

Studies of cyclic and linear poly(dimethyl siloxanes):

6. Effect of heat

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(Received 20 June 1980)

Cyclic and linear poly(dimethyl siloxanes) were heated under vacuum in the temperature range 623–693K for periods of hours or days in the absence of catalysts. The products were analysed by gas-liquid chromatography and gel permeation chromatography. The results for the linear poly(dimethyl siloxanes) were in full agreement with the published work of Thomas and Kendrick. The effect of heat on the cyclic poly(dimethyl siloxanes) was that predicted, assuming that similar siloxane bond interchange reactions take place to those believed to occur in the linear polymers. The cyclic poly(dimethyl siloxanes) produced mixtures of cyclic oligomers, together with polymeric products which have considerably higher molecular weights than the starting materials. It is proposed that these polymeric products consist of mixtures of ring molecules $[(CH_3)_2SiO]_x$. Some of these cyclic polymers are estimated to contain (on average) more than 10 000 skeletal bonds. Similar mixtures of cyclic oligomers and high molecular weight polymeric products were obtained by heating hexamethylcyclotrisiloxane and octamethylcyclotetrasiloxane.

INTRODUCTION

Atoms (or groups of atoms) linked together to form long chains are the basic units of familiar synthetic polymers. Such polymers may consist of simple linear molecules. Alternatively, the chains may be branched, or crosslinked to form network structures. Many thousands of polymers based on long chain molecules have been prepared and characterized, and some have been used commercially as plastics, fibres and rubbers^{1–3}.

During the past two decades, our experimental and theoretical investigations have been directed towards the preparation and characterization of a different type of synthetic polymer, where atoms (or groups of atoms) are linked together to form large rings^{4–12}. We have called such polymers *cyclic polymers*. They have a strikingly simple topology, differing from linear polymers in that they have no free ends. For practical purposes, true cyclic polymers may be considered to consist of mixtures of ring molecules containing (on average) at least 100 skeletal bonds. This restriction excludes the numerous macrocycles with less than 100 skeletal bonds that are described in the literature.

Cyclic poly(dimethyl siloxane) fractions were the first synthetic cyclic polymers to be prepared and characterized^{8–12}. They were recovered from ring-chain equilibration reactions, carried out in the presence of inert solvents^{13–15}. Already, more than fifty sharp fractions of cyclic poly(dimethyl siloxanes) (each on an average scale of 2 g) have been obtained in our laboratory using preparative gel permeation chromatography⁹. All these fractions consist of ring molecules with (on average) from 100 to 700 skeletal bonds. The cyclic poly(dimethyl siloxanes) have been characterized by: (i) cyclization studies^{6,7,14,15}; (ii) gel permeation chromatography^{14–16}; (iii) dilute solution and bulk viscometry^{8,11}; (iv) low-angle

neutron scattering investigations¹⁰; and (v) diffusion measurements¹².

In the future, it is expected that more complex topological structures involving cyclic polymers will be synthesized. For example, branched cyclic polymers (where the branches may be either ring or chain molecules), and crosslinked networks of cyclic polymers with no free ends. Some examples of possible arrangements of just two (or three) large cyclic molecules are shown diagrammatically in *Figure 1*. A number of circular deoxyribonucleic acids (DNAs) have already been found to be present in viruses, bacteria and mitochondria, and DNA molecules with the topological structures (I), (IIc) and (IIIc) in *Figure 1* have all been identified in natural systems^{17–21}. The first synthetic compound with the topology (IIc) was prepared by Wasserman²² and other examples of molecules with

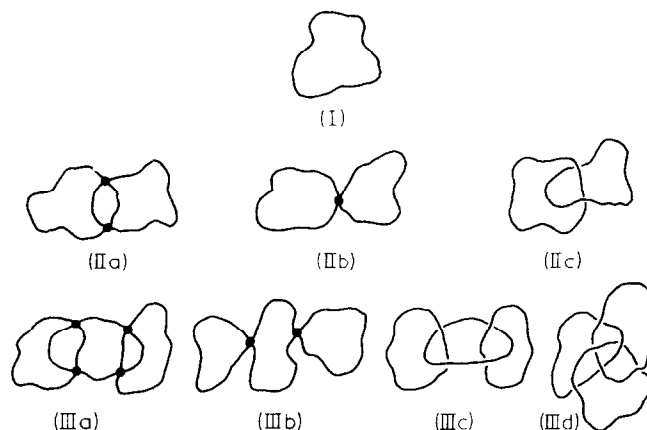


Figure 1 Possible structures formed from two (and three) large ring molecules

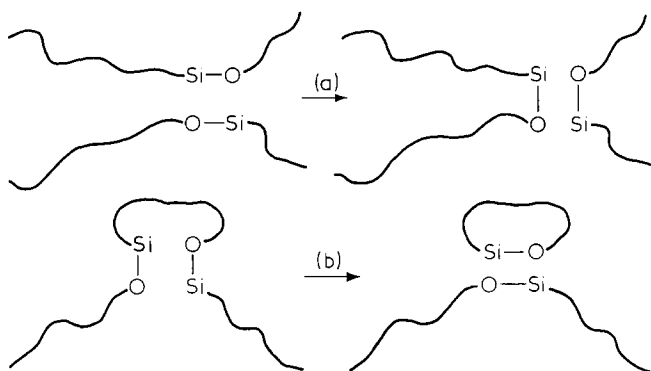


Figure 2 Siloxane bond interchange reaction for linear poly(dimethyl siloxanes). The intermolecular process (a) results in a broadening of the molecular weight distribution. The intramolecular process (b) gives a mixture of cyclic oligomers

this topology have been discussed by Schill²². In principle, cyclic polysiloxane molecules could be linked together chemically to produce a wide range of structures, including some of those shown in *Figure 1*.

Differences between the topologies of large ring molecules and long chain molecules can be illustrated by the following example. The random scission of a skeletal bond in a large ring molecule produces a chain molecule with an identical molecular weight, whereas random scission of a skeletal bond in a long chain molecule produces two shorter chain molecules. Thus, the mechanical degradation of cyclic and linear polymers (of similar molecular weight) by the random scission of their skeletal bonds would be expected to produce polymers which initially have markedly different molecular weight averages. Studies of such mechanical degradation have been initiated. Another simple consequence of the differences in topology is that there are no linear analogues of the possible catenated dimeric and trimeric cyclic polymers shown as (IIc), (IIId) and (IIId) in *Figure 1*. Furthermore, there is only one structure for the linked cyclic dimer molecule (IIb), whereas there are many possible isomeric structures for the linear analogue consisting of two chains joined together by any pair of monomeric units along their length.

The fact that cyclic and linear polymers do have some markedly different properties has been demonstrated recently by a study of the bulk viscosities of cyclic and linear poly(dimethyl siloxanes)¹¹. Cyclic fractions with substantially less than 100 skeletal bonds were found to have considerably higher bulk viscosities than their linear analogues. By contrast, cyclic fractions with substantially more than 100 skeletal bonds were found to have decidedly lower bulk viscosities than their linear analogues.

In this paper, it is shown that the effect of heat on cyclic and linear poly(dimethyl siloxanes), with similar molecular weights, produces polymeric products with quite different molecular weights and molecular weight distributions. These differences are believed to be a direct consequence of the different topologies of the large ring and long chain molecules.

The action of heat on linear polysiloxanes in sealed quartz tubes under vacuum and in the absence of additives or catalysts has been studied by Thomas and Kendrick^{24,25}. These authors found that linear poly(dimethyl siloxanes) depolymerize on heating at 693K for several hours to yield a mixture of volatile compounds, consisting almost entirely of low molecular

weight cyclics $[(CH_3)_2SiO]_x$, with hexamethylcyclotrisiloxane and octamethylcyclotetrasiloxane as the main components. In addition, polymeric products are formed with much broader molecular weight distributions than the starting materials, and usually (but not always) considerably lower molecular weights.

Thomas and Kendrick^{24,25} interpreted their results by proposing a siloxane bond interchange reaction involving the formation of a cyclic four-centre transition state, followed by the rearrangement of siloxane bonds. This mechanism is illustrated in *Figure 2*, which indicates how both broadening of molecular weight distributions and the production of volatile cyclics result when the linear polymers are heated. The siloxane bond interchange reaction has been discussed by other authors^{26,27}, and similar cyclic four-centre transition states have been suggested for bond interchange reactions in condensed phosphates²⁸ and in other inorganic polymers²⁹.

Cyclic poly(dimethyl siloxanes) would be expected to undergo similar bond interchange reactions to those of the linear polymers. Hence, as illustrated in *Figure 3*, the products resulting from heating cyclic poly(dimethyl siloxane) fractions are predicted to be a mixture of cyclic oligomers, together with cyclic polymer with a much higher molecular weight than the starting material. As will be discussed, chromatographic analyses of the products resulting from the heating of cyclic poly(dimethyl siloxanes) are in full agreement with this prediction.

EXPERIMENTAL

Materials and instrumental techniques

The cyclic and linear poly(dimethyl siloxane) fractions were prepared and characterized by methods described

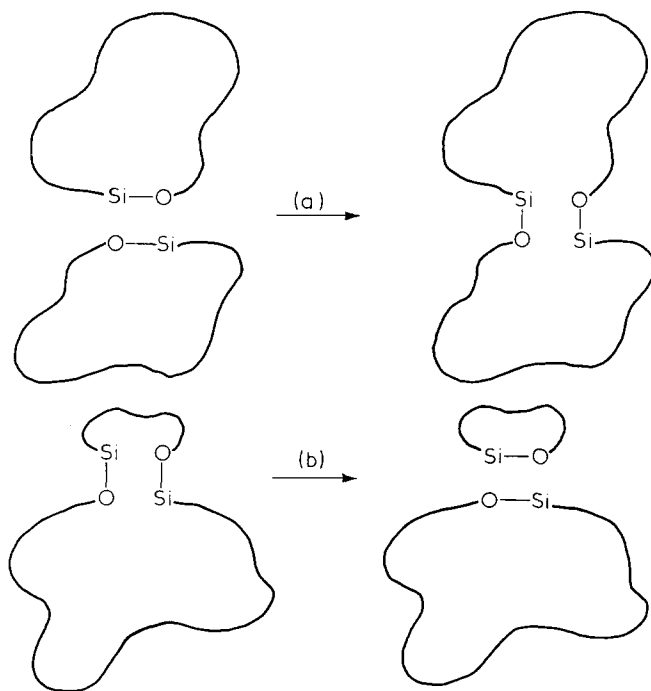


Figure 3 The siloxane bond interchange reaction for cyclic poly(dimethyl siloxanes). The intermolecular process (a) results in a much higher molecular weight cyclic polymer than that of the starting material. The intramolecular process (b) gives a mixture of cyclic oligomers

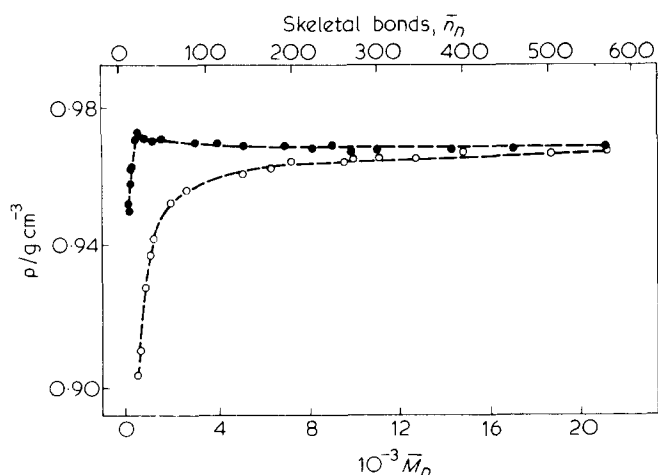


Figure 4 The densities ρ of cyclic (●) and linear (○) dimethyl siloxanes and poly(dimethyl siloxanes) at 298 K. The values are accurate to $\pm 0.002 \text{ g cm}^{-3}$

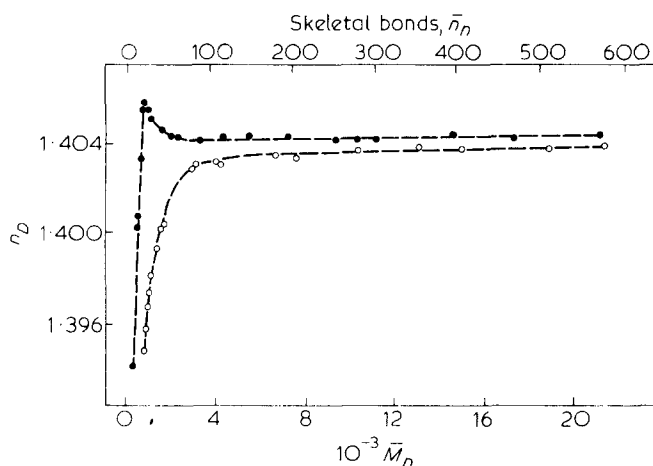
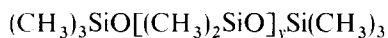


Figure 5 The refractive indices n_D of cyclic (●) and linear (○) dimethyl siloxanes and poly(dimethyl siloxanes) at 298 K

previously⁸⁻¹². Their densities and refractive indices were measured, and found to be in agreement with values obtained in previous work for other cyclic and linear fractions (see Figures 4 and 5). The cyclic fractions consisted of mixtures of ring molecules $[(\text{CH}_3)_2\text{SiO}]_x$, each containing $2x$ skeletal bonds. The linear fractions consisted of mixtures of chain molecules



each assumed to contain $2y$ skeletal bonds.

A gas-liquid chromatograph (g.l.c.) fitted with a heated katharometer detector, and two analytical gel permeation chromatographs (g.p.c.) were used to analyse oligomeric and polymeric dimethyl siloxanes. Toluene was the solvent for both g.p.c. instruments. One g.p.c. instrument was fitted with columns packed with Styragel (supplied by Waters Associates Ltd), with nominal porosities 25, 100, 300, 300 and 300 nm, respectively. The other was fitted with columns packed with PL-gel (supplied by Polymer Laboratories Ltd), with nominal porosities 10, 100 and 1000 nm, respectively.

Procedures

Samples of cyclic and linear oligomers and polymers (each on a scale of 0.1–10 g) were sealed in Pyrex glass tubes of appropriate size, following the removal of all

traces of gases and other volatile materials. The tubes were sealed under vacuum (at pressures lower than 0.1 N m^{-1}), and heated at temperatures in the range 623–693 K ($\pm 5 \text{ K}$) in a furnace. After cooling, the sample tubes were opened and the products dissolved in toluene or butanone, or some other suitable solvent, before analysing. In some cases, the products were analysed directly by g.l.c. without the addition of a solvent.

RESULTS AND DISCUSSION

Effect of heat on linear poly(dimethyl siloxanes)

Linear poly(dimethyl siloxane) fractions were heated at temperatures in the range 623–693 K for periods of time ranging from 1 h to several days. The products obtained were analysed by g.l.c. and g.p.c., and found to be those described by Thomas and Kendrick²⁴. For example, a g.p.c. of the products obtained by heating a linear fraction (with $\bar{n}_n = 172$ and $\bar{M}_w/\bar{M}_n = 1.20$) at 668 K for 3 days is shown in Figure 6. A polymeric product is obtained, which is assumed to be linear and is estimated to have a number-average molecular weight close to that of the original fraction ($\bar{n}_n = 168$) but with a much broader molecular weight distribution ($\bar{M}_w/\bar{M}_n = 1.67$). The low molecular weight products were analysed by g.l.c., and shown to be a mixture of cyclics $[(\text{CH}_3)_2\text{SiO}]_x$ (mainly $x = 3, 4, 5$ but with some $x = 6-9$). All these observations are in agreement with the results of Thomas and Kendrick²⁴, and can be interpreted in terms of the siloxane bond interchange reactions illustrated in Figure 2.

Effect of heat on cyclic poly(dimethyl siloxanes) and cyclic dimethyl siloxane oligomers

The products obtained by heating cyclic poly(dimethyl siloxane) fractions, under the same conditions as the linear fractions, were in agreement with those predicted assuming the siloxane bond interchange reactions illus-

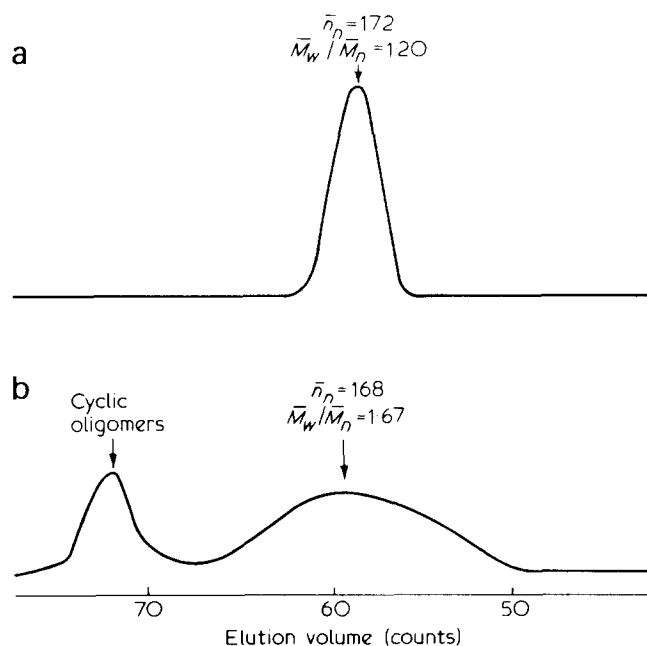


Figure 6 G.p.c. tracings of (a) a linear poly(dimethyl siloxane) fraction before heating, and (b) the products obtained after heating at 668 K for 3 days. The scale showing the elution volumes in counts is the same for both traces

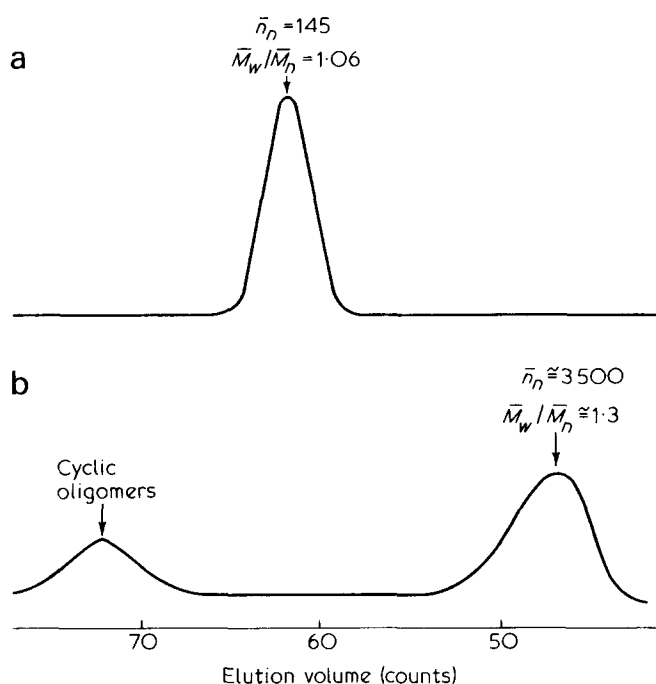


Figure 7 G.p.c. tracings of (a) a cyclic poly(dimethyl siloxane) fraction before heating, and (b) the products obtained after heating at 668K for 3 days. The scale showing the elution volumes in counts is the same for both traces, and the exclusion limit of the columns corresponds to ~ 43 counts

trated in Figure 3. For example, a g.p.c. of the products obtained by heating a cyclic fraction (with $\bar{n}_n = 145$ and $\bar{M}_w/\bar{M}_n = 1.06$) at 668K for 3 days is shown in Figure 7. The low molecular weight products, formed in $\sim 25\%$ yield, were analysed by g.l.c. and found to consist only of the cyclic oligomers $[(CH_3)_2SiO]_x$. These cyclics are predicted to result from the intramolecular reactions illustrated in Figure 3b. The other product (formed in $\sim 75\%$ yield) is identified with the high molecular weight cyclic poly(dimethyl siloxane), predicted to be formed by the intermolecular bond interchange reactions shown in Figure 3a. From its g.p.c. elution volume, it is estimated to have $\bar{n}_n \approx 3500$ and $\bar{M}_w/\bar{M}_n \approx 1.3$.

In principle, the reactions shown in Figure 3a could lead to the production of ring polymers containing a virtually unlimited number of skeletal bonds. In this connection, it is noted that g.p.c. analyses of the products from some of the cyclic poly(dimethyl siloxane) reactions gave products which were estimated to contain well over 10 000 skeletal bonds. Catenated cyclic molecules would be expected to be present in these products, including the species IIc and IIIc in Figure 1 (it is noted that species IIc can be formed from species IIIc).

The progress of some of the reactions was monitored by analysing samples after they had been heated at the same temperature for different periods of time. The g.p.c. tracings obtained by heating a cyclic fraction (with $\bar{n}_n = 88$ and $\bar{M}_w/\bar{M}_n = 1.07$) at 693K for periods of 3–28 h are shown in Figure 8. The yield and the number-average molecular weight of the polymeric product increased steadily over the time period, and at the end of the 28 h period there was no trace of the starting material.

High molecular weight polymeric products were also obtained by heating cyclic dimethyl siloxane oligomers. For example, hexamethylcyclotrisiloxane and octamethylcyclotetrasiloxane gave polymers which are believed to be cyclic and to contain at least 2000 skeletal bonds.

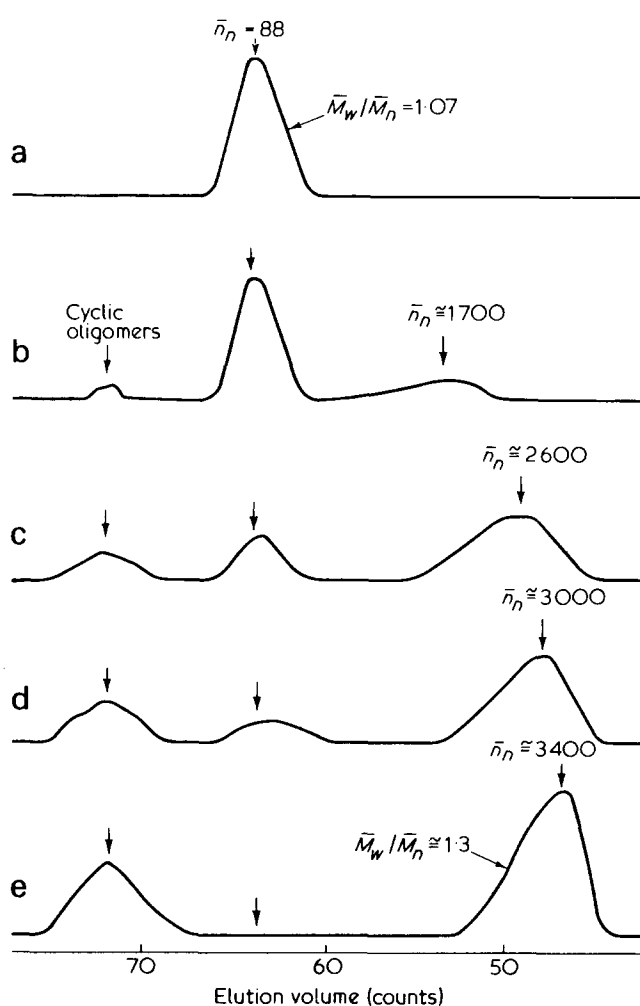


Figure 8 G.p.c. tracings of a cyclic poly(dimethyl siloxane) fraction before heating (a), and after heating at 693K for (b) 3 h, (c) 6 h, (d) 12 h and (e) 28 h. The scale showing the elution volumes in counts is the same for all the traces, and the exclusion limit of the columns corresponds to ~ 43 counts

Cyclic oligomers $[(CH_3)_2SiO]_x$ ($x = 3-9$) were also produced. These reactions are being studied in more detail at the present time. The high molecular weight polymeric products formed from the cyclic oligomers and from the cyclic poly(dimethyl siloxane) fractions are also being investigated.

ACKNOWLEDGEMENTS

We are indebted to the Science Research Council for a CASE studentship with ICI Fibres Ltd, Harrogate (for D.J.B.). We thank Dr K. Dodgson for helpful discussions, and Mr T. M. Elsworth and Mr C. J. Pellow for practical assistance.

REFERENCES

- Frith, E. M. and Tuckett, R. F. 'Linear Polymers', Longmans, Green and Co., London, New York, 1951
- Flory, P. J. 'Principles of Polymer Chemistry', Cornell Univ. Press, New York, 1953
- Cowie, J. M. G. 'Polymers: Chemistry and Physics of Modern Materials', International Textbook Co. Aylesbury, UK, 1973
- Flory, P. J. and Semlyen, J. A. *J. Am. Chem. Soc.* 1966, **88**, 3209
- Semlyen, J. A. *Trans. Faraday Soc.* 1967, **63**, 743; 1967, **63**, 2342; 1968, **64**, 1396

- 6 Parts 1-14 of the series 'Equilibrium Ring Concentration and the Statistical Conformations of Polymer Chains', published in *Polymer* (1969-76); Semlyen, J. A. and Wright, P. V. *Polymer* 1969, **10**, 543; Semlyen, J. A. and Walker, G. R. *Polymer* 1969, **10**, 597; Wright, P. V. and Semlyen, J. A. *Polymer* 1970, **11**, 462; Walker, G. R. and Semlyen, J. A. *Polymer* 1970, **11**, 472; Beevers, M. S. and Semlyen, J. A. *Polymer* 1971, **12**, 373; Semlyen, J. A. *Polymer* 1971, **12**, 383; Andrews, J. M. and Semlyen, J. A. *Polymer* 1972, **13**, 142; Beevers, M. S. and Semlyen, J. A. *Polymer* 1972, **13**, 385; Cooper, D. R. and Semlyen, J. A. *Polymer* 1972, **13**, 414; Beevers, M. S. and Semlyen, J. A. *Polymer* 1972, **13**, 523; Cooper, D. R. and Semlyen, J. A. *Polymer* 1973, **14**, 185; Andrews, J. M., Jones, F. R. and Semlyen, J. A. *Polymer* 1974, **15**, 420; Jones, F. R., Scales, L. E. and Semlyen, J. A. *Polymer* 1974, **15**, 738; Scales, L. E. and Semlyen, J. A. *Polymer* 1976, **17**, 601
- 7 Semlyen, J. A. *Adv. Polym. Sci.* 1976, **21**, 41
- 8 Dodgson, K. and Semlyen, J. A. *Polymer* 1977, **18**, 1265
- 9 Dodgson, K., Simpson, D. and Semlyen, J. A. *Polymer* 1978, **19**, 1285
- 10 Higgins, J. S., Dodgson, K. and Semlyen, J. A. *Polymer* 1979, **20**, 553
- 11 Dodgson, K., Bannister, D. J. and Semlyen, J. A. *Polymer* 1980, **21**, 663
- 12 Edwards, C. J. C., Stepto, R. F. T. and Semlyen, J. A. *Polymer* 1980, **21**, 781
- 13 Brown, J. F. and Slusarczuk, G. M. *J. Am. Chem. Soc.* 1965, **87**, 931
- 14 Wright, P. V. *D.Phil. Thesis* University of York, 1970
- 15 Wright, P. V. *J. Polym. Sci. (Polym. Phys. Edn)* 1973, **11**, 51
- 16 Semlyen, J. A. and Wright, P. V. in 'Chromatography of Synthetic Polymers and Biopolymers' (Ed. R. Epton) Ellis Horwood, Chichester, 1977, Vol 1
- 17 DuPraw, E. J. 'DNA and Chromosomes', Holt, Reinhart and Winston, Inc., New York, 1970
- 18 Bloomfield, V. A., Crothers, D. M. and Tinoco, I. in 'Physical Chemistry of Nucleic Acids', Harper and Row, New York, London, 1974
- 19 Freifelder, D. 'The DNA Molecule: Structure and Properties', W. H. Freeman and Co., San Francisco, 1978
- 20 Hudson, B. and Vinograd, J. *Nature* 1967, **216**, 650
- 21 Clayton, D. A. and Vinograd, J. *Nature* 1967, **216**, 652
- 22 Wasserman, E. *J. Am. Chem. Soc.* 1960, **82**, 4433
- 23 Schill, G. 'Catenanes, Rotaxanes, and Knots', Academic Press, New York, London, 1971
- 24 Thomas, T. H. and Kendrick, T. C. *J. Polym. Sci. (A-2)* 1969, **8**, 537
- 25 Thomas, T. H. and Kendrick, T. C. *J. Polym. Sci. (A-2)* 1970, **8**, 1823
- 26 Grassie, N. and MacFarlane, I. G. *Eur. Polym. J.* 1978, **14**, 875
- 27 Blazso, M., Garzo, G., Andrianov, K. A., Makarova, N. N., Chernavski, A. I. and Petrov, I. M. *J. Organometallic Chem.* 1979, **165**, 273
- 28 Thilo, E. in 'Advances in Inorganic Chemistry and Radiochemistry', (Eds H. J. Emeleus and A. G. Sharpe) Academic Press, New York, 1962, Vol 4
- 29 Eisenberg, A. *Inorganic Macromol. Rev.* 1970, **1**, 75