PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Self-Order in Flexible Non-Mesogenic Macromolecules [and Discussion]

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Phil. Trans. R. Soc. Lond. A 1994 **348**, 45-57
doi: 10.1098/rsta.1994.0080

Self-order in flexible non-mesogenic macromolecules†

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Some very flexible linear poly(di-n-alkylsiloxane)s and cyclolinear oligo- and polyorganosiloxanes, which do not contain classical rigid rodlike or disclike mesogens, similar to other semi-organic polymers like polyphosphazenes and polysilanes, can form thermodynamically stable two-dimensionally ordered thermotropic mesophases. In many respects the mesophases in polysiloxanes resemble columnar liquid crystals which seems to be the result of the amphiphilic constitution of the polyorganosiloxanes. The origin of the mesomorphic state seems to be closely related to the competition between the interaction of the polar inorganic backbones and those of the organic side chains facilitated by the high flexibility of the inorganic main chain. Similarily to discotic liquid crystals, mesophases in polysiloxanes consist mostly of columns packed hexagonally (or closely so) with lateral long-range positional order, but with only short-range order along the columns. The unique feature of the columnar mesophases is that the axes of macromolecules lie along the column axes. The influence of molecular structure and molecular mass of linear macromolecules is discussed. It has been demonstrated that the temperature interval of mesophase stability is critically dependent on the length of the alkyl side chains. Both the process of formation of the mesophase from the isotropic melt and the crystallization of the mesophase are nucleation controlled processes, although the crystallization of the mesomorphic state is characterized by some specific features. The phase behaviour of cyclolinear polyorganosiloxanes is described with particular emphasis on the temperature stability as a function of molecular structure, tacticity, substituents and flexible spacers.

1. Introduction

It is now generally accepted that in order to produce a thermotropic liquid crystalline (LC) polymer it is necessary to incorporate some rigid fragments, mesogens, into the main chain of macromolecules to arrive at a main-chain LC polymer, or to attach mesogens via some flexible spacers to a flexible backbone to arrive at a side-chain LC polymer (see, for example, McArdle 1989). While for the main-chain

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Phil. Trans. R. Soc. Lond. A (1994) **348**, 45–57
Printed in Great Britain

LC polymers more or less the entire macromolecules take part in the formation of the LC structure, for the side-chain LC polymers the anisotropic arrangement is built up only by mesogenic side chains without anisotropic packing of the backbone. It is also common knowledge that without any mesogenic units incorporated in macromolecules the formation of a thermotropic LC structure in polymers is unlikely.

However, it is also well established that some very flexible macromolecules without any mesogenic units in either the main chain, or in the side chains are also able to form thermodynamically stable thermotropic ordered phases possessing the level of organization intermediate between the crystalline and amorphous states (Wunderlich *et al.* 1989; Ungar 1993). Typically, the non-mesogenic macromolecules which are able to exist in the mesomorphic state are highly conformationally disordered, that is the main chain and side-chain bond conformations become disordered, while macromolecules are still in extended conformations. In spite of the conformational disordering they, nevertheless, possess two-dimensional long-range order through being, as a rule, in a hexagonally packed cylinders forming a lattice in the plane perpendicular to the axes of macromolecules, with only short-range order along the chain direction itself. Recently, it has been recognized that such two-dimensionally ordered hexagonal polymeric mesophases may be classified as a columnar LC phases (Skoulios & Guillon 1988; Siffrin *et al.* 1990; Ungar 1993).

A group of flexible polymers, for which mesomorphic columnar phases are especially characteristic is the group of macromolecules with an inorganic backbone framed with symmetrically substituted organic side groups, such as polyphosphazenes, polysilanes and polysiloxanes (see, for example, the review articles by Godovsky & Papkov (1989) and Ungar (1993)). All these macromolecules are rather flexible, which is reflected by low glass transition temperatures and low characteristic ratios $C = \langle r^2 \rangle / \langle r_0^2 \rangle$. In spite of the flexibility the temperature interval of mesophase stability in these polymers can be surprisingly large, being a strong function of such parameters as the molecular mass, length of the organic side chains, and the nature of substituents.

The purpose of this paper is to describe briefly earlier and recent results concerning the mesophase behaviour of only one of the member of this group of macromolecules, i.e. linear and cyclolinear polyorganosiloxanes to stimulate a discussion about self-order in non-mesogenic polymers.

2. Self-ordering in linear polydialkysiloxanes

(*a*) *General characteristics*

Linear polydialkysiloxanes (LPDAs) are very flexible macromolecules, because steric interactions in these macromolecules are reduced compared with those occurring in carbon chains due to the inequality of the Si and O valence angles ($\Theta_{\mathrm{O}} = 37°$, $\Theta_{\mathrm{Si}} = 70°$), the absence side groups at the O atom and relatively long Si–O (0.164 nm) and Si–C (0.190 nm) bonds (Stepto 1993). The rotational energy (barrier) about the Si–O bond is of the order of RT. With the increasing length of the alkyl substituents the rigidity of the chain, i.e. the characteristic ratio $\langle r^2 \rangle / \langle r_0^2 \rangle$, and the glass transition, T_g, changes as follows: PDMS: 1.6 and −123 °C, PDES: 1.75 and −139°C and PDPS: 2.0 and −109 °C (Godovsky

& Papkov 1989; Stepto 1993). Although further members of LPDASs have been synthesized recently (Moeller *et al.* 1992; Shiffrin 1993) their corresponding characteristics are still unknown. Normally, LPDASs are able to crystallize. The first important feature of LPDASs is their polymorphism. It is known that PDES exists in two crystalline polymorphs, α and β polymorphs, where each of the polymorphs undergoes a disordering transition from α_1 to α_2 and β_1 to β_2, correspondingly (Tsvankin *et al.* 1985; Godovsky & Papkov 1989; Koegler *et al.* 1990). Low temperature polymorphs have been also observed for PDPS (Godovsky & Papkov 1989; Shulgin *et al.* 1994) and other LPDASs (Moeller *et al.* 1992).

In PDES both α and β polymorphs can coexist in one sample, their ratio depends on cooling rate of the sample from the mesomorphic state (see below). Slow cooling results in increasing the amount of β polymorph, which is thermodynamically more stable and has the melting point 290 K. Besides, on annealing under appropriate conditions, the α_2 polymorph converts into the thermodynamically more stable β_2 polymorph (Papkov *et al.* 1984; Koegler *et al.* 1990; Shulgin *et al.* 1994). Molecular packing and chain conformations in both crystal modifications are rather different, and at the low temperature transitions in PDES the type of crystal lattice remains the same, despite jumplike changes of its parameters and crystalline density (Tsvankin *et al.* 1985). Nuclear magnetic resonance (Litvinov *et al.* 1985, 1989; Moeller *et al.* 1990), infrared (Papkov & Kvachev 1989) and Raman (Friedrich & Rabolt 1987) experiments showed the increase of molecular motion at α_1–α_2 and β_1–β_2 transitions resulting in dynamic conformational disordering. Light and electron microscopy show that in PDES chain-folded lamellae are typical morphological units for the α-polymorph, while for the more thermodynamically stable β-polymorph extended-chain lamellae can also exist (Papkov *et al.* 1984; 1987; Papkov & Obolonkova 1989; Koegler *et al.* 1990).

Before complete isotropization the high temperature polymorphs in LPDASs transform into a thermodynamically stable mesophase. Hence, the second especially interesting feature of the phase behaviour of LPDASs is their ability to exist in a mesomorphic state possessing an intermediate level of organization and properties between the crystalline and isotropic amorphous states. The brief characterization of this mesomorphic state is the main subject of this paper.

(*b*) *Thermotropic columnar mesophases in LPDASs*

(i) *Thermodynamics and kinetics*

High temperature polymorphs in LPDASs convert before complete isotropization into a thermodynamically stable phase, which is often referred to as the mesophase, α_m phase or μ phase. Although the isotropization of the mesophase occurs in a rather broad temperature range (for example, for PDES between about 300 and 320 K), this transition is a first-order thermodynamical transition. The heat of the transition to the isotropic state in PDES is about 0.3 kJ mol^{-1} being 12–15% of the heat of fusion of the high temperature α_2 and β_2 polymorphs. However, it contributes less than 5% to the total enthalpy of transformation from low temperature α_1 and β_1 polymorphs to the isotropic state. The changes in entropy (less than 1 J K^{-1} mol^{-1}) and density (less than 3%) at the isotropization temperature are small compared to those for the low and high temperature transformations α_1–α_2, α_2–α_m and β_1–β_2, β_2–β_m. These values are smaller than the clearing entropies of main chain or side-chain liquid crystal polymers (Wunderlich

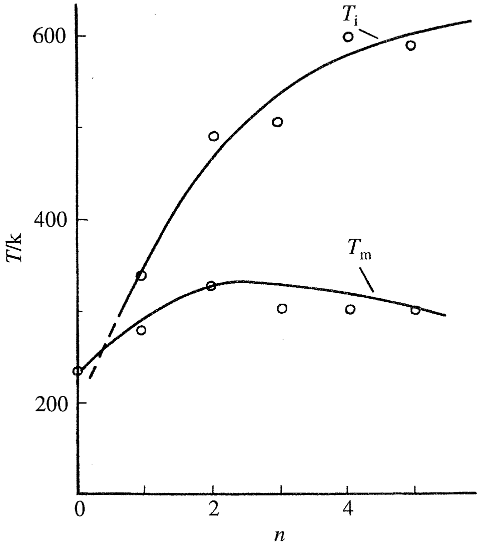


Figure 1. Dependence of melting point T_m and isotropization temperature T_i on number of CH$_2$-groups in the repeating unit of LPDASs $\{Si[(CH_2)_nCH_3]\}_p$. $n = 0$, PDMS; $n = 1$, PDES; $n = 2$, PDPS; $n = 3$, poly(di-n-butylsiloxane); $n = 4$, poly(di-n-pentylsiloxane); $n = 5$, poly(di-n-hexylsiloxane). Data for $n = 0, 1, 2$ from Godovsky & Papkov (1989); data for $n = 3, 4, 5$ from Moeller *et al.* (1992).

& Grebovicz 1984; Wunderlich *et al.* 1988). Similar relations are also characteristic of PDPS.

A very remarkable feature of the mesophase behaviour of LPDASs is a drastic dependence of the isotropization temperature T_i on the length of the side chain. Figure 1 shows dependencies of melting point T_m and T_i as a function of the length of alkyl side chains. As is seen, the temperature interval between T_m and T_i increases considerably as a result of a drastic increase of T_i. This increase seems to be the direct consequence of the enhanced rigidity of LPDASs macromolecules with the length of the side chains.

The isotropization temperature T_i is also very sensitive to the molecular mass. Figure 2 shows the strong influence of the molecular mass on T_i of fractionated samples of linear PDPS. A different dependence of the melting point and isotropization temperature on the molecular mass leads to a considerable increase of the temperature interval of the mesophase with increasing molecular mass. Such a dependence is closely related to the lamella-type morphology of the mesophase (Godovsky & Papkov 1989).

Kinetical analysis of the overall calorimetric transformation rate data obtained for PDES showed that the heat evolution resulting from the mesophase formation follows the Avrami equation with the morphological parameter n close to 2, which was interpreted as two-dimensional growth of lamellar structures on heterogeneous nuclei, which agrees with the direct microscopic measurements of the linear growth rates of the lamella-type mesophase domains (Papkov *et al.* 1987). Hence, the thermodynamical and kinetical analysis shows that the isotropization of PDES and other LPDASs can be classified as a first-order transformation with very low enthalpy and entropy changes.

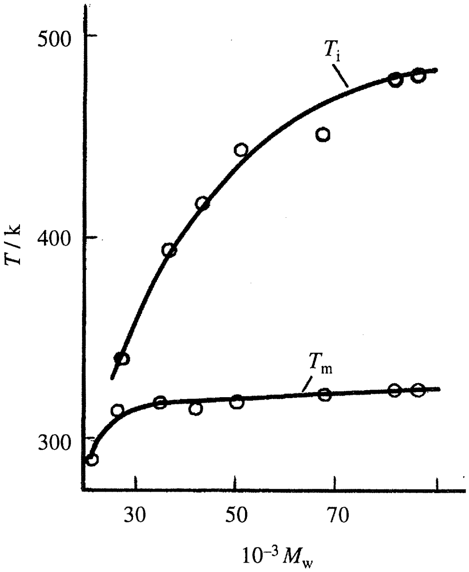


Figure 2. Dependence of melting point T_m and isotropization temperature T_i on molecular mass for fractionated PDPS (Godovsky & Papkov 1989).

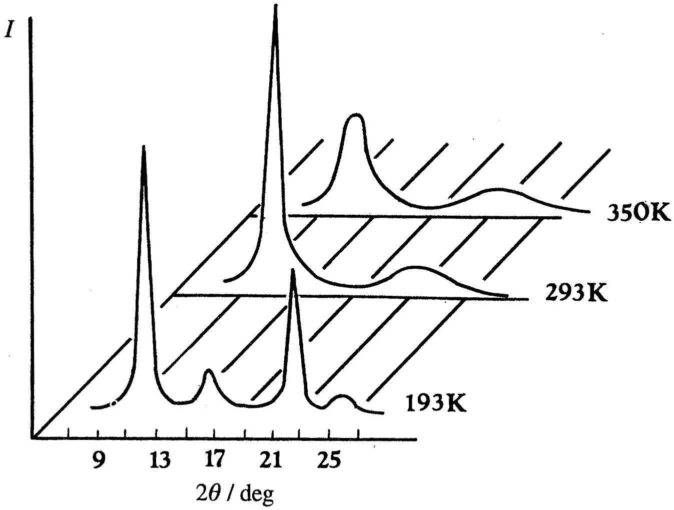


Figure 3. X-ray diffractograms of isotropic PDES in crystalline (193 K), mesophase (293 K) and isotropic (350 K) states (Tsvankin *et al.* 1985).

(ii) *Structure and morphology*

A characteristic feature of the X-ray diffractograms of the mesophases in PDES, PDPS and other LPDASs consists in the existence of two maxima (figure 3). One of them, very narrow and very intensive, is in the vicinity of $2\Theta = 8$–$12°$, and the second one, rather wide is near $2\Theta = 16$–$25°$. After isotropization there are two wide amorphous halos which are typical for the molten state of poly-organosiloxanes. X-ray fiber pattern of PDES shows sharp diffraction maxima on the zeroth layer line with only diffuse reflections on the first layer lines. The detailed analysis of the diffraction patterns led to the conclusion that such a mesophase possesses two-dimensional order in the plane perpendicular to the longitudinal axis of macromolecules while along the chain direction such a long-range order is absent and only short-range order exists. Although macromolecules are conformationally disordered, which, as mentioned above, is well documented by NMR and by vibrational spectroscopic methods, they are still extended either partly or considerably (up to complete extension) depending on the conditions of mesophase formation from the melt or on the nature of the high temperature polymorph from which they have transformed to the mesophase. It is now becoming increasingly accepted that the mesophase in LPDASs can be considered in the frame of the scheme of liquid crystalline polymers. According to the dimensionality of positional order, the thermotropic mesophase with apparently true long-range order in two dimensions can be categorized as a columnar liquid crystal phase (Ungar 1993). As has been suggested recently (Scoulios & Guillon 1988) the columnar liquid crystals can be formed either by discotic or by non-discotic amphiphilic molecules. Taking into account the amphiphilic character of LPDASs, as well as other mesomorphic semiorganic polymers, namely, polyphosphazenes and polysilanes, the mesophases in LPDASs can also be classified as the columnar liquid crystals. However, in contrast to the low molecular mass columnar liquid crystals, the unique feature of the polymer columnar mesophase is that the axes of macromolecules lie along the column axes (figure 4). Even if columnar structures are mostly hexagonal, other symmetries are also possible. The morphology of PDES, PDPS and other LPDASs has the appearance of lamella-type structures. The mesomorphic phase was found to grow from the isotropic melt in the form of lamellar domains. The thickness of the lamellar domains grown in PDES, within the temperature range 293–307 K, is about 2 μm. Such lamellar domains consist of layers with folded-chain or extended-chain macromolecules depending on the molecular mass and on the conditions of their formation. Because the enthalpy change resulting from the mesophase formation is very small the critical dimensions of nuclei should be considerably larger than that for crystallization. Because all other parameters are quite comparable with those for the crystalline nucleus, the critical dimensions of the mesomorphic nucleus should be one to two orders of magnitude larger. The corresponding estimates showed that the longitudinal dimensions of the critical nuclei at low undercooling are quite comparable with the completely extended chains for a typical molecular mass (Papkov *et al.* 1987). Direct SANS measurements showed that the radius of gyration in the mesomorphic state ($R_g = 175$ Å) differs drastically from that in the molten state ($R_g = 95$ Å) (Willenbacher 1990; see also Fisher *et al.* 1991). In accordance with the 'hairpin' model suggested for the structure of the mesophase in PDES ($M_w = 45.000$) the length of the extended part of one-folded chain $L_{st} = 520$ Å agrees very well with the half of the completely extended PDES chain ($L = 1160$ Å) (Willenbacher 1990; see also Fisher *et al.* 1991). It should also be mentioned that after melting of the thermodynamically stable β_2 polymorph with extended-chain mesophase lamella can occur. Hence, depending on the thermal treatment, a wide spectrum of mesophase lamellae can be obtained within the mesomorphic state of LPDASs.

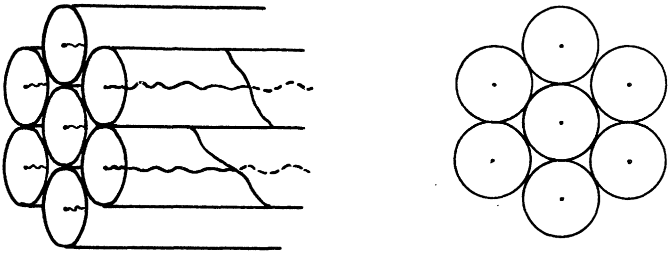


Figure 4. Schematic drawing of molecular packing in two-dimensionally ordered polymeric columnar mesophase.

(iii) *The effect of the mesophase on crystallization*

One of the interesting problems is the effect of mesophase formation on crystallization. It has been established that when the cooling rate of the isotropic melt is so high that the self-ordering can not occur during cooling the crystallization behaviour is similar to typical crystallizable polymers. In particular, upon such a quenching the melt of PDES can be transformed into the amorphous glassy state. In this case, on subsequent heating of the quenched sample a jump in the heat capacity at T_g and cold crystallization above T_g occurs. The degree of crystallinity which can be reached in this case is typical of crystalline polymers, in particular for polydimethylsiloxane (30–40%). However, when self-ordering occurs before crystallization, the sample can not be transformed into the amorphous state even by quenching. Typical values of the degree of crystallinity, if crystallization takes place after self-ordering, exceed 90%. On the other hand, in contrast to PDES, for PDPS, due to a large interval between the temperature of the mesophase formation from the melt and crystallization (see figure 1), it is impossible to obtain PDPS in the completely amorphous glassy state even by quenching its melt with liquid nitrogen. Hence, the preliminary self-ordering leads to extremely fast crystallization rates which excludes the possibility to reach the amorphous state or even to obtain the mesomorphic glassy state.

During crystallization the initial arrangement and orientation of the mesomorphic lamellar domains remains intact. The growth of the crystalline regions starts from a constant number of crystallization centres. The growth is not uniform and steady in time. Crystallization proceeds not as a sporadic crystallization of individual mesomorphic lamella but as a growth of the nucleated crystalline region via consecutive incorporation of adjacent crystallizing lamellae. Epitaxy and the strain induced at the phase boundary seems to play an imporatnt role during crystallization of the mesomorphic state. This is the reason why the thermal history of the sample has a strong effect on the transition kinetics. Finally, it is worth mentioning that the radius of gyration of the chain within the crystalline lamellae is very close to the value which was obtained for the mesomorphic lamellae (Willenbacher 1990; see also Fisher *et al.* 1991).

3. Self-ordering in cyclolinear polyorganosiloxanes

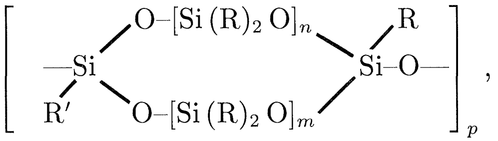
(*a*) *General description*

Cyclolinear polyorganosiloxanes (CLPOSs) consists of linear chains of repeated siloxane cycles of various dimensions bonded either by only oxygen atoms or by

Table 1. *Dependence of Kuhn segment on the chemical structure of CLPOSs*

polymer	Kuhn segment/Å
hexamethyltetrasiloxane	29
octamethylpentasiloxane	23
trans-decamethylhexasiloxane	40
trans-hexamethyldiphenylhexasiloxane	110

flexible spacers. The general formula of this class of polymers is



where R and R′ are alkyl or aryl substituents, $R = R'$ or $R = R'$, $n = 1, 2, 3$; $m = 1, 2, 3$. The number of the repeat cycles p in macromolecules may range from some dozens to several hundreds. Unlike LPDASs, in which the temperature interval of the mesophase stability depends only on the nature of the organic substituents of silicon atoms, in CLPOSs one can expect a considerable additional influence on the mesophase behaviour of the variable ratio of linear and silsesquioxanes fragments within the macromolecules as well as the variable spatial arrangement of the substituents within the organosilsesquioxane fragments. All these features show that the emergence and the existence range of the mesomorphic state in CLPOSs may be regulated by a larger number of molecular parameters in comparison with LPDASs. Although most of the CLPOSs macromolecules are rather flexible, one of their very important features is the considerable increase of rigidity with increasing number of and position of bulky phenyl substituents (table 1). Hence this factor, together with other molecular parameters of CLPOSs, can be used for widely varying the rigidity of cyclochain macromolecules and, in turn, for changing various characteristics of their mesomorphic state. Similarly to LPDASs, CLPOSs should also be conformationaly disordered, although until now there are no direct experimental NMR data. Typical phase behaviour of CLPOSs is shown in figure 5 (Godovsky *et al.* 1989; Godovsky & Papkov 1989). Besides glass transition at $T_g = 182$ K and melting point at $T_m = 220$ K there is a rather large exothermal peak in the vicinity of 600 K resulting from the isotropization, which is supported also by X-ray and polarizing light microscopy. Hence, the temperature interval of the mesophase stability of this polymer is extremely wide. The X-ray diffraction patterns of the mesomorphic and isotropic states are qualitatively analogous to that of LPDASs (figure 1).

(*b*) *Effect of the cycle dimension, substituents and tacticity*

The temperature interval of the mesophase is strongly dependent on the cycle dimension, substituents and tacticity. Below the role of these factors will be briefly considered.

Some results demonstrating the effect of the first two factors are listed in table 2. It is seen that the mesophase for methyl substituents occurs only for four- and six-membered cycles symmetrically incorporated into macromolecules.

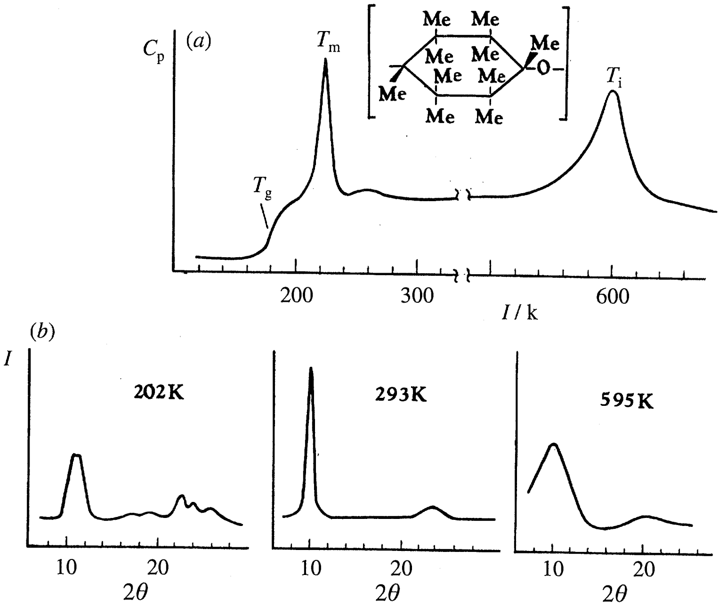


Figure 5. DSC curves of slowly cooled stereoregular transtactic poly[oxy(decamethylcyclohexasiloxane-2,8-diyl)] (*a*) and X-ray spectra in crystalline (202 K), mesophase (293 K) and isotropic (595 K) states (*b*) (Makarova *et al.* 1987).

Table 2. *Changes in mesophase temperature range depending on the size of cycles and the nature of substituents*

	size of cycles		
substituents	tetrasiloxane	pentasiloxane	hexasiloxane
methyl	10 K	no mesophase	> 250 K
methyl–phenyl	20 K	no mesophase	250 K
ethyl	400 K	250 K	above T_{cd}[a]

[a] T_{cd}, temperature of chemical decomposition.

The mesomorphic state is retained under partial substitution of methyl groups by the phenyl ones. Moreover, all macromolecules with ethyl substituents are mesomorphic, which demonstrates the very important role of organic substituents in the formation of the mesomorphic state which seems to arise from the increase of inter- and intramolecular interactions. Because of the atactic structure these macromolecules are not crystallizable, but can form the mesomorphic glasses.

The effect of phenyl substituents on the phase behaviour of a series of phenyl six-membered CLPOSs is shown in figure 6. Above T_m all these macromolecules can exist in the mesomorphic state, the temperature interval of mesophase stability being strongly dependent on the number of phenyl groups incorporated into the cycle. The isotropization temperature T_i of the polymers with a large number of phenyl groups is above the temperature at which they degrade chemically. A similar dependence of T_i on the number of phenyl substituents in the cycle is also found for polymers with tetrasiloxane cycles although the temperature interval

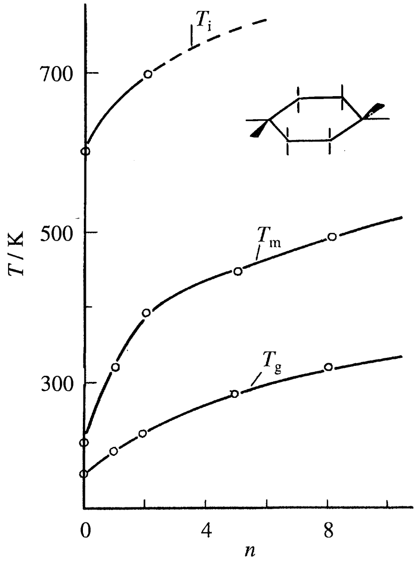


Figure 6. Dependence of the glass transition temperature T_g, melting point T_m and isotropization temperature T_i on the number of phenyl groups n in polymethyl(phenyl)cyclohexasiloxanes (Godovsky *et al.* 1989).

of the mesophase state in this case is considerably narrower (Makarova *et al.* 1989). Hence, by changing the ratio of the methyl to phenyl groups within the cycles it is possible to regulate the stability of the mesophase and the degree of mesomorphicity.

The structure of the mesophases in CLPOSs was analysed by means of the Stuart–Briegleb models and X-ray analysis (Makarova *et al.* 1989). Analysis of the models shows that the macromolecules of cyclotetrasiloxane units can be approximated by cylinders whose diameter increases with alkyl substituents as follows: methyl, $d = 11.0$; ethyl, $d = 13.0$; and n-propyl, $d = 14.5$ Å. It also clear from the models that, for example, the cyclotetramethylsiloxane chain is roughly composed of discs made up by the central siloxane cycles with methyl groups. From the shape of the chain and from a possible arrangement of two neighboring chains, one can represent, as a first approximation, such cyclochain molecules as a cylinders in which disclike cycles interpenetrate to attain a dense packing (figure 7). Although the diameter of the cylinder, d, increases steadily with alkyl substituents, the true intercylinder distances d_1 estimated from the position of the sharp mesophase peak in the X-ray spectrum are considerably smaller: methyl, $d_1 = 8.4$; ethyl, $d_1 = 8.8$; and n-propyl, $d_1 = 10.4$ Å. Hence, the columnar structure of the mesophase is pronounced, even more strikingly than in LPDASs because of some discotic-type configuration of the four-membered cyclochain macromolecules. Although the configuration of the six-membered macromolecules has a more complex character, nevertheless, it can also be represented by the columnar structure.

The four-membered methylcyclosiloxane polymer is able to form the mesophase only in the trans-tactic configuration (see below). On the other hand the six-membered methylsiloxane polymer can exist in the mesomorphic state irrespective of its tacticity, which reveals a very important role of the six-membered

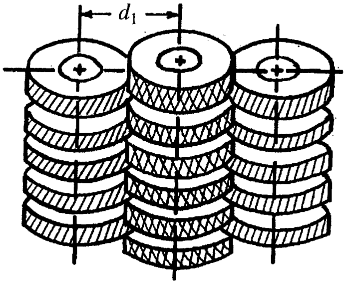


Figure 7. Schematic drawing of molecular packing of two-dimensionally ordered polyhexamethylcyclotetrasiloxane polymer chains (Godovsky *et al.* 1989).

cycle in self-ordering. Because of the flexible nature of the six-membered cycle with methyl substituents two effects can be observed. Firstly, when the mesophase transforms on cooling into solid, crystalline or glassy, state, the conformational interconversion process characteristic for the mesophase state should disappear. This disappearance must be accompanied by a decrease of the intensity of and broadening of the sharp mesophase diffraction peak as a result of a decrease of the correlation length of the lateral translational long-range order. X-ray analysis showed that for atactic polymer the intensity of a very intensive and very narrow mesophase peak slightly above T_g drops considerably and the peak is broadening. It means that in the vicinity of glass solidification the conformational interconversions in the cycles become more hindered and finally frozen. Secondly, because the cycles in macromolecules are bonded only by oxygen atoms some intercorrelation of the conformations of the neighbouring cycles should exist which, in turn, may promote self-ordering. However, this correlation must considerably decrease and finally disappear when the length of the flexible spacer between the neighbouring cycles in the macromolecules increases. The validity of this suggestion was tested on trans-tactic six-membered polymers in which a short dimethylsiloxane spacer was incorporated between each cycle. The following effects have been observed (Godovsky *et al.* 1989): a considerable reduction of T_i and the degree of mesomorphicity with increasing length of the spacer and a disappearance of both the ability to crystallize and to form a mesomorphic phase when the length of the spacer exceeds two repeating dimethylsiloxane units. Similar behaviour was also established for methyl–phenyl six-membered cycle polymers.

Because of the variable configuration of the substituents in the organosilsesquioxane fragments, different local tacticities are possible in CLPOSs, namely cis-tactic, trans-tactic and atactic. The role of tacticity is important both for crystallization and for the formation of mesomorphic states. The following picture is revealed (Makarova *et al.* 1987): (i) in six-membered cycle polymer the mesomorphic state exists irrespective of the chain tacticity, in contrast to the four-membered one, in which self-ordering occurs only for the trans-tactic conformation; (ii) for six-membered polymers at a comparable molecular mass the highest value of T_i is characteristic of trans-tactic polymer, the lowest – for cis-tactic, and atactic polymers possess intermediate values of T_i.

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Discussion

H. Fischer (*University of Bristol, U.K.*). You mentioned that the interchain distance in the mesomorphic state of polydialkylsiloxanes increases with the length of alkyl side chains. What kind of dependence should it be for the whole series from polydiethylsiloxane to, say, polydihexilsiloxane, keeping in mind that the macromolecules in the mesomorphic state are highly disordered conformationally including considerable disordering of their side chains.

Y.K. Godovsky. Unfortunately, X-ray data concerning the interchain distances in polydialkylsiloxanes have been obtained only for the first two members, namely PDES and PDPS. For higher members of the series synthesized recently such results are still absent. For the whole series it should look similar to the dependence of T_i as a function of the length of side chains.

H. Finkelmann (*University of Freiburg, Germany*). Have you observed macroscopic ordering during shear flow of your mesophase polysiloxanes?

Y. K. Godovsky. Application of shear to linear polydialkylsiloxanes, in particular to polydiethylsiloxane, which is the most thouroughly studied, in the mesophase state shows that the birefringence turns out to be more uniform. This seems to be a result of orientation by shearing. However, there is no indication that any macroscopic ordering occurs during shear experiments.

A. Keller (University of Bristol, U.K.). Are the siloxane chains in question, inlcuding those with cyclic chain members flexible? Do they form chain folded single crystals from solution? If so, why do they give rise to mesophases? To answer the last question is it feasible to envisage that the disubstitution on the Si atoms rigidifies the chain, but not in the absolute sense, but merely by creating a high activation barrier for rotation around backbone bonds? This would give it a high persistance length but nevertheless would allow it to display some properties characteristic of flexible chains, e.g. folding, once the barrier is overcome. Do you think such a picture is reasonable?

Y. K. Godovsky. High chain flexibility of linear polysiloxanes is well documented in low glass transition temperature and small characteristic ratio C^∞. Although with increasing length of the side chains both T_g and C^∞ also increases, nevertheless, T_g is still well below room temperature. There are no data concerning C^∞ for the members of the series higher than PDPS. Similar situation is also characteristic for cycylochain polysiloxanes, at least with methyl substituents. I am not sure that there are any data concerning the morphology of solution crystallization, however, crystallization of the melt without preliminary formation of the mesophase is accompanied by formation of typical crystallites with folded chains.

The general question, why these polysiloxanes, as well as polyphosphazenes and polysilanes, give rise to mesophases is still open. One can probably suggest the existence of some specific interaction between element-organic macromolecules resulting from the polarity of the siloxane bonds. This interaction increases with the length of the organic side chain. From this point of view your picture is quite reasonable.