Studies of cyclic and linear poly(dimethyl siloxanes): 1. Limiting viscosity number–molecular weight relationships

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The limiting viscosity numbers of ten cyclic and ten linear poly(dimethyl siloxane) fractions have been measured in a Θ-solvent (butanone at 293K) and in two 'good' solvents (toluene and cyclohexane at 298K). The dimethyl siloxane fractions studied were in the molecular weight range $800 < \bar{M}_w < 17\,000$. The data obtained are compared with related studies published in the literature. The ratio of the limiting viscosity numbers $[\eta]_r$ and $[\eta]_l$ of the cyclic and linear poly(dimethyl siloxanes) with $\bar{M}_w > 2500$ was found to be 0.67 in butanone at 293K. This value is identical (within experimental error) to the theoretical ratio $[\eta]_r/[\eta]_l = 0.66$ predicted by Bloomfield and Zimm and others for ring and chain polymers in Θ-solvents. The ratio $[\eta]_r/[\eta]_l$ was found to be somewhat smaller for the higher molecular weight polymers in the 'good' solvents.

INTRODUCTION

The pioneering investigations of Brown and Slusarczuk[1] some twelve years ago demonstrated that ring–chain equilibrates of poly(dimethyl siloxane) may contain a range of cyclic molecules $[(CH_3)_2SiO]_x$ with values of x from $x = 3$ to $x > 200$. The concentrations of cyclics in Brown and Slusarczuk's equilibrate and in other ring–chain equilibrates of poly(dimethyl siloxane) have been measured with considerable precision and they have been related to the statistical conformations of the corresponding open chain molecules[2–4]. Experimental methods used in these investigations include gas–liquid chromatography (g.l.c.), gel permeation chromatography (g.p.c.) and fractionation techniques. All these studies have been reviewed recently[5].

Although the preparation of large cyclic poly(dimethyl siloxanes) containing up to 500 skeletal bonds is well established, there have been no publications describing the properties of such ring compounds apart from two papers that describe their g.p.c. retention behaviour[4,6]. It is the purpose of this paper to report the limiting viscosity number–molecular weight relationships for cyclic poly(dimethyl siloxanes) $[(CH_3)_2SiO]_x$ with weight-average values of x in the range $10 < \bar{x}_w < 225$ and to compare the relationships with those found for the corresponding open chain molecules and with the theoretical predictions of Bloomfield and Zimm[7], Fukatsu and Kurata[8] and Yu and Fujita[9].

EXPERIMENTAL

Materials

A mixture of cyclic dimethyl siloxanes $[(CH_3)_2SiO]_4$ and $[(CH_3)_2SiO]_5$ was dried by refluxing over calcium hydride for 12 h and then fractionally distilled.

Linear poly(dimethyl siloxanes) with the general formula $(CH_3)_3SiO[(CH_3)_2SiO]_ySi(CH_3)_3$ were obtained from Hopkin and Williams Ltd as fractions with broad molecular weight distributions (Dow Corning DC 200 series Dimethicones). Several fractions were selected with number-average molecular weights $\bar{M}_n$ in the range $1500 < \bar{M}_n < 20\,000$.

Potassium silanolate initiator was prepared from potassium hydroxide and the cyclic dimethyl siloxane mixture by the method of Grubb and Osthoff[10].

Analytical grade solvents (acetone, butanone, toluene and cyclohexane) were used throughout. They were dried and distilled before use.

Preparation and fractionation of cyclic poly(dimethyl siloxanes)

Cyclic poly(dimethyl siloxanes) were prepared from oligomers $[(CH_3)_2SiO]_4$ and $[(CH_3)_2SiO]_5$ in a ring–chain equilibration reaction in toluene solution at 383K, using a method similar to that recommended by Brown and Slusarczuk[1]. The reaction mixture contained a total of 593 g of siloxanes, 10 g of diethylene glycol dimethyl ether (added as promotor) and $\sim 3 \times 10^{-4}$ mol potassium (as potassium silanolate). The total siloxane concentration was 235 g/dm^3. The mixture was allowed to reflux for several days under an atmosphere of dry nitrogen and the progress to equilibrium was monitored by g.l.c. and g.p.c. When equilibrium had been attained, the mixture was quenched by adding 10 g of glacial acetic acid and cooling to room temperature. Potassium salts were removed from the mixture by washing with three successive portions of distilled water. Then the toluene was removed by fractional distillation. The distributions of cyclic and linear poly(dimethyl siloxanes) in the equilibrate were determined by g.p.c. and were consistent with results obtained for equilibrations carried out under similar conditions[3,4].

Cyclics $[(CH_3)_2SiO]_x$ with $x = 3$ to $x = 6$ were removed from the quenched equilibrate by fractional distillation under reduced pressure. The cyclics and high molecular weight linear polymer in the residue were separated by precipitating the linear polymer from a hot solution of the residue in acetone (10% w/v) by allowing it to cool to room temperature and to stand for 24 h. The supernatant solution containing the cyclics was decanted from the linear polymer, and the acetone was removed by distillation under reduced pressure. The yield of large cyclic siloxanes obtained in this way was 74.0 g corresponding to a concentration of 29.3 g/dm^3 in the original equilibrate. The residue was analysed by g.p.c. and the observed distribution of cyclics was compared with the distribution calculated from Wright's experimental molar cyclization equilibrium constants[4]. Cyclics $[(CH_3)_2SiO]_x$, with values of x in the range $20 < x < 90$ were found to be present at their equilibrium concentrations. Cyclics with larger values of x were found to be present at concentrations somewhat lower than those predicted by the experimental molar cyclization equilibrium constants. The g.p.c. tracing of the linear high molecular weight polymer that had been precipitated as described above showed that ~5% of the large cyclic siloxanes were present in the chain fraction and that negligible amounts of linear polymer were present in the cyclic residue.

Over twenty cyclic siloxane fractions (each 1–3 g in weight) were obtained from ~50 g of the cyclic residue by distillation and fractional precipitation. Fractions of cyclics $[(CH_3)_2SiO]_x$ with weight-average values of x in the range $50 < \bar{x}_w < 225$ were obtained by fractional precipitation of the cyclic residue from 3% acetone solution at 293K using water as the non-solvent. The fractions were purified by reprecipitation. They were dried and residual solvent was removed by heating the samples under vacuum. Distilled fractions with weight-average values of x in the range $10 < \bar{x}_w < 32$ were obtained using a short path molecular still operating in the temperature range 373–500K at a pressure of 0.1 mmHg. Distilled fractions were analysed by g.l.c. and their number-average and weight-average molecular weights were determined from the chromatograms.

Preparation of linear poly(dimethyl siloxane) fractions

Fractions of linear poly(dimethyl siloxanes) $(CH_3)_3SiO[(CH_3)_2SiO]_ySi(CH_3)_3$ with weight-average values of y in the range $12 < \bar{y}_w < 45$ were obtained by fractional distillation of Dow Corning DC 200/20 Dimethicone and analysed by g.l.c. Fractions with weight-average values of y in the range $45 < \bar{y}_w < 225$ were obtained by fractional precipitation of samples of DC 200/200 and DC 200/100 Dimethicone from solution in butanone at 293K using methanol as the non-solvent. Each fraction was reprecipitated before being analysed.

Characterization of cyclic and linear fractions by g.p.c.

All the fractions of cyclic and linear poly(dimethyl siloxanes) used for the viscometric measurements were characterized by g.p.c. The g.p.c. instrument was equipped with five analytical columns of Styragel (a crosslinked polystyrene gel from Waters Associates Ltd). These columns were packed with gels having nominal porosities 25, 100, 300, 300 and 300 nm, respectively. Toluene was used as the solvent at a flow rate of ~1 cm^3/min. A Waters model R4 differential refractometer was used as the detector. The instrument was calibrated separately for cyclic and linear poly(dimethyl siloxanes) with number-average molecular weights in the range 300–18 000 and the g.p.c. calibration plots were linear and parallel in this range[4,6]. The g.p.c. tracings were corrected for imperfect resolution by the method of Pierce and Armonas[11] and then used to determine the number-average and weight-average molecular weights of the fractions. The molecular weights of distilled fractions obtained by g.p.c. were found to differ by less than 5% from those obtained by g.l.c.

Viscometric measurements

Dilute solution viscosities of the cyclic and linear poly(dimethyl siloxanes) were measured using a semimicro Ubbelohde suspended level viscometer (bulb capacity ~1 cm^3). Solvent efflux times were 121.0 sec for butanone at 293.00 ± 0.01K, 156.0 sec for toluene at 298.00 ± 0.01K and 283.0 sec for cyclohexane at 298.00 ± 0.01K. In consequence, no kinetic energy corrections were made. Solutions were prepared by weighing the solute and the solvent, and the concentrations c (in g/100 cm^3) were calculated from the specific gravities of the solute and solvent at the temperature of the experiment. Solution efflux times were found to be reproducible to ±0.2 sec and the mean time of at least four measurements was used to calculate the specific viscosity η_{sp} of each solution.

Measurements of the viscosity numbers of each cyclic and linear poly(dimethyl siloxane) fraction studied were made at four (or more) different concentrations. These concentrations were typically in the range 1–9 g/100 cm^3. In all cases, a least squares procedure was used to extrapolate values of the viscosity number η_{sp}/c for a particular fraction to zero concentration in order to determine the limiting viscosity number $[\eta]$ (see *Figure 1* for some examples).

It is noted that the units of limiting viscosity number used here are 100 cm^3/g. These units were chosen so that a direct comparison could be made with data published in the literature (see below). In order to convert $[\eta]$ values in this paper to units of m^3/kg it is necessary to multiply them by 0.1.

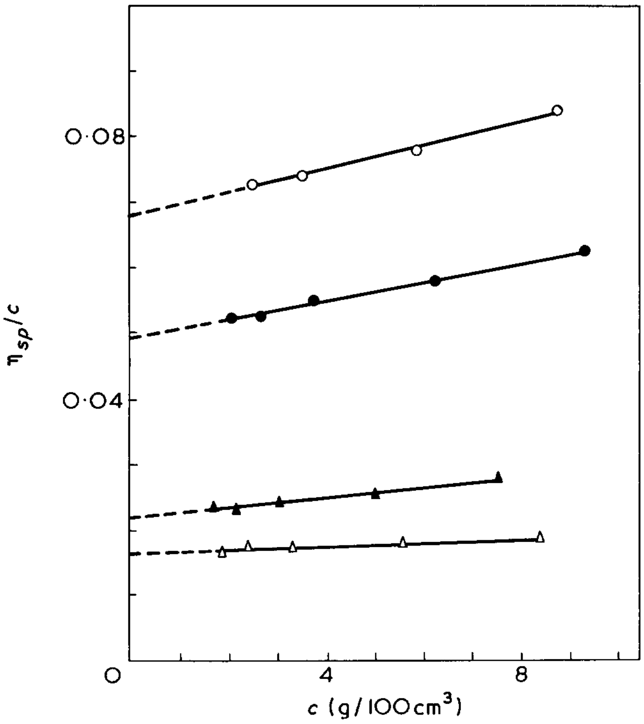

Figure 1 Examples of the dependence of viscosity number η_{sp}/c on the concentration c for fractions R6 (▲) and L1 (△) in butanone at 293K and fractions R8 (●) and L8 (○) in toluene at 198K. The concentrations are expressed in units of g/100 cm^3

Table 1 Molecular weights and limiting viscosity numbers [η] (in units of 100 cm^3/g) of the cyclic (R1–R10) and linear (L1–L10) poly(dimethyl siloxane) fractions

Fractions†	$\bar{M}_w$*	$\bar{M}_w/\bar{M}_n$*	[η] In butanone at 293K	[η] In toluene at 298K	[η] In cyclohexane at 298K
R1	800	1.07	0.0094	0.0084	0.0087
R2	1210	1.01	0.0119	0.0109	0.0104
R3	1580	1.01	0.0135	0.0129	0.0131
R4	1760	1.02	0.0149	0.0139	0.0143
R5	2310	1.03	0.0169	0.0166	0.0164
R6	3780	1.32	0.0219	0.0264	0.0271
R7	5990	1.41	0.0298	0.0331	0.0362
R8	10 040	1.38	0.0416	0.0493	0.0569
R9	13 400	1.28	0.0456	0.0705	0.0786
R10	16 570	1.22	0.0537	0.0787	0.0881
L1	1150	1.02	0.0164	0.0176	0.0169
L2	1220	1.03	0.0180	0.0178	0.0173
L3	1560	1.02	0.0204	0.0191	0.0187
L4	2030	1.02	0.0244	0.0237	0.0226
L5	2760	1.04	0.0273	0.0287	0.0310
L6	3580	1.14	0.0305	0.0362	0.0394
L7	5040	1.19	0.0403	0.0491	0.0547
L8	7540	1.32	0.0541	0.0677	0.0727
L9	11 040	1.24	0.0601	0.0956	0.1050
L10	16 690	1.29	0.0799	0.1300	0.1550

* M_n and M_w denote number-average and weight–average molecular weight respectively;

† fractions R1–R5 and L1–L5 were obtained by fractional distillation

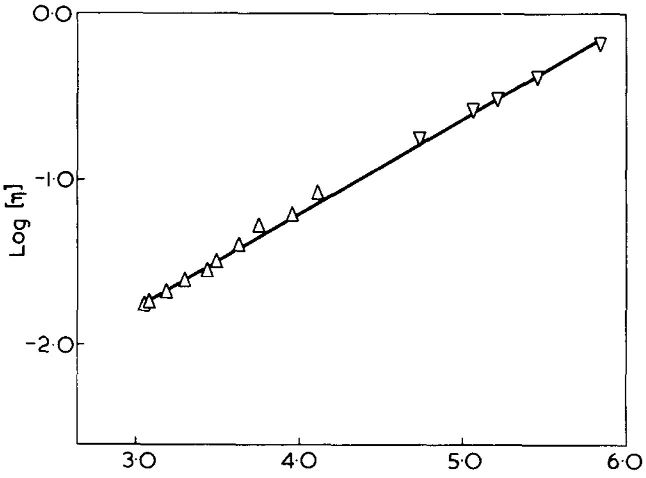

Figure 2 Plots of the logarithms of the limiting viscosity numbers [η] of linear poly(dimethyl siloxane) fractions against the logarithms of their number-average molecular weights $\bar{M}_n$ in butanone at 293K. △, determined in this study; ▽, obtained by Flory, Mandelkern, Kinsinger and Shultz[12]. ———,has been constructed by a least squares procedure using both sets of data

RESULTS AND DISCUSSION

The molecular weights and limiting viscosity numbers [η] of the cyclic and linear poly(dimethyl siloxane) fractions (R1–R10 and L1–L10) used in this study are presented in *Table 1*. The [η] values listed were measured in butanone at 293K (a θ-solvent for linear poly(dimethyl siloxane) at this temperature[12]), and in toluene and cyclohexane at 298K ('good' solvents for the linear polymer at this temperature[13]).

It is noted that the [η] values of the linear fractions in butanone at 293K agree with values predicted by the data of Flory, Mandelkern, Kinsinger and Shultz[12] (*Figure 2*). Furthermore, the [η] values of L6 and L7 in toluene at 298K are close to the values obtained for fractions of similar molecular weight by Bianci, Dalpiaz and Patrone[14]. However, L8–L10 do have somewhat higher [η] values and fractions L3–L5 do have somewhat lower [η] values than those predicted by the data of Bianci *et al.* (ref 14); whereas L1, L2 have [η] values close to that reported by Adank and Elias[15] for a fraction with a similar molecular weight.

The viscometric properties of the cyclic and linear poly(dimethyl siloxanes) in the different solvents are compared in *Figures 3* and *4*. The [η] values of the linear fractions in butanone, toluene and cyclohexane agree within experimental error for molecular weights below ~2000 (see *Figure 3*). Similar behaviour is observed for the cyclic polymers (*Figure 4*). For the fractions of higher molecular weight, a dependence of [η] on the nature of the solvent is observed, and the gradients of the plots of log [η] against log $\bar{M}_w$ are found to increase along the series butanone < toluene < cyclohexane, for both the cyclic and the linear polymers (see *Figures 3* and *4*). These increases are believed to be associated with expansion of the polymer molecules by excluded volume effects in the 'good' solvents (toluene and cyclohexane), and there is a substantial amount of experimental evidence to support this interpretation[16–20]. The chain lengths at which excluded volume effects become important would be expected to depend on the nature of the polymer[16]. The results presented here indicate that chain expansion becomes appreciable for both cyclic and linear poly(dimethyl siloxanes) with more than about 100 skeletal bonds. This finding is consistent with the conclusions of Wright[4], made on the basis of studies of the molar cyclization

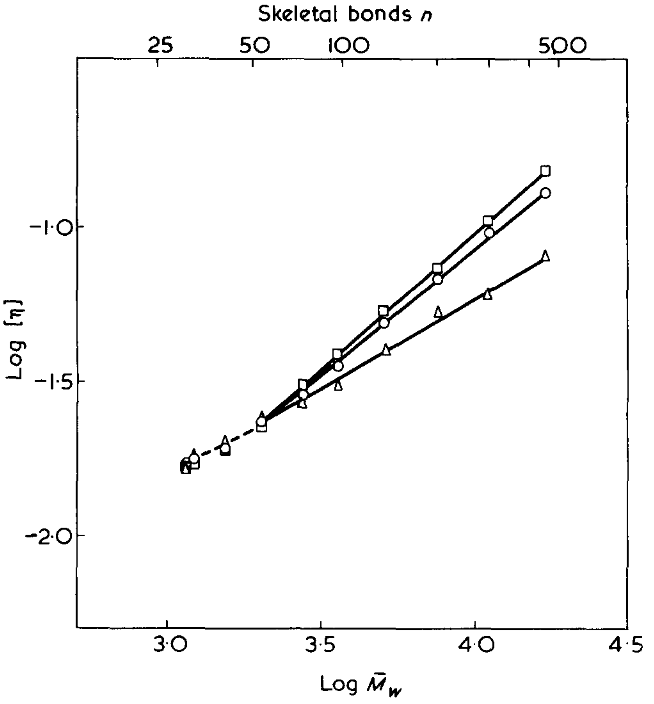

Figure 3 Plots of the logarithms of the limiting viscosity numbers [η] of the linear poly(dimethyl siloxane) fractions against the logarithms of their weight-average molecular weights $\bar{M}_w$ in butanone at 293K (△), toluene at 298K (○) and cyclohexane at 298K (□). ———, were constructed by a least squares procedure using the data of linear fractions L4–L10

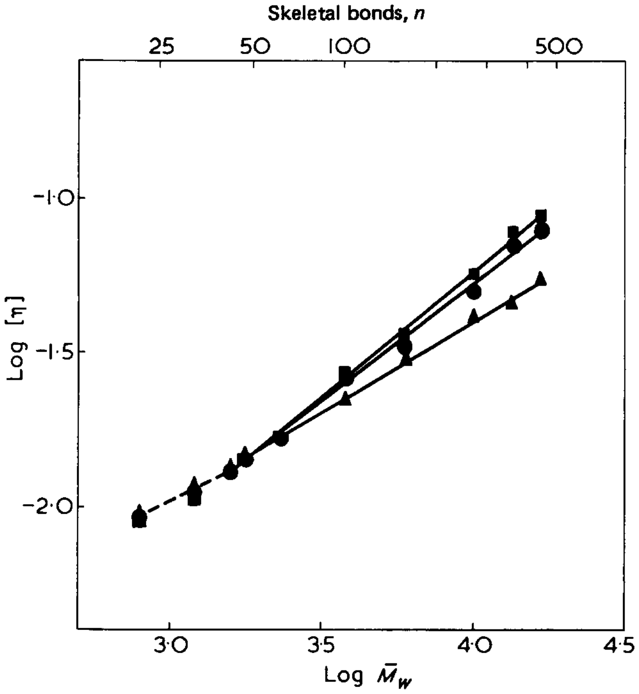

Figure 4 Plots of the logarithms of the limiting viscosity numbers $[\eta]$ of the cyclic poly(dimethyl siloxane) fractions against the logarithms of their weight-average molecular weights $\bar{M}_w$ in butanone at 293K (▲), toluene at 298K (●) and cyclohexane at 298K (■). ——, were constructed by a least squares procedure using the data of cyclic fractions R4–R10

equilibrium constants of poly(dimethyl siloxanes) in a 'good' and in a 'poor' solvent.

The limiting viscosity number–molecular weight relationships for cyclic and linear poly(dimethyl siloxanes) in butanone at 293K, toluene at 298K and cyclohexane at 298K (obtained from the least squares lines constructed using the values for R4–R10 and L4–L10) are as follows.

In butanone at 293K:
$[\eta]_r = 1.92 \times 10^{-4}\bar{M}_w^{0.58}$
$[\eta]_l = 2.80 \times 10^{-4}\bar{M}_w^{0.58}$
In toluene at 298K:
$[\eta]_r = 4.21 \times 10^{-5}\bar{M}_w^{0.77}$
$[\eta]_l = 4.21 \times 10^{-5}\bar{M}_w^{0.83}$
In cyclohexane at 298K:
$[\eta]_r = 2.72 \times 10^{-5}\bar{M}_w^{0.83}$
$[\eta]_l = 2.60 \times 10^{-5}\bar{M}_w^{0.89}$

where $[\eta]_r$ and $[\eta]_l$ denote the limiting viscosity number of the cyclic (i.e. ring) and linear poly(dimethyl siloxanes), respectively.

It is not the purpose of this paper to make a detailed comparison of the experimental data presented with the predictions of theory. However, the ratios of the limiting viscosity numbers of the cyclic and linear poly(dimethyl siloxanes) (deduced from the limiting viscosity number–molecular weight relationships presented above) will be quoted. Over the molecular weight range $2500 < \bar{M}_w < 16\,000$ the ratios $[\eta]_r/[\eta]_l$ are 0.675–0.670 in butanone at 293K, 0.659–0.597 in toluene at 298K and 0.655–0.584 in cyclohexane at 298K. The ratio in butanone agrees with that predicted for polymeric rings and chains at the Θ-point by Bloomfield and Zimm[7], Fukatsu and Kurata[8] and Yu and Fujita[9], namely $[\eta]_r/[\eta]_l = 0.662$. Furthermore, for the siloxanes with the highest molecular weights studied, the ratio $[\eta]_r/[\eta]_l$ is observed to decrease from ~0.67 in butanone, to ~0.60 in toluene and to ~0.58 in cyclohexane. This decrease of $[\eta]_r/[\eta]_l$ in 'good' solvents is in agreement with the theoretical predictions of Bloomfield and Zimm[7] and Yu and Fujita[9] but contrary to the predictions of Fukatsu and Kurata[8].

Further experimental and theoretical studies of cyclic and linear poly(dimethyl siloxanes) are in progress. It is hoped that a more detailed interpretation of their viscometric properties (and incidentally their g.p.c. retention behaviour[4,6]) may be made when more information relating to the properties of cyclic and linear poly(dimethyl siloxanes) becomes available.

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REFERENCES

1 Brown, J. F. and Slusarczuk, G. M. J. *J. Am. Chem. Soc.* 1965, **87**, 931
2 Flory, P. J. and Semlyen, J. A. *J. Am. Chem. Soc.* 1966, **88**, 3209
3 Semlyen, J. A. and Wright, P. V. *Polymer* 1969, **10**, 543
4 Wright, P. V. *J. Polym. Sci. (Polym. Phys. Edn)* 1973, **11**, 51
5 Semlyen, J. A. *Adv. Polym. Sci.* 1976, **21**, 41
6 Semlyen, J. A. and Wright, P. V. in 'Chromatography of Synthetic Polymers and Biopolymers', (Ed. R. Epton), Ellis Horwood, Chichester, 1977, Vol 1
7 Bloomfield, V. and Zimm, B. H. *J. Chem. Phys.* 1966, **44**, 315
8 Fukatsu, M. and Kurata, M. *J. Chem. Phys.* 1966, **44**, 4539
9 Yu, H. and Fujita, H., work cited by Yamakawa, H. in 'Modern Theory of Polymer Solutions', Harper and Row, New York, London, 1971, p 323
10 Grubb, W. T. and Osthoff, R. C. *J. Am. Chem. Soc.* 1955, **77**, 1405
11 Pierce, P. E. and Armonas, J. E. *J. Polym. Sci. (C)* 1968, **21**, 23
12 Flory, P. J., Mandelkern, L., Kinsinger, J. B. and Shultz, W. B. *J. Am. Chem. Soc.* 1952, **74**, 3364
13 Kuwahara, N., Miyake, Y., Kaneko, M. and Furuichi, J. *Rep. Prog. Polym. Phys. Jpn* 1962, **5**, 1
14 Bianchi, U., Dalpiaz, M. and Patrone, E. *Makromol. Chem.* 1964, **80**, 112
15 Adank, G. and Elias, H. G. *Makromol. Chem.* 1967, **102**, 151
16 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, New York, 1953
17 Berry, G. C. and Fox T. G. *J. Am. Chem. Soc.* 1964, **86**, 3540
18 Altares, T., Wyman, D. P. and Allen, V. R. *J. Polym. Sci. (A)* 1964, **2**, 4533
19 Bianci, U. and Peterlin A. *J. Polym. Sci. (A)* 1969, **2**, 563
20 Berry, G. C. *J. Chem. Phys.* 1967, **46**, 1338