Studies of cyclic and linear poly(dimethyl siloxanes): 2. Preparative gel permeation chromatography

K. Dodgson, D. Sympson and J. A. Semlyen
Department of Chemistry, University of York, Heslington, York YO1 5DD, UK
(Received 18 May 1978)

A preparative gel permeation chromatographic (g.p.c.) instrument has been constructed and used to separate broad fractions of cyclic poly(dimethyl siloxanes) into sharp fractions with heterogeneity indices $\bar{M}_w/\bar{M}_n = 1.05 \pm 0.02$. The number-average molecular weights $\bar{M}_n$ of the cyclic polymer fractions obtained were as high as 50 000, corresponding to number-average numbers of skeletal bonds $\bar{n}_n$ up to 1300. The concentrations of linear poly(dimethyl siloxanes) in all but the highest molecular weight cyclic polymer fractions prepared are believed to be negligible. The preparative g.p.c. instrument was also used to obtain some sharp fractions of linear poly(dimethyl siloxanes).

INTRODUCTION

Recently, we have reported the preparation and characterization of fractions of the first synthetic cyclic polymers[1]. These polymers consist of mixtures of cyclic poly(dimethyl siloxanes) $[(CH_3)_2SiO]_x$, containing up to about 1000 skeletal bonds. They are of considerable interest because they belong to a class of polymer that is different in type from the linear, branched and network polymers that have received such close attention over the past fifty years. In fact, a detailed knowledge of the properties and molecular conformations of cyclic polymers could lead to a better understanding of the behaviour of linear polymers, as well as to new insights into the properties of rubbers, gels and other systems where closed loops are known to be present. As a consequence, we have embarked on an investigation of synthetic cyclic polymers, beginning with the poly(dimethyl siloxanes) described in this paper. In connection with such an investigation, it is of interest to note that many natural forms of deoxyribonucleic acid (DNA) are cyclic macromolecules, as has been shown by electron microscopy and other methods (see, for example, refs 2–7). Furthermore, in recent years, there have been a number of interesting theoretical studies of the average conformations and physicochemical behaviour of large ring molecules, including those described in refs 8–22. We hope to test some of the results of these studies in the future using the synthetic cyclic polymers discussed here.

When investigating the properties of cyclic or linear polymers, it is clearly an advantage to use fractions that are as sharp as possible. As indicated previously[1,23–25], gas–liquid chromatography (g.l.c.) can be used to analyse individual dimethyl siloxane cyclics $[(CH_3)_2SiO]_x$ containing up to 100 skeletal bonds, and sharp fractions containing cyclics of this size can be prepared conveniently by vacuum fractional distillation. Such fractions have heterogeneity indices $\bar{M}_w/\bar{M}_n$ which are typically 1.02 ± 0.01. Larger cyclics can be fractionated using conventional methods (for example, by fractional precipitation using acetone and water[1]), but such methods are time consuming and broad fractions often result. It is the purpose of this paper to describe how gel permeation chromatography (g.p.c.) can be used to prepare sharp fractions of cyclic (and, incidentally, linear) poly(dimethyl siloxanes) with number-average numbers of skeletal bonds $\bar{n}_n$ in the range $100 < \bar{n}_n < 1000$. A preparative g.p.c. instrument was designed and constructed in our departmental workshops for this purpose. The fractions of cyclic and linear poly(dimethyl siloxanes) obtained had heterogeneity indices of 1.05 ± 0.02, which are considerably lower than those obtained using conventional fractionation methods[1].

EXPERIMENTAL

Materials

In the work described here, cyclic and linear poly(dimethyl siloxane) fractions with relatively broad molecular weight distributions were refractionated by preparative g.p.c. These broad fractions were obtained previously[1]. The cyclic fractions were recovered from a poly(dimethyl siloxane) cyclic–linear equilibration reaction in toluene solution at 383K. The linear fractions were made by fractional precipitation of Dow Corning DC200 series dimethicones obtained from Hopkin and Williams Ltd. The cyclic fractions consisted of rings $[(CH_3)_2SiO]_x$, and the linear fractions consisted of chains with the general formula $(CH_3)_3SiO[(CH_3)_2SiO]_y Si(CH_3)_3$. The number-average molecular weights $\bar{M}_n$ of the cyclic and linear fractions were in the range $4000 < \bar{M}_n < 15\,000$ and their heterogeneity indices were in the range $1.4 < \bar{M}_w/\bar{M}_n < 1.6$.

Analytical g.p.c.

All the fractions of cyclic and linear poly(dimethyl siloxanes) obtained from the preparative g.p.c. instrument were characterized by analytical g.p.c. The analytical instrument was equipped with five columns of Styragel (a cross-linked polystyrene gel from Waters Associates Ltd). These columns were packed with gels having nominal porosities 25, 100, 300, 300 and 300 nm, respectively. Freshly distilled 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.

0032–3861/78/111285–05$02.00

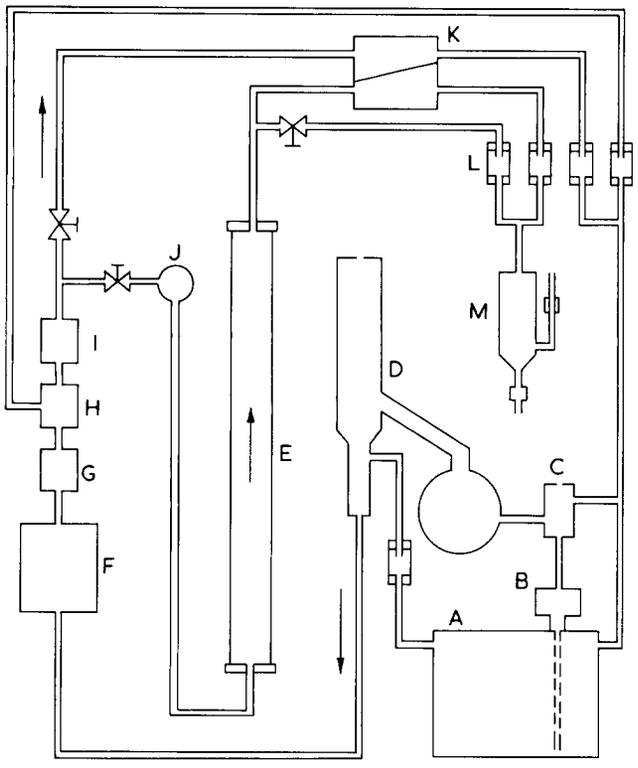

Figure 1 Schematic block diagram of the preparative g.p.c. instrument: A, solvent tank; B, still pump; C, constant level device; D, still; E, column; F, pressure pump; G, pulsation damper; H, pressure control valve; I, filter; J, sample injection valve; K, differential refractometer (and chart recorder); L, solvent and eluent flow sight glasses; M, solvent counter and fraction collector

The instrument was calibrated separately for cyclic and linear poly(dimethyl siloxanes). Plots of the logarithms of the number-average molecular weights, $\bar{M}_n$, against the g.p.c. distribution coefficients were found to be linear and parallel for the cyclics and linears in the range $300 < \bar{M}_n < 10\,000$ and, following Wright[26,27], the plots were taken to be parallel for values of $\bar{M}_n$ as high as 100 000. The g.p.c. tracings were corrected for imperfect resolution by the method of Pierce and Armonas[28], before being used to determine the number-average. weight-average and z-average molecular weights of the fractions.

Preparative g.p.c. instrument

A block diagram of the preparative g.p.c instrument is shown in *Figure 1.* The column used was ~120 cm in length and ~6 cm internal diameter. It was packed and supplied by Waters Associates Ltd. 2/5 of the column was packed with Styragel having a nominal porosity of 100 nm, and the remaining 3/5 was packed with Styragel having a nominal porosity of 300 nm. The resolution of the column was 4040 theoretical plates.

Toluene was used as the solvent, and it was delivered to the pressure pump from an automatic still. The still was constructed from stainless steel. It was heated by eight 150 watt immersion heaters mounted in an outer jacket containing a commercial heat transfer fluid 'Transcal 65' (supplied by Shell–Mex and BP Ltd). The level of toluene in the still was maintained by pumping it through a constant level device, as indicated in *Figure 1.*

The pressure pump, shown in *Figure 1,* was constructed with four bellows (each 2 cm in diameter). The cylinder stroke was adjustable over the range 0–0.8 cm giving solvent flow rates between 10–180 cm^3/min at pressures up to 7 x 10^5 Pa (~100 p.s.i.). The solvent flow was damped by an adjustable bellows system, and the solvent pressure was controlled by a diaphragm over-pressure release valve.

The solvent flow was directed through a filter, and split into reference and sample streams which were controlled by needle valves. The sample stream was directed through a six-port injection valve equipped with a sample loop having a nominal capacity of 10 cm^3, passed into the column and then a part of it directed into a Waters Model R4 differential refractometer detector (see *Figure 1*). The output of the column was fitted with a fraction cutter which was equipped with an adjustable photoelectric level detector and electrically operated release valve.

Preparative g.p.c. procedure

For each fractionation, the required amount of poly(dimethyl siloxane) (usually 1–2 g) was dissolved in approximately 12 cm^3 of toluene and filtered through a 10 μm sintered stainless steel filter. The solution was injected into the preparative g.p.c. instrument. The volume of solvent eluted from the column was measured in counts at each discharge of the fraction cutter. The flow rate of the instrument was nominally set at about 20 cm^3/min.

Fractionation of the sample was started when the chromatogram began to deflect from the baseline. Fractions were collected separately at each count until all the siloxane had eluted from the column. The volume of each fraction (corresponding to a single count) was 49.1 cm^3.

The fractions obtained were dried for about 12 h over anhydrous magnesium sulphate. Each poly(dimethyl siloxane) solution was filtered, and the siloxane recovered by removal of toluene using a rotary evaporator. Each fraction of siloxane obtained in this way was purified by washing with three successive portions of dried and distilled methanol. This procedure removed traces of contaminants (including benzaldehyde and benzoic acid, which were formed as oxidation products of toluene in the still). Finally, each fraction was dried by warming gently under vacuum at 313K.

RESULTS AND DISCUSSION

Preparation of cyclic and linear poly(dimethyl siloxane) fractions

The result of a typical preparative g.p.c. fractionation of a broad cyclic poly(dimethyl siloxane) fraction is shown in *Figure 2.* A total of eighteen sharp fractions were collected, and their individual analytical g.p.c. tracings obtained (see *Figure 2b*). After correction for imperfect resolution[26,28], the weight fraction and number-average number of skeletal bonds $\bar{n}_n$ of each of the cyclic fractions were determined from the tracings (see *Table 1*) The heterogeneity indices of all the cyclic fractions were found to be in the range $1.03 < \bar{M}_w/\bar{M}_n < 1.06$. Similar results were obtained for the preparative g.p.c. fractionation of broad linear poly(dimethyl siloxane) fractions (see *Table 2*).

Injections of more than ~ 2 g of cyclic and linear siloxane fractions into the preparative g.p.c. instrument resulted in broadening of the fractions collected. In order to obtain the maximum amount of a particular sharp cyclic fraction, several fractions of similar molecular weight from different preparative g.p.c. runs were combined and then refractionated. The procedure used is illustrated in *Figure 3.*

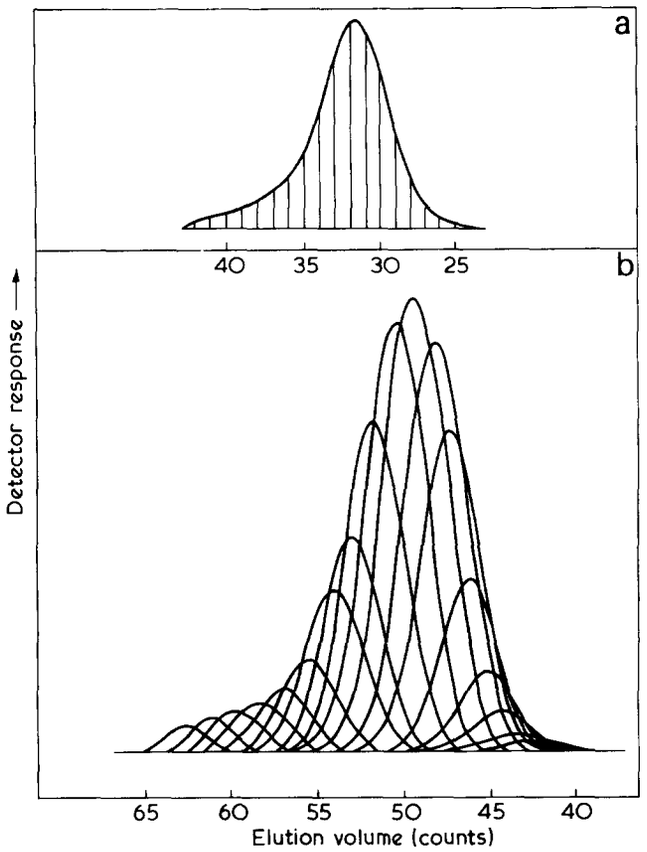

Figure 2 Fractionation of 1.59 g of a broad cyclic poly(dimethyl siloxane) fraction (with $\bar{M}_n$ = 9510 and $\bar{M}_w/\bar{M}_n$ = 1.59) by preparative g.p.c.: (a) preparative g.p.c. tracing of the broad cyclic sample showing the fractions collected; (b) analytical g.p.c. tracings of the individual fractions (see text)

Table 1 Number-average numbers of bonds $\bar{n}_n$ and weights of the cyclic poly(dimethyl siloxane) fractions obtained by preparative g.p.c. as shown in *Figure 2*

Preparative g.p.c. elution volumes of fractions collected (count numbers)	Number-average numbers of skeletal bonds in the cyclic fractions, $\bar{n}_n^*$	Weights (g) of the cyclic fractions computed from the tracings shown in *Figure 2*
25	1272	0.005
26	1098	0.007
27	904	0.019
28	759	0.038
29	662	0.096
30	527	0.166
31	468	0.219
32	397	0.245
33	339	0.238
34	277	0.185
35	217	0.121
36	170	0.088
37	132	0.049
38	107	0.029
39	78	0.026
40	61	0.022
41	47	0.018
42	40	0.017

* The heterogeneity indices of all the cyclic fractions were in the range $1.03 < \bar{M}_w/\bar{M}_n < 1.06$

Concentrations of linears in the cyclic fractions

As described above, low molecular weight cyclic fractions may be obtained from poly(dimethyl siloxane) cyclic–linear equilibrates by fractional distillation methods[1,26]. Analysis by g.l.c. gives tracings that show peaks which may be assigned to the individual cyclic molecules containing up to ~100 skeletal bonds. Furthermore, the g.l.c. tracings demonstrate that there are negligible amounts of linear siloxanes present. However, appreciable concentrations of linear siloxanes are expected to be present in the higher cyclic fractions prepared during the course of this work. In consequence, we have estimated their concentrations by carry-

Table 2 Number-average numbers of bonds $\bar{n}_n$ and weights of linear poly(dimethyl siloxane) fractions obtained by preparative g.p.c. of a sample of linear siloxane with $\bar{M}_n$ = 11 400 and $\bar{M}_w/\bar{M}_n$ = 1.34

Preparative g.p.c. elution volumes of fractions collected (count numbers)	Number-average numbers of skeletal bonds in the linear fractions $\bar{n}_n^*$	Weights (g) of the linear fractions
29	546	0.073
30	481	0.127
31	422	0.193
32	351	0.199
33	278	0.142
34	233	0.107
35	175	0.074
36	129	0.045

* The heterogeneity indices of all the linear fractions were in the range $1.04 < \bar{M}_w/\bar{M}_n < 1.07$

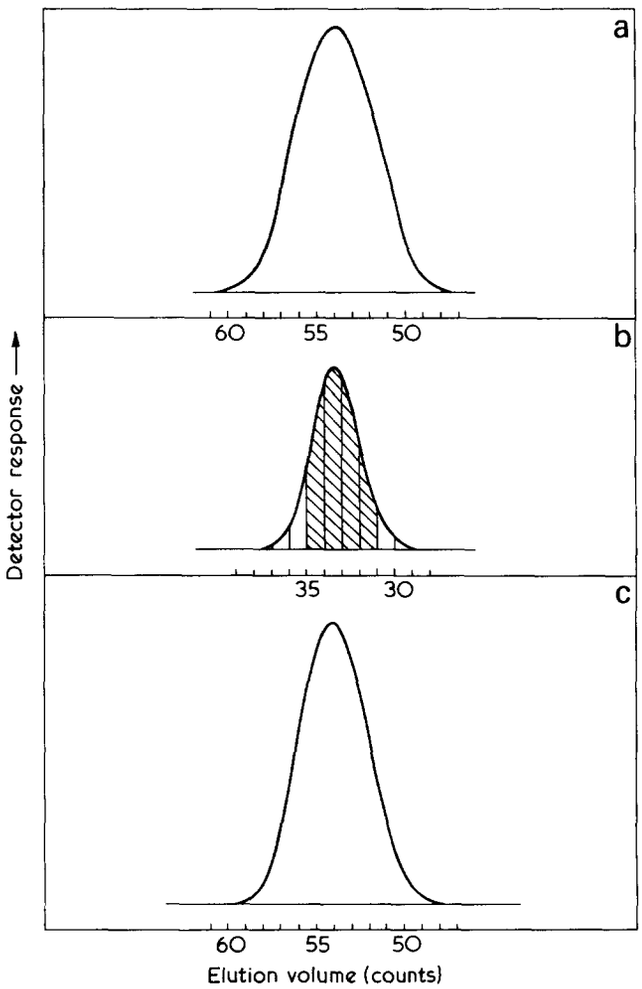

Figure 3 (a) Analytical g.p.c. tracing of a combined cyclic poly(dimethyl siloxane) fraction with $\bar{M}_w/\bar{M}_n$ = 1.10. (b) Preparative g.p.c. tracing of the combined cyclic fraction showing the part retained as a single fraction (shaded area). (c) Analytical g.p.c. tracing of the new cyclic fraction retained in (b). It has $\bar{M}_w/\bar{M}_n$ = 1.05 and a number-average number of skeletal bonds $\bar{n}_n$ = 195

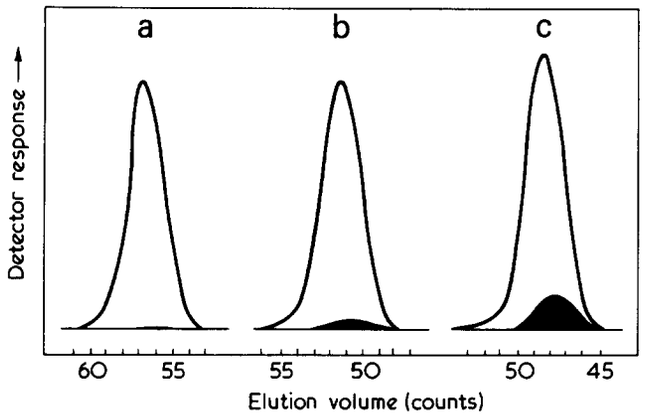

Figure 4 Analytical g.p.c. tracings (corrected for imperfect resolution) of three cyclic poly(dimethyl siloxane) fractions with number-average numbers of skeletal bonds: (a) $\bar{n}_n = 107$; (b) $\bar{n}_n = 227$; (c) $\bar{n}_n = 468$. The shaded areas show the calculated concentrations of linear poly(dimethyl siloxanes) in the cyclic fractions (see text)

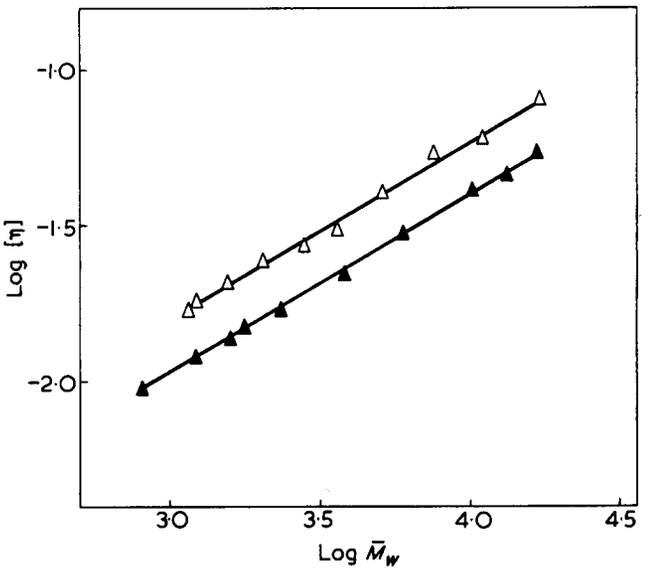

Figure 5 Plots of logarithms of the limiting viscosity numbers $[\eta]$ of the cyclic (▲) and linear (△) poly(dimethyl siloxane) fractions in butanone at 293K against the logarithms of their weight-average molecular weights $\bar{M}_w$. The plots have been obtained by using data published in ref 1

ing out a detailed analysis of the particular cyclic–linear equilibrate from which the cyclic fractions were derived. The equilibrate used contained a total of 593 g of dimethyl siloxanes at a concentration of 235 g/dm^3 in toluene solution at 383K[1]. All but the lowest molecular weight linears, present in the equilibrate as 53.6 g/dm^3, were separated from the cyclics by fractional precipitation. Their weight-average molecular weight $\bar{M}_w$ was determined viscometrically in toluene solution at 298K using the limiting viscosity number–molecular weight relationship of Haug and Meyerhoff[29,30]:

$$[\eta] = 0.828 \times 10^{-4} \bar{M}_w^{0.72} \quad (1)$$

The $\bar{M}_w$ value found (viz 371 600) corresponds to an extent of reaction of functional groups $p = 0.9996$ in the linear part of the poly(dimethyl siloxane) in the cyclic–linear equilibrate. Following Flory[31], the weight fraction w_y of a y-meric siloxane in the linear part of the equilibrate was calculated using a relationship which has been shown to apply for cyclic–linear poly(dimethyl siloxane) equilibrates by Wright[26] and others[32,33]:

$$w_y = y(1-p)^2 p^{y-1} \quad (2)$$

The concentrations of the x-meric cyclic siloxanes in the equilibrate were calculated from published molar cyclization equilibrium constants K_x for cyclics in toluene at 383K[24,26]. Hence, the relative concentrations of x-meric cyclics and y-meric linears were computed for the relatively high molecular weight cyclic fractions obtained by preparative g.p.c.

The calculated concentrations of linear siloxane in three cyclic fractions are shown in the analytical g.p.c. tracings shown in *Figure 4*. For the cyclic fraction (a) $\bar{n}_n = 107$ and the calculated percentage concentration of linear siloxanes $p_l = 0.2\%$. For the cyclic fraction (b) $\bar{n}_n = 277$ and $p_l = 3.3\%$. For the cyclic fraction (c) $\bar{n}_n = 468$ and $p_l = 11.9\%$.

However, the concentrations of linear siloxanes shown in *Figure 4* are believed to represent upper limits. The higher cyclic fractions obtained from the original equilibrate were isolated by fractional precipitation procedures[1], that preferentially precipitate linears relative to cyclics of similar molecular weight.

This conclusion is supported by the results of viscometric studies of the cyclic and linear fractions[1]. Measurements of limiting viscosity numbers were made in butanone at 293K (a θ solvent for linear poly(dimethyl siloxane) at this temperature)[34]. In *Figure 5*, the logarithms of the limiting viscosity numbers $[\eta]$ of the cyclic and linear fractions are plotted against the logarithms of their weight-average molecular weights. The ratio $[\eta]_r/[\eta]_l$ (where the subscripts r and l denote cyclics (i.e. rings) and linears, respectively) is 0.67 for poly(dimethyl siloxanes) with weight-average numbers of skeletal bonds $\bar{n}_w$ in the range $30 < \bar{n}_w < 500$. This experimental value of $[\eta]_r/[\eta]_l$ is identical (within experimental error) to that predicted theoretically by Bloomfield and Zimm[35], Fukatsu and Kurata[36] and Yu and Fujita[37], and namely 0.662. If appreciable amounts of linears had been present in the higher cyclic fractions, an experimental ratio $[\eta]_r/[\eta]_l$ substantially larger than 0.67 would have been expected.

ACKNOWLEDGEMENTS

We are indebted to the Science Research Council for a Research Fellowship (to K. D.). We thank Mr T. M. Elsworth for practical assistance with the work.

REFERENCES

1 Dodgson, K. and Semlyen, J. A. *Polymer* 1977, **18**, 1265
2 Fiers, W. and Sinsheimer, R. L. *J. Mol Biol.* 1962, **5**, 408, 424
3 Kleinschmidt, A. K., Burton, A. and Sinsheimer, R. L. *Science* 1963, **142**, 961
4 Freifelder, D., Kleinschmidt, A. K. and Sinsheimer, R. L. *Science* 1964, **146**, 254
5 Dulbecco, R. and Vogt, M. *Proc. Natl. Acad. Sci.* 1963, **50**, 236
6 Weil, R. and Vinograd, J. *Proc. Natl. Acad. Sci.* 1963, **50**, 730
7 Radloft, R., Bauer, W. and Vinograd, J. *Proc. Natl. Acad. Sci.* 1967, **57**, 1514
8 Casassa, E. F. *J. Polym. Sci. (A)* 1965, **3**, 605
9 Bloomfield, V. and Zimm, B. H. *J. Chem. Phys.* 1966, **44**, 315
10 Fukatsu, M. and Kurata, M. *J. Chem. Phys.* 1966, **44**, 4539
11 Simon, E. *J. Chem. Phys.* 1970, **52**, 3879
12 Kumbar, M. M. *J. Chem. Phys.* 1971, **55**, 5046

13 Solc, K. *Macromolecules* 1972, **5**, 705
14 Bixon, M. *J. Chem. Phys.* 1973, **58**, 1459
15 Kumbar, M. M. *J. Chem. Phys.* 1973, **58**, 2874
16 Solc, K. *Macromolecules* 1973, **6**, 378
17 Solc, K. and Gobush, W. *Macromolecules* 1974, **7**, 814
18 Naghizadeh, J. and Sotobayashi, H. *J. Chem. Phys.* 1974, **60**, 3104
19 Kumbar, M. M. *J. Chem. Phys.* 1975, **59**, 5620
20 Freed, K. F., Edwards, S. F. and Warner, M. *J. Chem. Phys.* 1976, **64**, 5132
21 Boots, H. and Deutch, J. M. *Macromolecules* 1977, **10**, 1163
22 Howell, C. D. and Eichinger, B. E. *Macromolecules* 1978, **11**, 276
23 Semlyen, J. A. and Wright, P. V. *Polymer* 1969, **10**, 543
24 Wright, P. V. *J. Polym. Sci. (Polym. Phys. Edn)* 1973, **11**, 51
25 Semlyen, J. A. *Adv. Polym. Sci.* 1976, **21**, 41
26 Wright, P. V. *D. Phil. Thesis,* University of York, 1970
27 Semlyen, J. A. and Wright, P. V. in 'Chromatography of Synthetic Polymers and Biopolymers' (Ed. R. Epton), Ellis–Horwood Ltd, Chichester, vol. 1, 1977
28 Pierce, P. E. and Armonas, J. in 'Analytical Gel Permeation Chromatography' (Eds J. F. Johnson and R. S. Porter) Interscience, New York, 1968
29 Haug, V. A. and Meyerhoff, G. *Makromol. Chem.* 1962, **53**, 91
30 Crescenzi, V. and Flory, P. J. *J. Am. Chem. Soc.* 1964, **86**, 138
31 Flory, P. J. in 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, New York, 1953
32 Scott, D. W. *J. Am. Chem. Soc.* 1946, **68**, 2294
33 Carmichael, J. B. and Winger, R. *J. Polym. Sci. (A)* 1965, **3**, 971
34 Flory, P. J., Mandelkern, L., Kinsinger, J. B. and Shultz, W. B. *J. Am. Chem. Soc.* 1952, **74**, 3364
35 Bloomfield, V. and Zimm, B. H. *J. Chem. Phys.* 1966, **44**, 315
36 Fukatsu, M. and Kurata, M. *J. Chem. Phys.* 1966, **44**, 4539
37 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