

CYCLIC POLYMERS

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Abstract - The possibility of a cyclic polymer rather than a linear polymer being produced in a polymerization reaction is discussed with reference to the poly(1,3-dioxolane) system. It is emphasised that, in general, new experimental methods are required for distinguishing between cyclic and linear polymers. Some progress towards the establishment of such methods has followed the preparation of sharp fractions of cyclic poly(dimethyl siloxanes). The properties of these cyclic polymers have been contrasted with those of the corresponding linear polymers, including their gel permeation chromatographic distribution coefficients, their bulk and solution viscosities, their radii of gyration and their translational friction coefficients. References are made to the other known synthetic and natural cyclic polymers, namely cyclic polystyrene, circular deoxyribonucleic acids and the large sulphur rings, which are predicted to be present in liquid sulphur.

INTRODUCTION

In principle, the polymerization of a monomer could lead to the production of a high molecular weight cyclic polymer, rather than to a conventional linear polymer. In fact, there have been suggestions that certain polymerization reactions do result in the formation of cyclic polymers. One example is the polymerization of the heterocyclic monomer 1,3-dioxolane, and this will now be discussed.

The polymerization reactions of 1,3-dioxolane have been studied under a variety of conditions. In our investigations, monomer-polymer equilibration reactions at 333K (under the catalytic influence of boron trifluoride diethyl etherate) were carried out both for the undiluted monomer and for the monomer in solution in dichloroethane (Refs. 1 & 2). Oligomers present in the monomer-polymer equilibrates were shown to be the cyclics $(\text{CH}_2\text{OCH}_2\text{CH}_2\text{O})_x$, by mass spectroscopy and nuclear magnetic resonance spectroscopy. The concentrations of the individual cyclics with $x = 1-8$ were measured by gas-liquid chromatography, and the molar cyclization equilibrium constants K_x were deduced assuming equilibria between ring and chain molecules. Values for the average number of monomeric units in the

polymer were obtained by gel permeation chromatography, by assuming the polymer to be linear and to have a most probable distribution of chain lengths. The K_x values for the individual cyclics with $x = 2-8$ were found to be the same within experimental error for the undiluted equilibrate (containing 81% by weight of polymer) and in the solution equilibrate (containing 14% by weight of polymer). Furthermore, K_x values for larger cyclics with $x = 5-8$ were found to be in good agreement with theoretical K_x values calculated using the Jacobson and Stockmayer (Ref. 3) cyclization theory, which assumes that chains corresponding to rings obey Gaussian statistics. All these results provide convincing evidence that equilibria between cyclic oligomers and linear polymers are established under the conditions described, and that the poly(1,3-dioxolane) obtained in our laboratory is not a cyclic polymer.

By contrast, the polymerization of 1,3-dioxolane (and also of 1,3-dioxepan) under vacuum in dichloromethane with anhydrous perchloric acid as catalyst has been studied by Plesch and Westermann (Refs. 4-7). These authors concluded that cyclic polymers had been formed by ring-expansion mechanisms. Detailed investigations of the equilibrium concentrations of individual cyclic oligomers have not yet been carried out for these systems. Such investigations should provide a method for establishing whether the proposed ring-ring equilibria are set up, or whether there are ring-chain equilibria, as in the equilibrium polymerization of 1,3-dioxolane involving boron trifluoride diethyl etherate as catalyst (Refs. 1 & 2). In this connection, it is noted that the concentrations of cyclic oligomers in the equilibrium polymerization of 1,3,6,9-tetraoxacycloundecane (under the influence of trifluoromethanesulphonic acid, with dichloromethane as solvent), as measured by Rentsch and Schulz (Ref. 8), are typical values for ring-chain equilibria (Ref. 2). This result, together with their published gel permeation chromatographic analyses, indicate that their polymer is linear and not cyclic.

From these examples, it follows that the establishment of new methods for identifying and characterising cyclic polymers could prove to be most helpful. In particular, methods are required that could identify a polymeric product (of known molecular weight) as a cyclic or as a linear polymer. In connection with our general studies of the preparation and properties of cyclic polymers, we have prepared and characterised cyclic poly(dimethyl siloxane). Here, the properties of cyclic poly(dimethyl siloxane) will be compared with those of the corresponding linear polymer. The results show that the two types of polymer can indeed be readily distinguished, and the methods described should be applicable generally to other pairs of cyclic and linear polymers.

CHARACTERISATION AND PROPERTIES OF CYCLIC AND LINEAR
POLY(DIMETHYL SILOXANES)

Cyclic poly(dimethyl siloxane) fractions have been prepared in our laboratory (Refs. 9-14) by recovering them from dimethyl siloxane ring-chain equilibrates carried out in solution in inert solvents. Analytical and separative methods used in the preparation include fractional distillation, gas-liquid chromatography, fractional precipitation, and analytical and preparative gel permeation chromatography. Many sharp fractions have now been obtained, each on a scale of several grams. The fractions consist of cyclics $((\text{CH}_3)_2\text{SiO})_x$ with (on average) up to 700 skeletal bonds, and with heterogeneity indices substantially less than 1.1.

The concentrations of cyclics and linears in the dimethyl siloxane ring-chain equilibrates were calculated using the Jacobson and Stockmayer (Ref. 3) cyclization theory for the cyclics, and Flory's (Ref. 15) equations for the linear species. Application of the Jacobson and Stockmayer theory to the larger cyclics was straightforward, as chains corresponding to rings should obey Gaussian statistics (Ref. 16). The concentrations of smaller rings ($x < 15$) were calculated using the Flory, Crescenzi and Mark (Ref. 17) rotational isomeric state model of poly(dimethyl siloxane), without recourse to the Gaussian assumption (Refs. 18 & 19). All the gel permeation chromatographic instruments were calibrated from information obtained by gas-liquid chromatography (for cyclics with 100 or less skeletal bonds), from cyclization data and from vapour pressure osmometric measurements (Refs. 10-12, & 20).

The properties of the cyclic poly(dimethyl siloxane) fractions have been investigated and compared with those of the corresponding linear polymers. For example, the ratio of the limiting viscosity numbers of the ring and linear polymers was measured in a θ -solvent, and found to be in agreement with the value of 0.66, predicted theoretically by Bloomfield and Zimm (Ref. 21) and others (Refs. 22 & 23). In addition, small-angle neutron scattering investigations gave a value of 1.9 ± 0.2 for the ratio $\langle s^2 \rangle_{z,l} / \langle s^2 \rangle_{z,r}$ of the squares of the z-average radii of gyration of linear and ring poly(dimethyl siloxanes) in benzene- d_6 . This may be compared with the value of 2.0 predicted theoretically for 'flexible' high molecular weight linear and cyclic polymers under θ -point conditions by Kramers (Ref. 24) and others (Refs. 25-27).

A comparison of the experimental and theoretical ratios is shown in Table 1, together with the results of bulk viscometric investigations, gel permeation chromatographic (g.p.c.) studies and diffusion measurements in dilute solution. In every case, the experimental conditions were such as to effectively eliminate excluded volume effects. Unless otherwise stated, all the ratios in Table 1 refer to cyclic and linear polymers containing the same number of skeletal bonds. The theoretical ratio for the bulk viscosities was calculated by Bueche (Ref. 34) assuming no entanglements, and the experimental bulk viscometric ratio refers to poly(dimethyl siloxanes)

containing (on average) from 430 to 650 skeletal bonds. Limits of accuracy have been placed on all the experimental ratios, and the temperatures of the measurements were in the range 292-298K.

Among the experimental methods discussed, neutron scattering provides possibly the best test for discriminating between cyclic and linear polymers. Plots of the inverse scattering intensities $c/I(Q)$ (where c is the polymer concentration) against the squares of the scattering vectors Q^2 for the cyclic poly(dimethyl siloxane) fractions show the characteristic pronounced upward curvature (Ref. 28), predicted for cyclic polymers by Casassa (Ref. 26). By contrast, there is little curvature in the corresponding plots for the linear poly(dimethyl siloxane) fractions (Ref. 28).

The bulk viscosities η of cyclic and linear poly(dimethyl siloxane) fractions, with weight average molecular weights \bar{M}_w , at 298K are shown in Fig. 1. Cyclic fractions with (on average) substantially less than 100 skeletal bonds have considerably higher bulk viscosities than the corresponding linear fractions. Whereas, cyclic fractions with (on average) substantially more than 100 skeletal bonds have markedly lower bulk viscosities than their linear analogues.

Comparisons of other properties of cyclic and linear poly(dimethyl siloxanes) will not be described here. Instead, references will be made to all the other known synthetic and natural cyclic polymers.

TABLE 1. Properties of cyclic and linear poly(dimethyl siloxanes)

Ratio of the property for ring (r) and linear (l) polymers	Experimental Value	Theoretical Prediction
Number-average molecular weights of rings and chains with the same g.p.c. distribution coefficients M_r/M_l	20,29 1.24 (+0.04)	30-32 1.26
Limiting viscosity numbers $[\eta]_r/[\eta]_l$	13 0.67 (+0.01)	21-23 0.66
Mean-square radii of gyration $\langle s_{z,r}^2 \rangle / \langle s_{z,l}^2 \rangle$	28 0.53 (+0.05)	24-26 0.50
Bulk viscosities η_r/η_l	33 0.51-0.45 (+0.02)	34 0.50
Translational friction coefficients f_r/f_l	35 0.84 (+0.01)	21,22,36 0.85

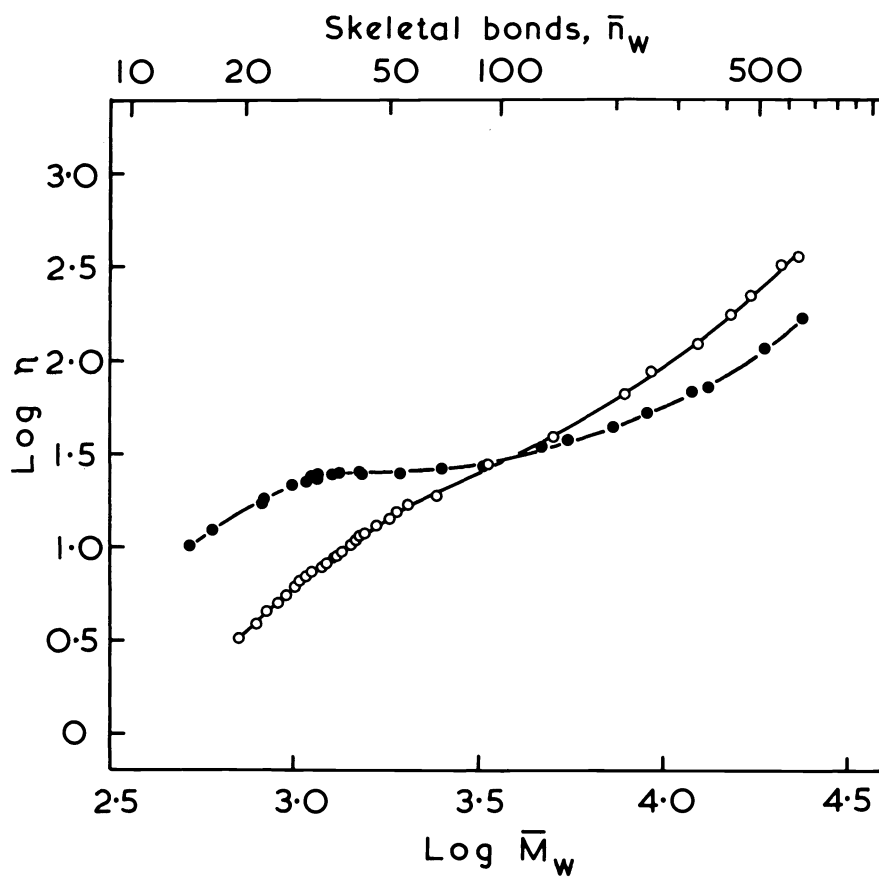


Fig. 1. Plots of the logarithms of the bulk viscosities η of the cyclic (●) and linear (○) poly(dimethyl siloxanes) at 298K against the logarithms of their weight average molecular weights \bar{M}_w .

OTHER CYCLIC POLYMERS

In addition to ring-chain equilibrates of poly(dimethyl siloxane), many other ring-chain equilibrates have been found to contain large ring molecules. Among those that have been analysed are certain polyesters (Refs. 37 & 38), polyamides (Refs. 39 & 40) and polyethers, such as poly(1,3-dioxolane) (Refs. 1 & 2) and poly(1,3,6,9-tetraoxacycloundecane) (Ref. 8) which were discussed above. In all these systems, individual cyclics with up to ca.50 skeletal bonds, and sometimes more, have been separated by gas-liquid chromatography and gel permeation chromatography. However, substantial quantities of cyclic polymers (with more than 100 skeletal bonds) have not yet been isolated from any of these equilibrates.

Several years ago, Jones (Ref. 41) published a study of cyclic concentrations in a block copolymer of polystyrene-poly(dimethyl siloxane), which he had prepared in our laboratory by an anionic polymerization method. Cyclics containing up to ca.150 skeletal bonds were identified by gel permeation chromatography alone. Recently, Geiser and Höcker (Ref. 42) and Hild and his coworkers (Ref. 43) have reported the preparation of substantial quantities of cyclic polystyrene, again using anionic polymerization methods. Their fractions are believed to consist of ring molecules containing up to ca.450 skeletal bonds, and incorporating residual molecules from the coupling agents used to effect cyclization (Refs. 42 & 43).

The preparation of the first synthetic cyclic polymers followed the discovery of ring macromolecules in nature. Circular deoxyribonucleic acids (DNA) have been found to be present in a variety of living systems, including viruses and bacteria (Refs. 44-46). The circular nature of the DNA structures has been strikingly demonstrated by electron microscopy (see, for example, Refs. 47 & 48).

Another natural source of cyclic polymers is believed to be liquid, elemental sulphur. Calculations of ring concentrations in liquid sulphur have been carried out (Refs. 49-52) using the Jacobson and Stockmayer (Ref. 3) cyclization theory, together with a rotational isomeric state model based on the available molecular structural information. It has been concluded that rings with more than 100 skeletal bonds are present at concentrations of ca.2% by weight in liquid sulphur close to the critical polymerization temperature of 433K (Refs. 51 & 52). The recent Voyager space missions have signalled information to earth which suggests that the surface of Jupiter's moon Io contains vast quantities of liquid sulphur (Ref. 53). Io may prove to be carrying the largest amounts of cyclic polymers in our solar system.

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