Studies of cyclic and linear poly(dimethyl siloxanes): 10. Calculations of radii of gyration

C. J. C. Edwards, D. Rigby* and R. F. T. Stepto
Department of Polymer Science and Technology, The University of Manchester Institute of Science and Technology, Manchester M60 1QD, UK

K. Dodgson† and J. A. Semlyen
Department of Chemistry, University of York, York, Y01 5DD, UK
(Received 1 July 1982)

A Monte Carlo method has been devised for calculating the conformation-dependent properties of cyclic poly(dimethyl siloxanes) (PDMS), using Flory, Crescenzi and Mark's rotational isomeric state model. Calculated values of the mean-square radii of gyration $\langle s_r^2 \rangle$ of ring molecules unperturbed by excluded volume effects and containing 8–100 skeletal atoms are compared with the $\langle s_l^2 \rangle$ values for the corresponding unperturbed chain molecules. Exact enumeration methods were also employed for rings $[(CH_3)_2SiO]_{w/2}$ with $w \leqslant 24$ and the results found to be in close agreement with those obtained by the Monte Carlo method. The ratio $\langle s_l^2 \rangle / \langle s_r^2 \rangle$ was found to attain limiting values close to 2.0 for $w > 30$, in agreement with theoretical predictions.

Keywords Cyclic poly(dimethyl siloxane); linear poly(dimethyl siloxane); Monte Carlo calculations; radii of gyration; Metropolis sampling; rotational isomeric state model

INTRODUCTION

Previous publications in this series have described the preparation and some of the properties of the first synthetic cyclic polymers containing more than 100 skeletal bonds[1-9]. These polymers are cyclic poly(dimethyl siloxanes) and many sharp fractions have already been obtained (each on a scale of several grams) containing average numbers of skeletal bonds up to 700. The cyclic polymers have been characterized and investigated using a variety of experimental methods, including dilute solution viscometry[1], analytical gel permeation chromotography[2], small-angle neutron scattering[3], bulk viscometry[4], light scattering[8], and diffusion measurements[5,7,9].

From these investigations, experimental values have been derived for some physical properties of large ring molecules relative to those of the corresponding linear species, enabling comparisons to be made with theoretical predictions. For example, the ratio of the z-average mean-square radii of gyration of ring (r) and linear (l) poly(dimethyl siloxanes) $\langle s_r^2 \rangle_z / \langle s_l^2 \rangle_z$ was measured by neutron scattering methods[3] and found to be 0.53 ± 0.05 in agreement with the theoretically predicted ratio of 0.50[10-15]. Furthermore, the ratio of the limiting viscosity numbers $[\eta]_r/[\eta]_l$ was found to 0.67 ± 0.01 for the poly(dimethyl siloxanes) in a θ solvent[1], compared with the theoretical value of 0.66 calculated for 'flexible' cyclic polymers[10,16-18]. In addition, the ratio of the translational friction coefficients f_r/f_l was shown to be 0.84 ± 0.01 for the poly(dimethyl siloxanes) in accord with the theoretically predicted value of $8/3\pi$ $(=0.85)$[10,16,17,19,20]. The theoretical studies[10-20] deal only with predictions of the ratios of the physical properties of cyclic polymers to those of their linear counterparts and they use simplified chain models. The absolute values of the radii of gyration of cyclic polymers with realistic chain structures still remain to be investigated.

Here, we present the results of computational studies of the radii of gyration of ring and chain poly(dimethyl siloxanes). There have been a number of studies of the radii of gyration and related parameters of ring and chain polymers by other authors[21-29]. In this paper, the radii of gyration of cyclic and linear poly(dimethyl siloxanes) (PDMS) have been calculated using Flory, Crescenzi and Mark's (FCM)[30] rotational isomeric state model (RISM) of the linear polymer.

The largest ring and chain molecules considered here contain 100 skeletal atoms and it has been shown experimentally that excluded volume effects are negligible for such polymers[5,31,32]. Hence, all the radii of gyration have been calculated as being unperturbed by long range intramolecular interactions. The matrix algebraic methods of Flory and Jernigan[33-35] have been used to calculate the radii of gyration of the linear chains and a Monte Carlo method employing Metropolis sampling[36-40] has been used for the cyclic molecules. For

* Present address: Department of Materials Science and Metallurgical Engineering, University of Cincinnati, Cincinnati, Ohio 45221, USA.
† Present address: Department of Chemistry, Sheffield City Polytechnic, Sheffield, S11WB, UK.

0032-3861/83/040391-04$03.00
© Butterworth and Co. (Publishers) Ltd.

Table 1 Values of the mean-square radius of gyration $\langle s_r^2 \rangle$ calculated by the complete enumeration method, for various end-to-end separations (r_e)

Value of w in cyclic $[(CH_3)_2SiO]_{w/2}$	$\langle s_r^2 \rangle$/nm^2		
	r_e = 0.1 nm	r_e = 0.2 nm	r_e = 0.3 nm
8	–	–	0.045
10	–	0.055	0.063
12	0.072	0.076	0.078
14	0.097	0.106	0.111
16	0.125	0.124	0.127
18	0.139	0.139	0.142
20	0.164	0.173	–
22	0.234	0.242	–
24	0.237	0.253	–

rings with up to 24 skeletal atoms the Monte Carlo results have been confirmed by using complete enumerations of the chain conformations.*

The radius of gyration of a ring or chain polymer is a quantity of particular interest, as it is closely related to a number of parameters amenable to experimental measurement, including gel permeation chromotographic elution volumes[31,41–45] and bulk viscosities[4,46]. In this paper, the calculated ratios of the radii of gyration of linear and cyclic PDMS are compared with the experimental values for polymers of similar molar mass, as found by neutron scattering[3].

COMPUTATIONS

The rotational isomeric state model

The FCM RISM was first set up to calculate the unperturbed dimensions of PDMS chains[47] and the temperature coefficient of the unperturbed dimensions[48]. It has since been used to interpret the conformation-dependent properties of linear PDMS including dipole moments[49]; as well as the molar cyclization equilibrium constants of small and medium sized dimethyl siloxane rings formed in PDMS ring-chain equilibrates[50,51].

In the FCM RISM of PDMS, the Si–O bond lengths are taken to be 0.164 nm and the bond angle supplements at silicon and oxygen atoms are assigned the values 70° and 37° respectively. Each skeletal bond is assigned to one of three discrete rotational isomeric states situated in *trans*($\varphi = 0°$), *gauche*+($\varphi = 120°$) and *gauche*−($\varphi = 240°$) positions (denoted t, g^+, g^-). The statistical weight matrix that takes account of the mutual interdependence of adjacent pairs of skeletal bonds centred on silicon atoms takes the form

$$\mathbf{U}' = \begin{array}{c} \\ t \\ g^+ \\ g^- \end{array} \begin{array}{c} \begin{array}{ccc} t & g^+ & g^- \end{array} \\ \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & 0 \\ 1 & 0 & \sigma \end{bmatrix} \end{array}$$

The corresponding statistical weight matrix that takes account of the mutual interdependence of adjacent pairs of skeletal bonds centred on oxygen atoms takes the form

$$\mathbf{U}'' = \begin{array}{c} \\ t \\ g^+ \\ g^- \end{array} \begin{array}{c} \begin{array}{ccc} t & g^+ & g^- \end{array} \\ \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \delta \\ 1 & \delta & \sigma \end{bmatrix} \end{array}$$

The statistical weight parameters σ and δ were assigned the values 0.238 and 0.0402 respectively at the temperature considered (298 K). These values were obtained from the Boltzmann factors $\sigma = \exp(-\Delta E_\sigma/kT)$ and $\delta = \exp(-\Delta E_\delta/kT)$ defined in the FCM model[30].

Calculation of the radii of gyration of the PDMS chains

The unperturbed mean-square radii of gyration of PDMS chains $[(CH_3)_2SiO]_{w/2}$ containing w skeletal atoms were calculated using the FCM RISM by matrix methods described by Flory[35]. In general these methods can be used to evaluate the even moments of properties which depend on sums of scalar products of skeletal bond vectors. To evaluate odd-moments of such properties and quantities such as the Kirkwood impermeable hydrodynamic radius, Monte Carlo methods[32,39,40,52,53] have to be employed.

Calculation of the radii of gyration of the PDMS rings

The matrix algebraic methods developed by Flory and Jernigan[33–35] cannot be applied to calculate the radii of gyration of ring molecules, because the individual conformations of the rings cannot be defined *a priori*. However, Monte Carlo methods can be applied as has been demonstrated in a number of computational studies, including investigations of freely-jointed ring molecules[27–29], ring molecules confined to a lattice[23,25] and off-lattice cyclic polymers[24,26]. The calculations involving lattices have the advantage that the ends of a chain molecule forming a ring can meet exactly, and the computation is simplified.

However, in general, chains confined to lattices do not provide good models for real polymer molecules. For example, PDMS has unequal skeletal bond angles at silicon and oxygen, so that it cannot be superimposed on a regular lattice. In off-lattice calculations, a condition for ring formation by the chain molecules is required. Generally, this is taken as being when the end separation of end-to-end distances of a chain molecule falls within a certain value[50,51]. In this case, 0.2 nm was chosen, corresponding to rather more than the S–O bond length of 0.164 nm. Hence, ring formation is assumed when one end of the chain falls within a sphere of radius 0.2 nm, centred around the terminal atom at the other end of the siloxane chain. The effects of changes in the radius of the sphere r_e from 0.1–0.3 nm were examined for chains corresponding to rings with 8–24 skeletal atoms. Relatively little variation was found, as shown in *Table 1*. The greatest differences were for $w = 10$ and $w = 14$.

More stringent tests of ring formation, including analysis of the relative orientations of terminal bonds were carried out for the cyclics $[(CH_3)_2SiO]_{w/2}$ (with $w = 8$–24) and were found to have relatively little effect on the radii of gyration. The relative insensitivity of $\langle s_r^2 \rangle$ to the variation of the magnitude and valence angles associated with the one bond which closes the ring is not unexpected as $\langle s_r^2 \rangle$ depends on the separations of all pairs of skeletal atoms in the molecule. For these relatively small rings, Monte Carlo methods were not employed.

* In keeping with earlier papers in this series, the term 'conformation' is used to specify the shape of a molecule using the rotational isomeric state model. Some of the present authors prefer the term 'spatial configuration' (c.f. Flory[35], p 15).

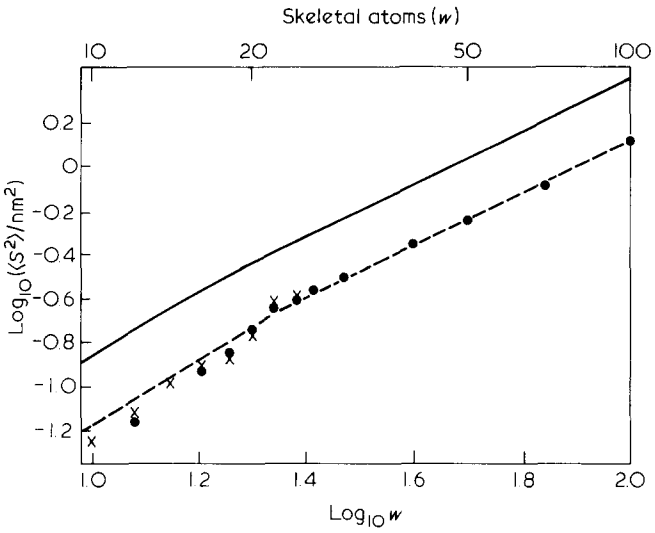

Figure 1 Logarithms of radii of gyration ($\langle s^2\rangle$) in nm^2 plotted against logarithms of numbers of skeletal atoms (w) for cyclic and linear PDMS at 298 K. Values of $\langle s_r^2\rangle$ were calculated by the complete enumeration (x) and Monte Carlo methods (●) assuming a value of r_e = 0.2 nm (see text)

Instead, the statistically-weighted ring fraction of the 3^{w-3} conformations of $[(CH_3)_2SiO]_{w/2}$ chains, containing w skeletal atoms, were computed using the DEC computer at the University of York. This direct computational method has been described elsewhere[50,51].

The Monte Carlo technique employed for the larger rings has previously been used to compute the properties of isolated chains[39], and chain molecules adsorbed onto a surface[38]. An initial conformation corresponding to a ring is generated and the conformational energy calculated using the FCM RISM. Then, a new conformation is generated by changing the rotational states of a small number of contiguous bonds in the existing conformation and this process is repeated until a new cyclic conformation is obtained. The number of contiguous bonds, which were altered in this way, was typically seven. It was found that if fewer bonds were changed, the conformation was not sufficiently altered to produce a different cyclic conformation; if too many bonds were changed, the computational time required to perform all the necessary coordinate transformations became prohibitive. If the energy difference (ΔE) between the old and the new conformation is negative, the new conformation is accepted and the average value of its radius of gyration is computed. If $\Delta E > 0$, the new conformation is accepted and the average value of the If the new conformation is rejected, the old conformation is counted into the sample again. For large sample sizes, this process leads to a Boltzmann distribution of conformations. Sample sizes generated using the University of Manchester Computer Centre CDC 7600 computer varied from 2×10^5 for $w=12$ to 8×10^3 for $w=100$.

The Metropolis sampling technique has two main advantages over a purely random sampling method for the present application. Firstly, the random method gives unpredictable convergence to the average value of the property being calculated. Secondly, the amount of computer time required to find a ring molecule by searching at random through a series of chain conformations is orders of magnitude greater than the time required to generate a new conformation from a preformed ring.

CALCULATED RADII OF GYRATION

The calculated mean-square radii of gyration of ring (r) and linear (l) PDMS are shown in *Figure 1*. The solid curve for linear PDMS was obtained by using the methods of Flory and Jernigan[33-35], as described. The dashed curve for cyclic PDMS was constructed assuming the ratio $\langle s_l^2\rangle/\langle s_r^2\rangle$ to be constant for all chain lengths and to be equal to 2.0, as predicted theoretically for high molar mass, 'flexible' linear and cyclic polymers[10-15]. The agreement between the $\langle s_r^2\rangle$ values computed by the complete enumeration method and the Monte Carlo method is satisfactory for rings with $w=16$–24 and provides support for the validity of the Metropolis method in the present application. For the largest values of w, calculated $\langle s_r^2\rangle$ values are in good agreement with theoretical expectation. However, for $w<ca.\,20$ substantially smaller values of $\langle s_r^2\rangle$ are calculated than predicted.

In *Figure 2*, the ratio $\langle s_l^2\rangle/\langle s_r^2\rangle$ is plotted against $1/w$. In the region $30<w<100$, the calculated ratio lies in the range 2.0 ± 0.10. This is in agreement with the theoretically predicted value[10-15].

Furthermore, it is in agreement with the experimental value of 1.9 ± 0.2 for linear and cyclic PDMS with $130<\bar{n}_z<550$, as found by small angle neutron scattering measurements in dilute solution[3]. In general, the calculated ratio $\langle s_l^2\rangle/\langle s_r^2\rangle$ is substantially greater than 2.0 for values of $w<20$, with indications from the complete enumeration results that the increase is not monotonic.

Figure 3 shows the characteristic ratio $\langle s^2\rangle/nl^2$ plotted *versus* $1/w$ for linear polymethylene (PM), polyoxyethylene (POE), and both cyclic and linear PDMS. The RISM's used for the PM and POE chains are described elsewhere[35] and the values shown were computed using the matrix methods of Flory and Jernigan[33-35]. Mattice[26] had previously used such plots as a method of linearly extrapolating characteristic ratios for freely-rotating chains, to infinite chain length. However, *Figure 3* shows that for the more realistic chain models used here, linear behaviour at large w does not necessarily result from this type of plot. The data for POE fall on a good straight line, but the data for PM and linear PDMS give pronounced curves. Intercepts for the linear

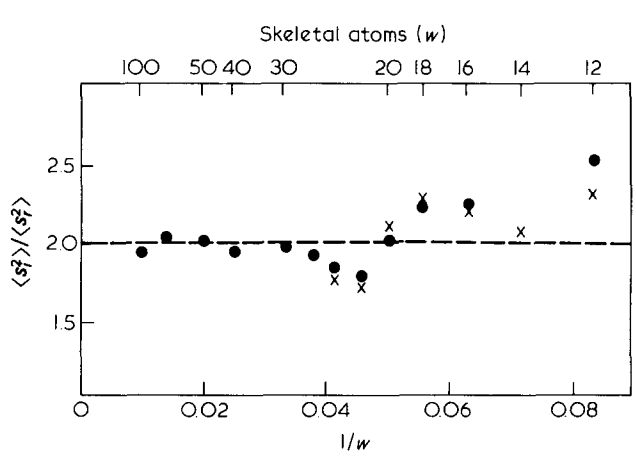

Figure 2 The ratio of the mean-square radii of gyration ($\langle s_l^2\rangle/\langle s_r^2\rangle$) for linear and cyclic PDMS at 298 K, calculated by the complete enumeration (x) and Monte Carlo methods (●)

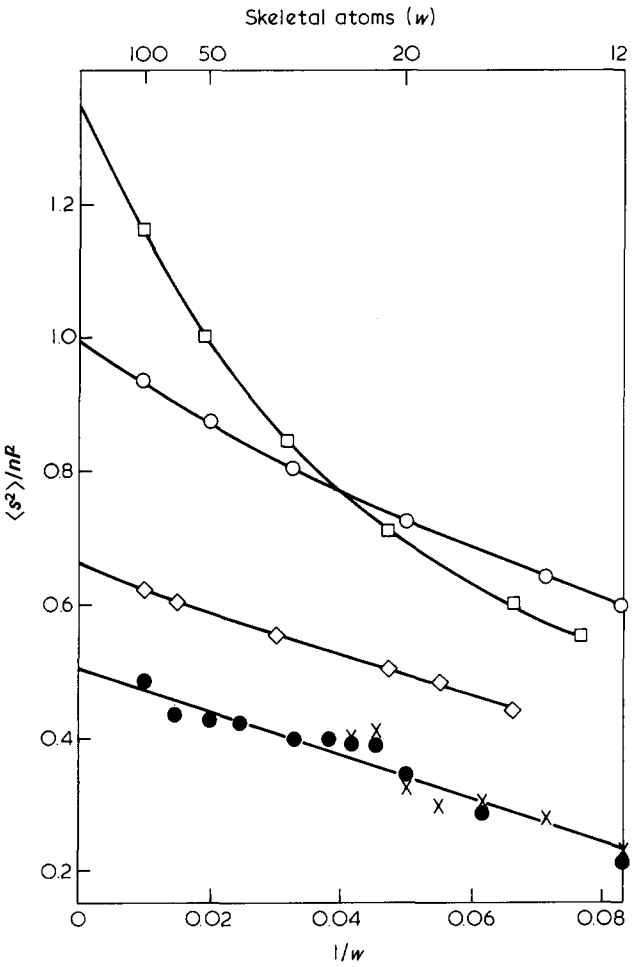

Figure 3 Characteristic ratios $\langle s^2 \rangle / nl^2$ (where $n(= w - 1)$ is the number of skeletal bonds of root mean-square length l) plotted against $1/w$ for linear polymethylene (PM) (□), linear polyoxyethylene (POE)(◇), linear PDMS (○) and cyclic PDMS (●) at 298 K

polymers are taken as the characteristic ratios of chains of 2000 skeletal bonds. The data for cyclic PDMS give an approximately straight line when plotted in this way and the solid line through the data has been drawn using a least-squares procedure. The intercept of 0.5 can be compared with the value of 0.99 for linear PDMS to give an estimate of the limiting value of the ratio $\langle s_l^2 \rangle / \langle s_r^2 \rangle = 1.98$ which is in good agreement with the theoretical value mentioned earlier[10-15].

CONCLUSIONS

The data presented here are the first calculations of the dimensions of cyclic PDMS using the FCM RISM and a Monte Carlo method to investigate rings containing up to 100 skeletal bonds. The calculated ratio of the mean-square radii of gyration $\langle s_l^2 \rangle / \langle s_r^2 \rangle$ for the ring and chain molecules was found to be 2.0 ± 0.1 for $w > 30$ in agreement with experiment[3] and with theoretical predictions[10-15]. Substantially greater values of the ratio were found for values of $w < 20$ and such values were also calculated by the complete enumeration computational method, which counts all the conformations defined by the RISM. In the paper to follow, calculations of the shapes of PDMS rings and chains will be described.

ACKNOWLEDGEMENTS

C. J. C. Edwards and D. Rigby and K. Dodgson wish to acknowledge financial support from the Science and Engineering Research Council during the period of this research.

REFERENCES

1 Dodgson, K. and Semlyen, J. A. *Polymer* 1977, **18**, 1265
2 Dodgson, K., Sympson, D. and Semlyen, J. A. *Polymer* 1978, **19**, 1285
3 Higgins, J. S., Dodgson, K. and Semlyen, J. A. *Polymer* 1979, **20**, 553
4 Dodgson, K., Bannister, D. J. and Semlyen, J. A. *Polymer* 1980, **21**, 663
5 Edwards, C. J. C., Stepto, R. F. T. and Semlyen, J. A. *Polymer* 1980, **21**, 781
6 Bannister, D. J. and Semlyen, J. A. *Polymer* 1981, **22**, 377
7 Edwards, C. J. C., Stepto, R. F. T. and Semlyen, J. A. *Polymer* 1982, **23**, 865
8 Edwards, C. J. C., Stepto, R. F. T. and Semlyen, J. A. *Polymer* 1982, **23**, 869
9 Edwards, C. J. C., Bantle, S., Burchard, W., Stepto, R. F. T. and Semlyen, J. A. *Polymer* 1982, **23**, 873
10 Yamakawa, H. 'Modern Theory of Polymer Solutions', Harper and Row, New York, London, 1971
11 Kramers, H. A. *J. Chem. Phys.* 1946, **14**, 415
12 Casassa, E. F. *J. Polym. Sci. (A)* 1965, **3**, 605
13 Zimm, B. H. and Stockmayer, W. H. *J. Chem. Phys.* 1949, **17**, 1301
14 Boots, H. and Deutch, J. M. *Macromolecules* 1977, **10**, 1163
15 Prentis, J. J. *J. Chem. Phys.* 1982, **76**, 1574
16 Bloomfield, V. and Zimm, B. H. *J. Chem. Phys.* 1966, **44**, 315
17 Fukatsu, M. and Kurata, M. *J. Chem. Phys.* 1966, **44**, 4539
18 Yu, H. and Fujita, H. work cited in Ref. 10, p 321–323
19 Kumbar, M. *J. Chem. Phys.* 1971, **55**, 5046
20 Kumbar, M. *J. Chem. Phys.* 1973, **59**, 5620
21 Naghizadeh, J. *J. Chem. Phys.* 1968, **48**, 1961
22 Solc, K. and Gobush, W. *Macromolecules* 1974, **7**, 814
23 Naghizadeh, J. and Sotobayashi, H. *J. Chem. Phys.* 1974, **60**, 3104
24 Bruns, W. and Naghizadeh, J. *J. Chem. Phys.* 1976, **65**, 747
25 Solc, K. *Macromolecules* 1978, **6**, 378
26 Mattice, W. L. *Macromolecules* 1980, **13**, 506
27 Chen, Yi-der *J. Chem. Phys.* 1981, **74**, 2034
28 Chen, Yi-der *J. Chem. Phys.* 1981, **75**, 2447
29 Chen, Yi-der *J. Chem. Phys.* 1981, **75**, 5160
30 Flory, P. J., Crescenzi, V. and Mark, J. E. *J. Am. Chem. Soc.* 1964, **86**, 146
31 Wright, P. V. *J. Polym. Sci., Polym. Phys. Edn.* 1973, **11**, 51
32 Edwards, C. J. C., Rigby, D. and Stepto, R. F. T. *Macromolecules* 1981, **14**, 1808
33 Flory, P. J. *Proc. Natl. Acad. Sci., USA* 1964, **51**, 1060
34 Flory, P. J. and Jenigan, R. L. *J. Chem. Phys.* 1965, **42**, 3509
35 Flory, P. J. 'Statistical Mechanics of Chain Molecules', Interscience, New York, 1969
36 Metropolis, N., Rosenbluth, A. W., Rosenbluth, M. N., Teller, A. H. and Teller, E. *J. Chem. Phys.* 1953, **21**, 1087
37 Lal, M. and Spencer, D. 'Applications of Computer Techniques in Chemical Research', (Ed. P. Hepple), Applied Science Publishers, 1972
38 Lal, M. and Stepto, R. F. T. *J. Polym. Sci., Polym. Symp.* 1977, **61**, 401
39 Winnik, M. A., Rigby, D., Stepto, R. F. T. and Lemaire, B. *Macromolecules* 1980, **13**, 699
40 Rigby, D. *PhD Thesis* University of Manchester, 1981
41 Semlyen, J. A. *Adv. Polym. Sci.* 1976, **21**, 41
42 Casassa, E. F. and Tagami, Y. *Macromolecules* 1969, **2**, 14
43 Casassa, E. F. *Sep. Sci.* 1971, **6**, 305
44 Casassa, E. F. *Macromolecules* 1976, **9**, 182
45 Semlyen, J. A. and Wright, P. V. in 'Chromatography of Synthetic Polymers and Biopolymers', (Ed. R. Epton), Ellis Horwood, Chichester, 1977, vol 1
46 Beuche, F. *J. Chem. Phys.* 1964, **40**, 484
47 Crescenzi, V. and Flory, P. J. *J. Am. Chem. Soc.* 1964, **86**, 141
48 Mark, J. E. and Flory, P. J. *J. Am. Chem. Soc.* 1964, **86**, 138
49 Sutton, C. and Mark, J. E. *J. Am. Chem. Soc.* 1971, **54**, 5011
50 Scales, L. E. and Semlyen, J. A. *Polymer* 1976, **17**, 601
51 Beevers, M. S. and Semlyen, J. A. *Polymer* 1972, **13**, 385
52 Hill, J. L. and Stepto, R. F. T. *Trans. Faraday Soc.* 1971, **67**, 3202
53 Mokrys, I. J., Rigby, D. and Stepto, R. F. T. *Ber Bunsenges. Phys. Chem.* 1979, **83**, 446