_T$  (or  $R_{iso}$ ) =  $a + bT + eT^2$

Fraction	$R_T$			$R_{iso}$		
	$a \times 10^6$ (cm <sup>-1</sup> )	$-b \times 10^6$ (cm <sup>-1</sup> K <sup>-1</sup> )	$e \times 10^8$ (cm <sup>-1</sup> K <sup>-2</sup> )	$a \times 10^6$ (cm <sup>-1</sup> )	$-b \times 10^6$ (cm <sup>-1</sup> K <sup>-1</sup> )	$e \times 10^9$ (cm <sup>-1</sup> K <sup>-2</sup> )
A	78.0	0.5490	0.1135	35.9	0.3117	0.7661
B	102.5	0.6978	0.1357	55.3	0.4289	0.9395
C	115.7	0.7808	0.1482	68.7	0.5113	1.0590
D	82.0	0.4540	0.08583	22.9	0.1336	0.3256
D <sub>1</sub>	73.6	0.4466	0.08261	53.5	0.3329	0.6449
E	95.9	0.4509	0.09902	-26.4	-0.1706	-0.1203
E <sub>1</sub>	97.8	0.5000	0.1014	6.58	0.03166	0.1951
Toluene	26.3	0.003028	0.03559	-102.7	-0.6283	-0.7657

fitted to a polynomial in composition. The coefficients are given in Table 7 and enable  $d\tilde{n}/dc$  to be calculated at any particular concentration.

*Coefficient of isothermal compressibility.* The values of  $\beta$  were obtained from the values for the pure components ( $\beta_1$  and  $\beta_2$ ) using equation (4) [see Appendix for derivation] in which  $X$  and  $V$  denote mol fraction and molar volume, respectively:

$$\beta = (1/V)(\beta_1 V_1 X_1 + \beta_2 V_2 X_2) \quad (4)$$

*Weight average molecular weights.* The values of  $\bar{M}_w$  in Table 1 were obtained from equation (5) in which  $\bar{M}_w$  is denoted by  $M_2$ :

$$Kc_2/R_c = 1/M_2 + 2A_2c_2 + 3A_3c_2^2 \quad (5)$$

Here  $A_2$  and  $A_3$  are the second and third virial coefficients. The factor  $K$  is not constant, but varies with concentration. Its values were calculated from:

$$K = (2\pi^2 N_A^{-1} \lambda_0^{-4})[\tilde{n}(d\tilde{n}/dc)]_{T,p}^2 \quad (6)$$

Here  $N_A$  is the Avogadro number and  $\tilde{n}$  is the refractive index of the mixture.

The concentration fluctuation Rayleigh ratio  $R_c$  was obtained from:

$$R_c = R_{iso} - R_d \quad (7)$$

$R_{iso}$  for a mixture was determined as for a pure component. The density fluctuation Rayleigh ratio  $R_d$  was obtained by calculation via equations (2), (3) and (4). Bullough<sup>5</sup> has

Table 6 Coefficients of isothermal compressibility  $\beta$  (cm<sup>2</sup> dyn<sup>-1</sup>) for PDMS fractions and toluene as a function of temperature in accord with  $\beta = a + bT + eT^2$

Fraction	$a \times 10^{10}$ (cm <sup>2</sup> dyn <sup>-1</sup> )	$-b \times 10^{11}$ (cm <sup>2</sup> dyn <sup>-1</sup> K <sup>-1</sup> )	$e \times 10^{14}$ (cm <sup>2</sup> dyn <sup>-1</sup> K <sup>-2</sup> )
A	4.343	0.3611	0.8784
B	6.247	0.4730	1.034
C	7.600	0.5551	1.149
D	3.262	0.1760	0.3858
D <sub>1</sub>	6.395	0.3795	0.7096
E	-2.532	-0.1908	-0.1696
E <sub>1</sub>	1.394	0.05174	0.2110
Toluene	-6.141	-0.3874	-0.4896

**Table 7** Refractive indices ( $\tilde{n}$ ) at  $\lambda_0 = 436$  nm for solutions of PDMS (concentration  $c_2$ ) dissolved in toluene and solutions of toluene (concentration  $c_1$ ) dissolved in PDMS, according to:  $\tilde{n} = a + bc_2 + ec_2^2$  and  $\tilde{n} = a + bc_1 + ec_1^2$ 

Fraction	Temperature (K)	Silicone in toluene			Toluene in silicone		
		$a$	$-b$ ( $\text{g}^{-1} \text{cm}^3$ )	$e \times 10^2$ ( $\text{g}^{-2} \text{cm}^6$ )	$a$	$b$ ( $\text{g}^{-1} \text{cm}^3$ )	$e \times 10^2$ ( $\text{g}^{-2} \text{cm}^6$ )
A	298	1.51507	0.12967	0.26752	1.40222	0.12846	0.27899
	308	1.51137	0.13018	0.21485	1.39888	0.12988	0.22654
	323	1.50542	0.13085	0.17227	1.39385	0.13126	0.18886
	343	1.49763	0.13198	0.13078	1.38730	0.13312	0.13321
B	298	1.51507	0.12473	0.22403	1.40438	0.12630	0.23796
	308	1.51133	0.12515	0.18445	1.40114	0.12739	0.20268
	320	1.50841	0.12595	0.17757	1.39619	0.12844	0.19320
	343	1.49797	0.12725	0.17398	1.38996	0.12983	0.19664
C	298	1.51512	0.12237	0.30393	1.40594	0.12366	0.34431
	308	1.51134	0.12252	0.27623	1.40289	0.12444	0.30948
	323	1.50539	0.12244	0.22622	1.39821	0.12552	0.25217
	343	1.49761	0.12302	0.19428	1.39185	0.12693	0.21332
D	298	1.51509	0.11721	0.06270	1.40733	0.12431	0.07518
D <sub>1</sub>	298	1.51514	0.11737	0.17124	1.40778	0.12281	0.19457
	308	1.51513	0.11753	0.15947	1.40479	0.12328	0.18141
	323	1.50542	0.11754	0.16617	1.40042	0.12336	0.20078
	343	1.49760	0.11770	0.17924	1.39459	0.12369	0.20371
E	298	1.51507	0.11219	0.07216	1.40840	0.12294	0.08794
E <sub>1</sub>	298	1.51518	0.11555	0.18297	1.40882	0.12245	0.21787
	308	1.51131	0.11559	0.19361	1.40600	0.12145	0.22802
	323	1.50538	0.11514	0.17751	1.40183	0.12158	0.20315
	343	1.49767	0.11538	0.25736	1.39653	0.12056	0.30233

proposed an amended form of equation (7), viz:

$$R_c = R_{\text{iso}} - R_d(1 + 4Y) \quad (8)$$

where:

$$Y = c_2 \tilde{n} (d\tilde{n}/dc)_{p,T} / \rho (\partial \epsilon / \partial \rho)_T \quad (9)$$

Use of the Eykman equation enabled  $Y$  and hence the amended form of  $R_c$  to be obtained. Using as solutes simple organic compounds of known low molecular weight, Sicotte and Rinfret<sup>6</sup> found equation (8) more accurate than the normal expression, equation (7). We have found the difference in  $M_2$  for our rather higher molecular PDMS samples to be only ~5% when comparing the two approaches. However, for fraction A, the value of  $M_2$  yielded by equation (7) was actually slightly smaller than the measured number average molecular weight. Hence, we conclude that for low molecular weight solutes equation (8) is the more appropriate expression in principle. The weight average molecular weights in *Table 1* were obtained by this means.

It has been proposed as a useful approximation that the third and second virial coefficients are interrelated by:

$$A_3/A_2^2 M_2 = 1/3 \quad (10)$$

Consequently equation (5) assumes the square root form:

$$(Kc_2/R_c)^{1/2} = (1/M_2)^{1/2} [1 + M_2 A_2 c_2] \quad (11)$$

A plot of the left-hand side of equation (11) *versus*  $c_2$  should be linear, with intercept  $= (1/M_2)^{1/2}$  and (slope  $\times$  intercept)  $= A_2$ . Actually, it is unnecessary to assume the validity of

the factor 1/3 in equation (10) in order to arrive at the same conclusion. Thus, binomial expansion applied to equation (5) gives:

$$(Kc_2/R_c)^{1/2} = (1/M_2)^{1/2} [1 + M_2 A_2 c_2 + \left(\frac{3}{2} A_3 M_2 - \frac{1}{2} A_2^2 M_2^2\right) c_2^2 + \dots] \quad (12)$$

and truncation at squared and higher powers of  $c_2$  reduces equation (12) to equation (11). Empirically, such square root plots are considered<sup>7</sup> to be sensibly linear up to higher concentrations than the normal ones [equation (5)] and hence may permit a better means of estimating  $M_2$  and  $A_2$ .

We have examined this possibility with regard to solutions of all five PDMS samples, each at three different temperatures. *Figure 1*, curves A and B, display a similar behaviour over the whole composition range for both types of plot. The linear regions are shown on a larger scale in *Figures 2a* and *2b*. It is seen that  $M_2$  and  $A_2$  can be evaluated from data relating to concentrations not exceeding  $\sim 0.2 \text{ g cm}^{-3}$ . Moreover, this approximate limiting concentration applies to all the samples, i.e. it is not dependent on the molecular weight of the PDMS for the range of  $M_2$  studied. Consistency of the molecular weights is evident by the fact that plots at different temperatures yielded a common intercept. Thus, for sample B at 25°, 50° and 70°C, the plots yielded  $M_2 = 610$ , 608 and 609 respectively.

Plots covering the linear region according to equations (5) and (11) afforded values of  $A_2$  differing by no more than 0.5%. The data are listed in *Table 8*. We have also attempted

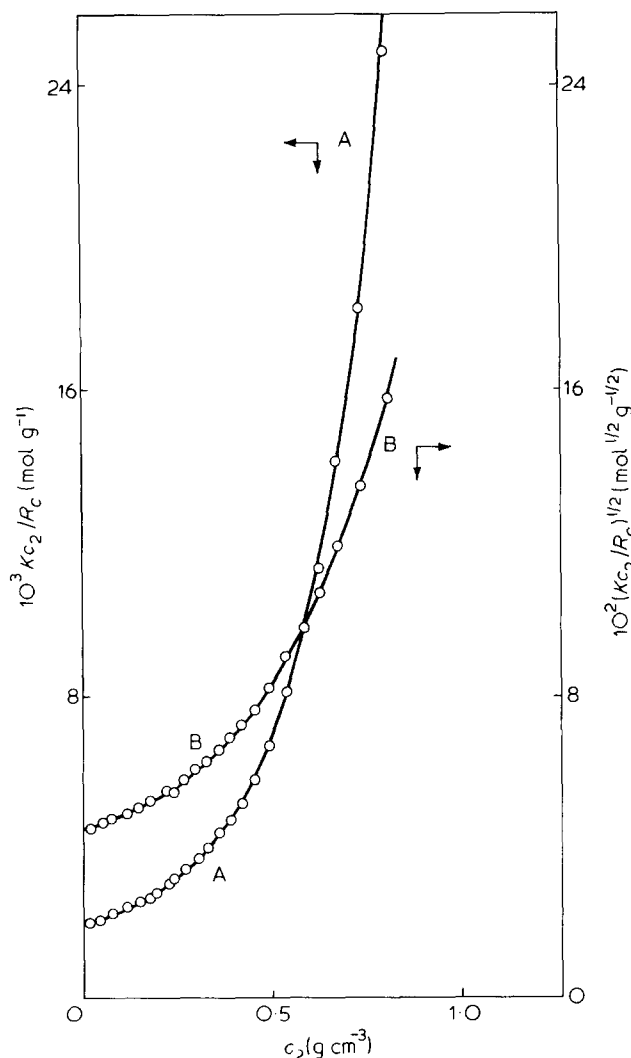


Figure 1 Reduced light scattering versus concentration over complete concentration range for fraction A dissolved in toluene at 50°C. A, normal plot according to equation (5); B, square root plot according to equation (12)

to obtain  $A_2$  by the 'pairs of concentration' method outlined (in a different context) elsewhere<sup>8</sup>. Essentially, light scattering data for pairs of successive concentrations  $(c_2)_i$ ,  $(c_2)_{i-1}$  and  $(c_2)_{i-1}$ ,  $(c_2)_{i-2}$  etc. are used in conjunction with the following expression, which derives readily from equation (5):

$$\frac{\{[K_i(c_2)_i/(R_c)_i] - [K_{i-1}(c_2)_{i-1}/(R_c)_{i-1}]\}}{[(c_2)_i - (c_2)_{i-1}]} = 2A_2 + 3A_3[(c_2)_i + (c_2)_{i-1}] \quad (13)$$

A plot of the left-hand side of equation (13) versus  $[(c_2)_i + (c_2)_{i-1}]$  should be linear, yielding  $2A_2$  as the intercept and  $3A_3$  as the slope. An illustrative plot is given in Figure 3. For this and the remaining fourteen plots,  $A_2$  and  $A_3$  were evaluated by least squares analysis. Although these values of  $A_2$ , which are also included in Table 8, agree reasonably in several instances with those obtained via equations (5) and (11), the considerable scatter of data points in Figure 3 suggests that this accord is rather fortuitous. Hence, we prefer to place reliance solely on the  $A_2$  values yielded via equations (5) and (11). There are no values with which to compare the magnitudes of  $A_3$  yielded by plots such as Figure 3. For this reason, but primarily because of the

scatter in the plots, values of  $A_3$  have been excluded from Table 8.

Since refractometric and light scattering measurements encompassed the whole range of concentration, it was possible to recast light scattering plots in a form invoking toluene as solute and PDMS as solvent. An example is given in Figure 4, where the dilute region is seen to display more scatter than the corresponding region with PDMS as solute (e.g. Figure 1). For the fifteen sets of data, extrapolation to  $c_1 = 0$  should yield the same intercept in each case, viz.  $1/92.1$ , where 92.1 is the molecular weight,  $M_1$ , of toluene. In fact the intercepts gave values of  $M_1$  lying between 84.7 and 131. In view of the extremely small molecular weight of the solute, we do not regard these results as unreasonable. Scatter of data points in the dilute solution region precludes an accurate estimate of  $A_2$ . However, we note that in every instance  $A_2$  is negative.

The variation of intrinsic viscosity with weight average molecular weight for the PDMS fractions in toluene at 25°C is shown in Figure 5, from which the Mark-Houwink relationship is derived as:

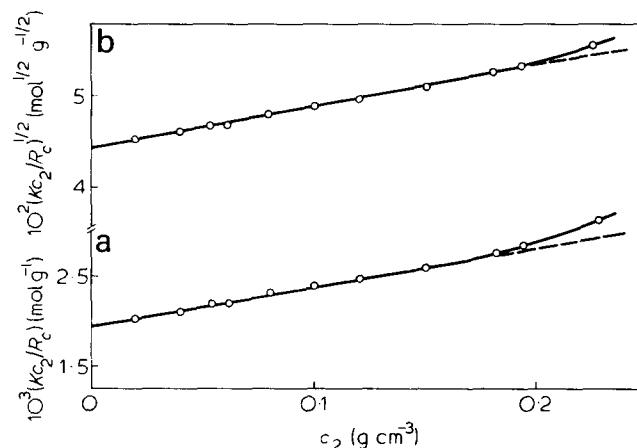


Figure 2 a, dilute region of Figure 1, curve A; b, dilute region of Figure 1, curve B

Table 8 Second virial coefficients (via light scattering) for solutions of PDMS in toluene

Silicone fraction	Temperature (K)	$A_2 \times 10^3$ (cm <sup>3</sup> g <sup>-2</sup> mol)	
		via equations (5) or (11)	via equation (13)
A	298	1.68	1.57
	323	1.94	1.78
	343	2.05	1.60
B	298	1.62	1.61
	323	1.82	1.89
	343	1.97	1.69
C	298	1.55	1.56
	323	1.75	1.68
	343	1.87	2.02
D <sub>1</sub>	298	1.40	1.47
	323	1.66	1.81
	343	1.83	1.51
E <sub>1</sub>	298	1.37	1.41
	323	1.58	1.59
	343	1.72	1.27

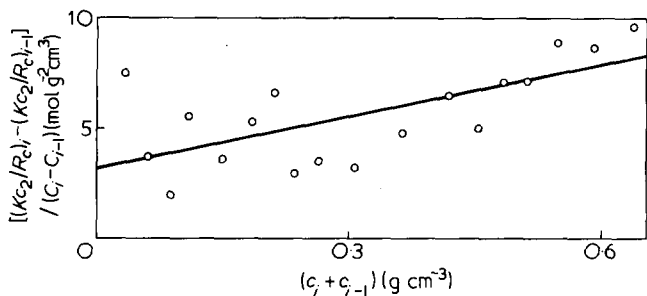


Figure 3 Plot according to equation (13) for solutions of fraction A in toluene at 25°C. Line obtained by least squares analysis

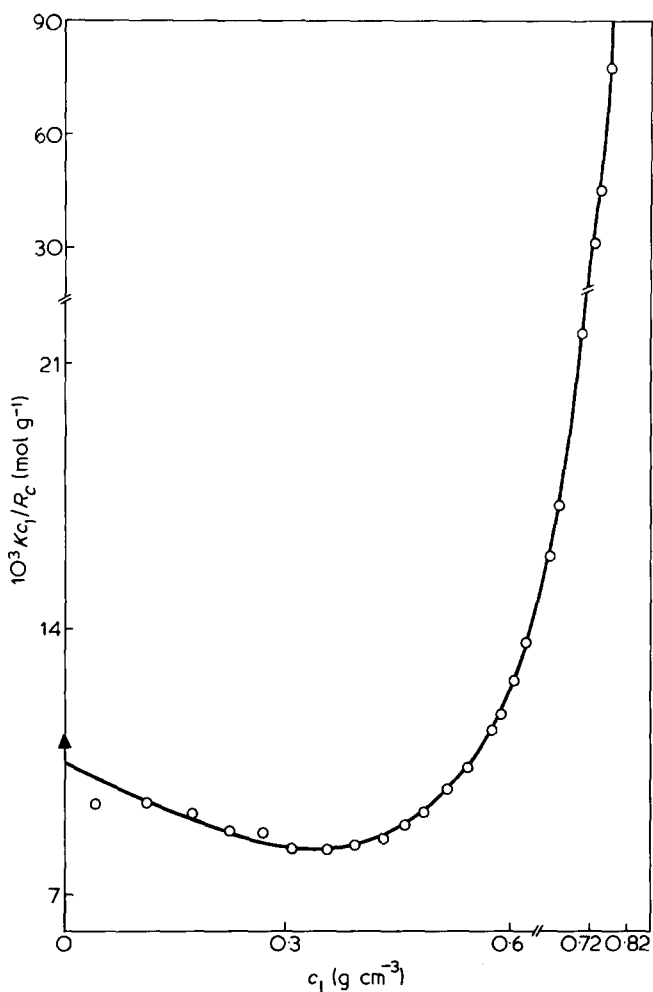


Figure 4 Reduced light scattering versus concentration over complete concentration range for toluene dissolved in fraction A at 50°C.  $\blacktriangle$  denotes reciprocal of correct molecular weight of toluene

$$[\eta] \text{ (cm}^3 \text{ g}^{-1}) = 1.35 \times 10^{-3} \bar{M}_w^{1.01} \quad (14)$$

Literature values of  $[\eta]$  under the same conditions are also included in Figure 5.

## DISCUSSION

The measured parameters have been fitted by least squares to polynomials in terms of independent variables such as concentration or temperature (Tables 2–7). The coefficients listed (e.g.  $a$ ,  $b$  and  $e$ ) do not always display a regular variation with chain length of PDMS. However, when the actual conditions are specified, a regular variation becomes appa-

rent. For example, in Table 2, the coefficients  $a$  and  $b$  in conjunction with a specified temperature of 303K yield values of  $\rho_2 = 0.8816, 0.8972, 0.9083, 0.9228$  and  $0.9299 \text{ g cm}^{-3}$  throughout the sequence of increasing molecular weight for fractions A, B, C, D<sub>1</sub> and E<sub>1</sub> respectively. Here, we shall consider experimental data in relation to corresponding literature values. Frequently, the latter are available only for high molecular weight PDMS and hence interpolation is made.

### (1) Density

Figure 6 shows  $\rho_2$  as a function of  $1/\bar{M}_n$ . A common straight line may be drawn through the present and literature data. Slight departure from linearity is apparent only for  $\bar{M}_n < \sim 416$ . The limiting value at  $(1/\bar{M}_n) = 0$  is  $0.9679 \text{ g cm}^{-3}$  at 30°C, which is close to the value of  $\rho_2 = 0.9692 \text{ g cm}^{-3}$  obtained by Nilsson and Sunderlöf<sup>15</sup> for a PDMS of molecular weight  $6.3 \times 10^4$ . For this sample, these workers report:

$$\rho_2 \text{ (g cm}^{-3}) = 1.2571 - 9.5 \times 10^{-4} T(\text{K})$$

The corresponding relationship from the present data is obtained from the limiting value of  $\rho_2$  at each of ten temperatures.

$$\rho_2 \text{ (g cm}^{-3}) = 1.2179 - 8.244 \times 10^{-4} T(\text{K})$$

At 25°C, the values of  $\rho_2$  and  $\bar{M}_n$  give the molar volume of each fraction. Taking fractions in pairs, division of the difference in molar volume by the difference in average chain length yields  $75.7 \text{ cm}^3 \text{ (mol of segment)}^{-1}$  for PDMS. For

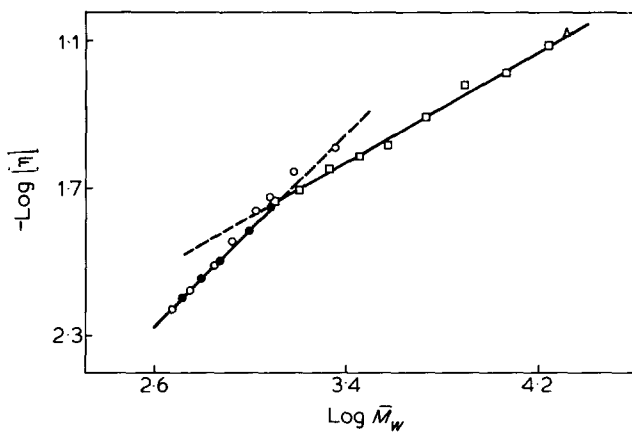


Figure 5 Dependence of  $[\eta]$  on  $\bar{M}_w$  for PDMS in toluene at 25°C.  $\bullet$ , present data;  $\circ$ , ref 9;  $\square$ , ref 10;  $\triangle$ , ref 11

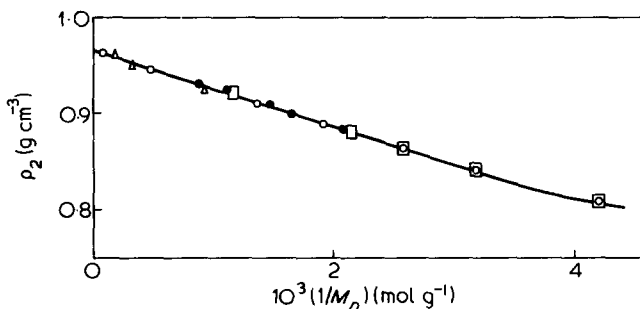


Figure 6 Variation of density with chain length for PDMS at 30°C.  $\bullet$ , present data;  $\circ$ , ref 12;  $\triangle$ , ref 13;  $\square$ , ref 14

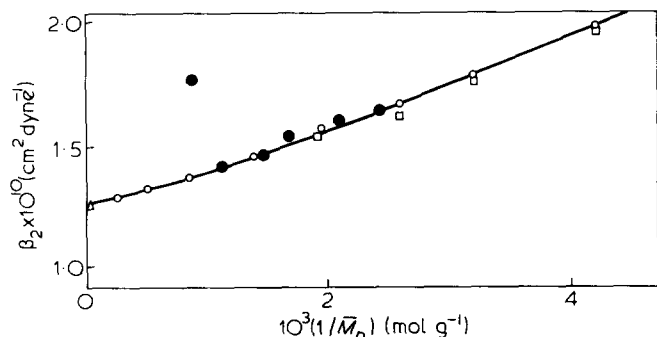


Figure 7 Coefficient of isothermal compressibility as a function of chain length for PDMS at 30°C. ●, present data; ○, ref 12; □, ref 14; △, ref 16

oligomers of smaller  $\bar{M}_n$  than those used here, McLure *et al.*<sup>14</sup> obtained a corresponding value of 76.4 cm<sup>3</sup> (mol of segment)<sup>-1</sup>.

### (2) Coefficient of isothermal compressibility

Figure 7 gives  $\beta_2$  as a function of  $1/\bar{M}_n$  at 30°C. The present data and literature ones fall on a common line, slight departure from linearity being as in the previous section (1). The datum for fraction E<sub>1</sub> is markedly off the line due to the anomalous value of  $\nu_u$  on which  $\beta_2$  depends. Figure 7 includes an additional point relating to a sample of  $\bar{M}_n$  smaller than that of fraction A, viz. unfractionated Dow Corning PDMS fluid DC200/2. The value of  $\beta_2$  was obtained by light scattering as for the five fractions, and  $\bar{M}_n$  was estimated from the measured refractive index ( $\lambda_0 = 436$  nm). The results fall well into the general pattern displayed by the other samples in Figure 7.

The limiting value of  $\beta_2$  at  $(1/\bar{M}_n) = 0$  is  $1.25 \times 10^{-10}$  cm<sup>2</sup> dyn<sup>-1</sup>, which accords exactly with the directly measured value reported by Kim and Ogino<sup>16</sup> for PDMS of molecular weight  $5.1 \times 10^4$ . For this sample, the data of these workers yield:

$$\beta_2(\text{cm}^2 \text{ dyn}^{-1}) = -1.843 \times 10^{-10} + 1.02 \times 10^{-12} T(\text{K})$$

The corresponding relationship from the present data using limiting values of  $\beta_2$  at each of nine temperatures is:

$$\beta_2(\text{cm}^2 \text{ dyn}^{-1}) = -1.756 \times 10^{-10} + 0.992 \times 10^{-12} T(\text{K})$$

These two relationships are practically identical.

### (3) Intrinsic viscosity/molecular weight relationship

In view of the near monodispersity of the samples, the Mark-Houwink constants on the basis of  $\bar{M}_n$  are practically the same as those already presented in equation (14), which related to  $\bar{M}_w$ . The data of Barry<sup>9</sup> also give an exponent  $\nu \approx 1.0$  within the molecular weight region of 458–840, but  $\nu$  falls to 0.66 at high molecular weight. The reported<sup>17</sup> value of  $\nu = 0.50$  under the same conditions for low molecular weight PDMS constitutes an exceptional finding for this polymer.

We have reported previously<sup>18</sup> that  $\nu = 0.50$  for oligomeric nylon-6, a higher value of  $\nu$  holding for medium-high molecular weight polymer. In other systems<sup>19</sup> a normal (0.7–0.8) value of  $\nu$  extends down even to low molecular weights. Hence the contention<sup>20</sup> that oligomers in good solvents behave as if they were under  $\theta$ -conditions (i.e.  $\nu = 0.50$ ) does not seem to be of universal applicability. In particular, the present oligomeric PDMS is unusual in that in the low mole-

cular weight region  $\nu$  increases to a high value (1.01), rather than exhibiting a change to a low value (0.50). This high value of  $\nu$  lends support to the view<sup>21</sup> that oligo-PDMS is helical. Although this view is based on light scattering plots indicative of association, our present light scattering data actually give no indication of association. A rod-like form for oligo-PDMS is an (unverified) assumption, which has been adopted in Corresponding States Theory calculations<sup>22</sup>

### (4) Refractive index and refractive index increment

Plots (not indicated here) of  $\tilde{n}_2$  as a function of PDMS chain length for data at 30°C and  $\lambda_0 = 436$  nm and 589 nm are linear, as is also the plot for  $\lambda_0 = 546$  nm, which was obtained by calculation on the basis of a Cauchy dispersion. In order of increasing  $\lambda_0$ , the limiting values at  $(1/\bar{M}_n) = 0$  of  $\tilde{n}_2$  are 1.4131, 1.4040 and 1.4019. For  $\lambda_0 = 436$  nm and 546 nm at 30°C, others<sup>15</sup> have obtained  $\tilde{n}_2 = 1.4122$  and 1.4039 respectively for PDMS of  $M_2 = 6.3 \times 10^4$ . The makers' specification for high molecular weight PDMS at 25°C and 589 nm is  $\tilde{n}_2 = 1.403$ .

The present data afford the following temperature dependence of the limiting value of  $\tilde{n}_2$ :

$$\lambda_0 = 436 \text{ nm}, \tilde{n}_2 = 1.4874 - 2.458 \times 10^{-4} T(\text{K})$$

$$\lambda_0 = 546 \text{ nm}, \tilde{n}_2 = 1.5156 - 3.680 \times 10^{-4} T(\text{K})$$

$$\lambda_0 = 589 \text{ nm}, \tilde{n}_2 = 1.5262 - 4.074 \times 10^{-4} T(\text{K})$$

The corresponding relationships quoted by Nilsson and Sunderlöf<sup>15</sup> are:

$$\lambda_0 = 436 \text{ nm}, \tilde{n}_2 = 1.5303 - 3.90 \times 10^{-4} T(\text{K})$$

$$\lambda_0 = 546 \text{ nm}, \tilde{n}_2 = 1.5219 - 3.90 \times 10^{-4} T(\text{K})$$

The accord is good for  $\lambda_0 = 546$  nm, but not for  $\lambda_0 = 436$  nm. We are concerned solely with oligo-PDMS and the refractive data for them are probably reliable, despite the lack of accord at  $\lambda = 436$  nm between literature data and limiting values interpolated from the present results. With respect to high molecular weight PDMS only, the following discussion suggests that the literature value (at  $\lambda_0 = 436$  nm) of  $d\tilde{n}_2/dT = -3.90 \times 10^{-4} \text{ deg}^{-1}$  is probably preferable to our own of  $-2.46 \times 10^{-4} \text{ deg}^{-1}$ .

We have verified that  $d\tilde{n}/dc_2$  at  $c_2 = 0$ , obtained by differentiation of the polynomial in  $c_2$ , agrees well with the value obtained by using experimental values of  $\tilde{n}$  at different concentrations and taking the value of  $\Delta\tilde{n}/c_2 = 0$  in the corresponding linear plot. Values of  $d\tilde{n}/dc_2$  versus  $1/\bar{M}_n$  thus yield at each  $T$  the refractive index increments in the limit of  $c_2 = 0$  and  $(1/\bar{M}_n) = 0$ . The temperature coefficient of these is found to be  $5.26 \times 10^{-5} \text{ cm}^3 \text{ g}^{-1} \text{ deg}^{-1}$  as compared to the literature value<sup>15</sup> of  $9.5 \times 10^{-5} \text{ cm}^3 \text{ g}^{-1} \text{ deg}^{-1}$  found for high molecular weight polymer. The latter value agreed to within 2–3% of the temperature coefficient of  $d\tilde{n}/dc_2$  determined by calculation via the Gladstone–Dale equation. This calculation necessitates a knowledge of  $\rho_2$ ,  $d\rho_2/dT$ ,  $\tilde{n}_2$ ,  $d\tilde{n}_2/dT$ ,  $\tilde{n}_1$  and  $d\tilde{n}_1/dT$ . Using our values of these quantities yields a calculated value ( $6.11 \times 10^{-5} \text{ cm}^3 \text{ g}^{-1} \text{ deg}^{-1}$ ), which is  $\sim 14\%$  higher than the experimental temperature coefficient. If our  $d\tilde{n}_2/dT$  is replaced by the value of Nilsson and Sunderlöf and our remaining experimental quantities in the calculation are retained in the calculation, the resultant temperature coefficient of  $d\tilde{n}/dc_2$  ( $= 8.7 \times 10^{-5} \text{ cm}^3 \text{ g}^{-1} \text{ deg}^{-1}$ )

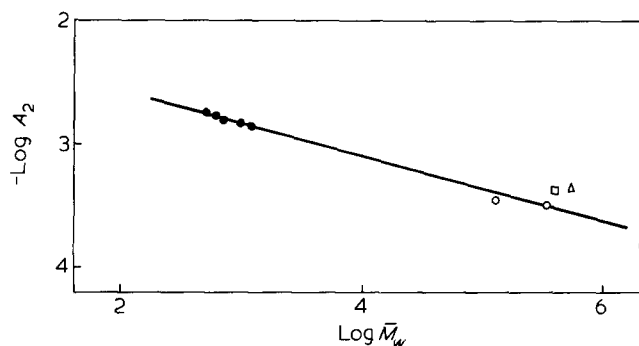


Figure 8 Dependence of  $A_2$  on  $\bar{M}_w$  for PDMS in toluene at 25°C. ●, present data; △, ref 17; □, ref 23; ○, ref 24

differs by only ~5% from the experimental value of Nilsson and Sunderlöf.

#### (5) Second virial coefficient

The dependence of  $A_2$  on  $\bar{M}_w$  for solutions in toluene at 25°C is shown in Figure 8. The four literature values included do not exhibit alone any regular dependence among them, but one of the values relating to a sample of  $\bar{M}_w = 3.53 \times 10^5$  has an  $A_2$  value which agrees well with that interpolated from the present data for oligomers.

The present data at three different temperatures may be represented as:

$$A_2 \propto \bar{M}_w^\gamma \quad (15)$$

The values of  $\gamma$  are found to be  $-0.25$ ,  $-0.22$  and  $-0.20$  at 25°C, 50°C and 70°C respectively and are unchanged, when the dependence is expressed in terms of  $\bar{M}_n$ . As seen in Table 8,  $A_2$  increases with  $T$  at any fixed molecular weight. The systems are thus above the upper critical solution temperature, but are not yet approaching the lower critical solution temperature, since  $A_2$  would decrease with  $T$  if the latter were the situation.

At a particular temperature, any enhancement of polymer-polymer interaction must occur at the expense of reduced polymer-solvent contacts. Since the latter are reflected in the magnitude of  $A_2$ , the increased polymer-polymer interaction associated with increasing chain length of polymer, causes a reduction in  $A_2$  and a resultant negative value of  $\gamma$  in equation (15).

The three quoted values of  $\gamma$  show that the fall in  $A_2$  with  $\bar{M}_w$  is less pronounced at high temperature than at a lower temperature. Qualitatively, this is explicable as follows. At a fixed temperature,  $\gamma$  manifests the decrease in polymer-solvent interaction accompanying an increase in  $\bar{M}_w$ . At a higher temperature this decrease, (whilst still obtaining), is less marked, because it is offset partially by the effect of temperature in increasing independently polymer-solvent interaction. Consequently, the value of  $-\gamma$  at 70°C is less than that at 25°C. Accordingly, one would predict that at temperatures approaching the upper critical solution temperature the reverse situation could hold with regard to the change in  $\gamma$ .

#### ACKNOWLEDGEMENTS

We thank Drs. K. Dodgson and J. A. Semlyen of the University of York, UK, for their helpful discussion. MBS acknowledges financial support provided to her by Universiti Kebangsaan Malaysia under the aegis of its Staff Training Scheme.

#### REFERENCES

- Koningsveld, R., Kleintjens, L. A. and Schoffeleers, H. M. *Pure Appl. Chem.* 1974, **39**, 1
- Scholte, Th. G. *J. Polym. Sci. A-2* 1971, **9**, 1553
- Scornaux, J. and Van Leemput, P. *Makromol. Chem.* 1976, **177**, 2721
- Einstein, A. *Ann. Physik* 1910, **33**, 1275
- Bullough, R. K. *J. Polym. Sci.* 1960, **46**, 517
- Sicotte, Y. and Rinfret, M. *Trans. Faraday Soc.* 1962, **58**, 1090
- Casassa, E. F. and Berry, G. C. in 'Polymer Molecular Weights' Pt 1, (Ed. P. E. Slade, Jr.), Ch 5, Marcel Dekker, New York, 1975
- Huglin, M. B. *Pure Appl. Chem.* 1977, **49**, 929
- Barry, A. J. *J. Appl. Phys.* 1946, **17**, 1020
- Dodgson, K. and Semlyen, J. A. *Polymer* 1977, **18**, 1265
- Takimoto, H. H., Forbes, C. T. and Laudenslager, R. K. *J. Appl. Polym. Sci.* 1961, **5**, 153
- Weissler, A. *J. Am. Chem. Soc.* 1949, **71**, 93
- Katauda, T. and Ueda, S. *J. Polym. Sci. Polym. Lett. Edn* 1966, **4**, 317
- McLure, I. A., Pretty, A. J. and Sadler, D. A. *J. Chem. Eng. Data* 1977, **22**, 372
- Nilsson, R. and Sunderlöf, L. *Makromol. Chem.* 1963, **66**, 11
- Kim, B. Y. and Ogino, K. *Polym. J.* 1979, **11**, 449
- Price, F. P. and Bianchi, J. P. *J. Polym. Sci.* 1955, **15**, 355
- Hague, P., Huglin, M. B., Johnson, B. L. and Smith, J. *J. Appl. Polym. Sci.* 1968, **12**, 2105
- Huglin, M. B., Whitehurst, D. H. and Sims, D. *J. Appl. Polym. Sci.* 1968, **12**, 1889
- Bianchi, U., Dalpiaz, M. and Patrone, E. *Makromol. Chem.* 1964, **80**, 112
- Adank, G. and Elias, H. *Makromol. Chem.* 1967, **102**, 151
- Flory, P. J. and Shih Hsiang *Macromolecules* 1972, **5**, 761
- Kuwahara, N., Okazawa, T. and Kaneko, M. *J. Polym. Sci. C.* 1968, **23**, 543
- Kubota, K., Kubo, K. and Ogino, K. *Bull. Chem. Soc. Jpn.* 1976, **49**, 2410

#### APPENDIX

##### Derivation of equation (4)

At a constant temperature,  $T$ , consider  $n_1$  moles of component 1 and  $n_2$  moles of component 2. Then:

$$\text{total volume} = n_1 \bar{V}_1 + n_2 \bar{V}_2$$

where  $\bar{V}_1$  and  $\bar{V}_2$  denote, respectively, the partial molar volumes of the two components. The molar volume ( $V$ ) of the mixture is the total volume divided by the total number of moles, viz:

$$V = 1/(n_1 + n_2) [n_1 \bar{V}_1 + n_2 \bar{V}_2] = X_1 \bar{V}_1 + X_2 \bar{V}_2 \quad (A1)$$

where  $X$  denotes mol fraction.

By definition, the coefficient of isothermal compressibility,  $\beta$ , is:

$$\beta = (-1/V)(\partial V/\partial p)_T \quad (A2)$$

$$= -(\partial \ln V/\partial p)_T \quad (A3)$$

Substituting for  $V$  from equation (A1) into equation (A3) gives for the mixture:

$$\begin{aligned} \beta &= -(\partial \ln [X_1 \bar{V}_1 + X_2 \bar{V}_2] / \partial p)_T \\ &= [-1/(X_1 \bar{V}_1 + X_2 \bar{V}_2)] [X_1 (\partial \bar{V}_1 / \partial p)_T + X_2 (\partial \bar{V}_2 / \partial p)_T] \\ &= (-1/V) [X_1 (\partial \bar{V}_1 / \partial p)_T + X_2 (\partial \bar{V}_2 / \partial p)_T] \quad (A4) \end{aligned}$$

Invoking equation (A2) for each component and approximating partial molar volumes to molar volumes  $V_1$  and  $V_2$  yields from equation (A4):

$$\beta = (1/V)(X_1 V_1 \beta_1 + X_2 V_2 \beta_2)$$