Liquid Crystalline Cyclic Polymers

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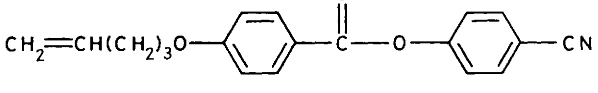
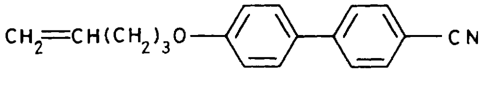
Cyclic poly(hydrogenmethylsiloxane) fractions $[H(Me)SiO]_x$ with $4 < \bar{x} < 24$ ($\bar{x}$ = number-average degree of polymerisation) have been prepared by a pyrolysis reaction and interacted with suitable mesogenic alkenes to form liquid crystalline cyclic polymers; some of the properties of these polymers are reported here and compared with those of their open chain analogues.

All polymers were once thought to be based on long chain molecules (which could be branched or cross-linked into networks).[1] However, in recent years the first examples of synthetic cyclic polymers have been prepared and characterised and their properties studied.[2] In particular, a range of cyclic silicones $[R(Me)SiO]_x$, where R = Me,[3] $CH_2=CH$,[4] and Ph,[5] have been obtained as sharp fractions (heterogeneity indices of *ca.* 1.05) containing up to 1 000 skeletal bonds. Some of the properties of these cyclic polymers are markedly different from those of their linear analogues, suggesting that it would be of interest to prepare and investigate the first cyclic polymer liquid crystals.

The preparation of small cyclic silicones with up to five mesogenic side-chains has been reported previously.[6] Cyclic poly(hydrogenmethylsiloxane) (PHMS) $[H(Me)SiO]_x$ in base catalysed ring-chain equilibrates,[7,8] kinetically controlled cationic polymerizations,[8,9] and dilute solution hydrolysis of methyldichlorosilane $H(Me)SiCl_2$,[8,10] have been investigated by GLC. These ring polymers are suitable for interactions with mesogenic molecules because they contain reactive Si–H bonds. The thermal depolymerization of poly(dimethylsiloxane) to yield cyclic oligomers has been extensively studied,[11] and for the present purposes cyclic PHMS was prepared by a similar route. These products were compared with cyclic PHMS prepared as described above, and characterized by GLC, gel permeation chromatography, and ^1H and ^{29}Si NMR spectroscopy. The results now reported are



Cyanoester (I)



Cyanobiphenyl (II)

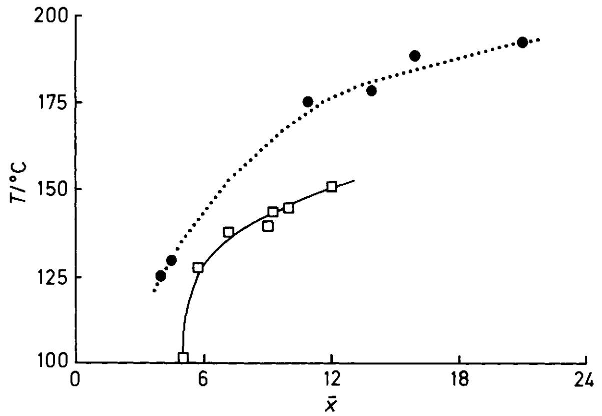


Figure 1. Mesophase–isotropic transition temperatures for cyclic (●) and linear (□) polymers containing the cyanoester mesogenic groups.

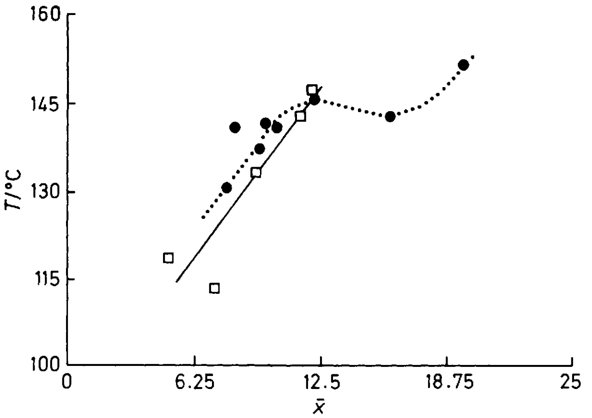


Figure 2. Mesophase–isotropic transition temperatures for cyclic (●) and linear (□) polymers containing the cyanobiphenyl mesogenic groups.

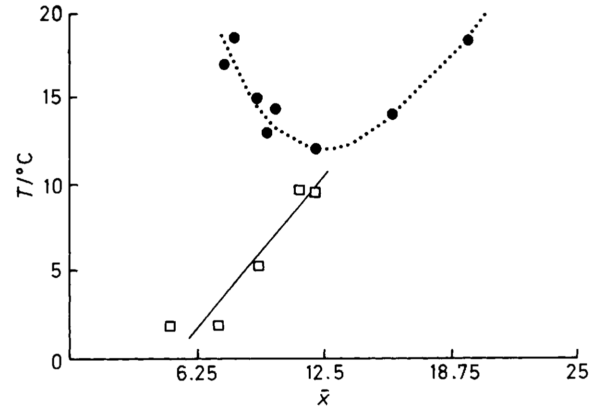


Figure 3. Glass transition temperatures for cyclic (●) and linear (□) polymers containing the cyanobiphenyl mesogenic groups.

from some investigations of cyclic silicones containing up to 24 mesogenic side-chains.

Poly(hydrogenmethylsiloxane) (PHMS) resins of high molar mass were prepared by the hydrolysis of methyldichlorosilane $H(Me)SiCl_2$. These resins were then heated to over 850 K under high vacuum. Sudden cooling of the gaseous depolymerization products permitted the isolation of cyclic PHMS from the condensate. Narrow molar mass distribution fractions of the cyclic PHMS were obtained by molecular distillation.

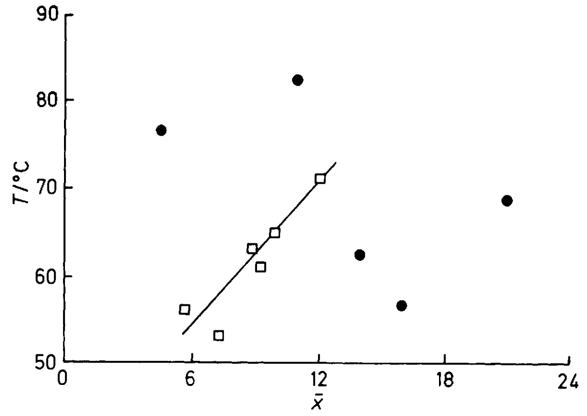


Figure 4. Crystalline–mesophase transition temperatures for cyclic (●) and linear (□) polymers containing the cyanoester mesogenic groups.

Some open chain analogues of these materials were prepared by re-equilibration of a polydisperse trimethylsilyl terminated PHMS material† in the presence of sufficient hexamethyldisiloxane to produce PHMS chains $(Me)_3SiO[H(Me)SiO]_xSi(Me)_3$ containing (on average) approximately ten monomer units. Narrow molar mass distribution fractions of these materials with $4 < \bar{x} < 13$ ($\bar{x}$ = number-average degree of polymerisation) were also obtained by molecular distillation.

The cyclic and linear fractions were characterised by GLC, gel permeation chromatography, and ^{1}H and ^{29}Si NMR. Both the refractive indices and the densities of the fractions were measured. The well-defined maxima[4,12] in the plots of both refractive indices and densities against $\bar{x}$ for cyclic dimethyl- and vinylmethyl-siloxanes at $\bar{x} = 11$ were not observed[8] for the cyclic hydrogenmethylsiloxanes. However, the $[H(Me)SiO]_x$ fractions with $\bar{x} \approx 11$ were observed to be much less stable than the others, forming gels after a period of 3—4 weeks.

Side-chain liquid crystalline cyclic polymers and their open chain analogues were prepared by means of a standard hydrosilylation reaction[13] using both the cyclic and the linear polymers. The results shown in Figures 1—4 relate to products obtained using the side-chain precursors (**I**) and (**II**).

The polymeric products formed from (**I**) were crystalline, while those from (**II**) were glassy materials. The phase transition temperatures were recorded by differential scanning calorimetry (DSC), and the phases examined using a hot stage microscope. While all materials exhibited focal-conic fan textures resembling those given by the smectic A mesophase, other physical measurements (such as *X*-ray crystallography) would however be required to confirm that the phases of the materials of cyclic structure are not discotic. However, the materials were not nematic.

The generally higher mesophase–isotropic transition temperatures of the cyclic relative to the linear analogues (Figures 1 and 2) may be attributed in part to the absence of trimethylsilyl end groups in the cyclics. Such end groups would be expected to dilute the mesophase, thereby lowering the transition temperatures of the linear relative to those of the corresponding cyclic materials.

Discontinuities were observed at $\bar{x}$ = 12 in the plots of temperature *vs.* $\bar{x}$ for the liquid crystalline cyclic polymer fractions in the case of (i) the mesophase–isotropic transition temperatures for rings containing the cyanobiphenyl

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† Provided by Dow Corning Ltd.

mesogenic group (Figure 2) and (ii) the glass transition temperatures (Figure 3) for rings containing the cyanobiphenyl mesogenic group. For rings containing the cyanoester mesogenic groups (Figure 4), a sudden fall in the crystal–mesophase transition temperature occurs between $\bar{x} = 10$ and 13, giving a clear minimum at $\bar{x} = 16$. No such discontinuity is observed for the mesophase–isotropic transition temperatures of cyclics prepared from the cyanoester moiety (Figure 1).

Calculations of the sizes and shapes of polysiloxane molecules[14] as a function of ring size using rotational isomeric state models have led to the interpretation of the maxima and minima in the properties of cyclic siloxanes, at $x = 11$, as arising from the unequal bond angles at the silicon and oxygen atoms. As a result, silicone rings adopt a low energy, all *trans* conformation at $x = 11$. The conformations of the liquid crystalline cyclic polymers described here remain to be interpreted theoretically, but investigations are in progress to establish whether the discontinuities referred to here also have their origins in conformational effects.

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