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# Analogy between liquid crystal side chain polysiloxanes and liquid crystal twins with siloxane spacers

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# Analogy between liquid crystal side chain polysiloxanes and liquid crystal twins with siloxane spacers

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The goal of this present work was to compare the properties of dimers with a siloxane spacer to those of side chain polysiloxanes including the same mesogenic groups and the same dilution with dimethylsiloxane segments. A systematic study of the influence of the dilution parameter on the mesomorphic and structural properties of dimers and diluted side chain polysiloxanes, as well as on the behaviour of their solutions with low molar mass liquid crystals is reported.

## 1. Introduction

Dimeric liquid crystalline compounds are formed through rigid mesogen–flexible spacer–rigid mesogen sequence (twins for short). Most studies have focused interest on series using flexible polymethylene chains of various lengths as spacers. These dimers are often regarded as low molar mass model compounds for thermotropic liquid crystalline main chain polymers having alternating sequences of similar mesogenic units and spacers [1–5]. They duplicate especially well the influence of the length of the aliphatic spacer on the thermal behaviour of these main chain polymers.

Dimeric compounds [6–8], as well as main chain polymers [8–12], with a siloxane containing spacer have also been reported. Such highly flexible siloxane spacers are obviously different from methylene spacers and significant variations in LC properties depending on the nature of the spacer can be observed. Thus, a comparative study of dimers and main chain polymers, both containing siloxane spacers, revealed a real discrepancy in their mesomorphic behaviours [8]. Correlatively, it seems that in this case dimers cannot appear as models for thermotropic main chain polymers.

This paper is concerned with another approach, namely the comparison of the properties of twins with a siloxane spacer to those of side chain polysiloxanes. Dimers and side chain polysiloxanes bearing the same mesogenic groups and including the same proportion of mesogens and of siloxane parts have been synthesized and characterized. Comparisons of the mesomorphic and structural properties among siloxane dimers and side chain polysiloxanes, as well as of the behaviour of their solutions with low molar mass liquid crystals have been achieved. In addition, this work presents a systematic study of the influence of the dilution of the mesogenic groups with siloxane moieties in polymeric and in dimeric compounds.

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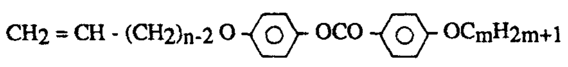
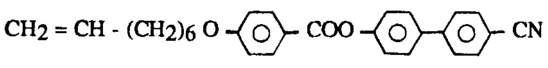
## 2. Materials

The starting materials were:

(i) Vinylic compounds (**1**):



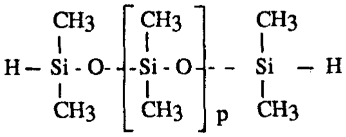
labelled $V_{n,m}$ with $n=4$ or 6 and $m=1$ or 4



labelled $V_{8,\mathrm{CN}}$

The synthesis of these vinylic units have already been described [13, 14].

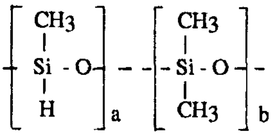
(ii) Oligosiloxanes (**2**):



$$\mathrm{H-\underset{CH_3}{\overset{CH_3}{Si}}-O-\left[\underset{CH_3}{\overset{CH_3}{Si}}-O\right]_p-\underset{CH_3}{\overset{CH_3}{Si}}-H}$$

from Petrarch Inc. Syst. and [15].

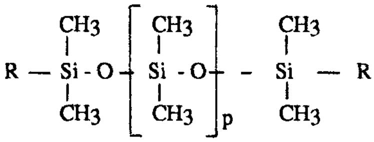
(iii) Polysiloxanes (**3**):
one homopolymethylhydrogenosiloxane;
and three statistical copolymers with various ratios of methylhydrogenosiloxane and dimethylsiloxane units from Petrarch Inc. Syst.



$$\left[\underset{H}{\overset{CH_3}{\mathrm{Si}}}-\mathrm{O}\right]_a-\left[\underset{CH_3}{\overset{CH_3}{\mathrm{Si}}}-\mathrm{O}\right]_b$$

The fixation of the vinylic units (**1**) to the Si–H groups of oligosiloxanes (**2**) and polysiloxanes (**3**) was performed via a classical hydrosilylation reaction [13] leading to:

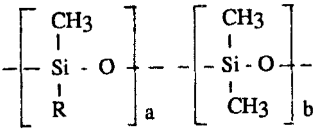
(i) The following twins:



$$\mathrm{R-\underset{CH_3}{\overset{CH_3}{Si}}-O-\left[\underset{CH_3}{\overset{CH_3}{Si}}-O\right]_p-\underset{CH_3}{\overset{CH_3}{Si}}-R}$$

where $R$ represents a mesogenic group. (These compounds were purified by at least three precipitations from a concentrated THF solution into methanol.)

(ii) The following polymers:



$$\left[\underset{R}{\overset{CH_3}{\mathrm{Si}}}-\mathrm{O}\right]_a-\left[\underset{CH_3}{\overset{CH_3}{\mathrm{Si}}}-\mathrm{O}\right]_b$$

In both cases, we can define the average number of mesogenic groups per Si atom as follows:

(i) For polymers

$$x=a/(a+b)$$

$x=1$ corresponds to the homopolysiloxane, $x=0{\cdot}5$; $0{\cdot}3$; $0{\cdot}09$ correspond to the copolysiloxanes with dimethylsiloxane units. The selected polymers are labelled $P_{n,m,\text{per cent}}$, $P_{8,\text{CN},x\,\text{per cent}}$.

(ii) For twins

$$x'=2/(p+2)$$

$x'=1$ corresponds to a disiloxane segment as the spacer, $x'=0{\cdot}66$ to a trisiloxane segment, $x'=0{\cdot}5$ to a tetrasiloxane segment, and $x'=0{\cdot}33$ to an hexasiloxane segment. The corresponding twins are labelled DI for $x'=1$, TRI for $x'=0{\cdot}66$, TETRA for $x'=0{\cdot}5$ and HEXA for $x'=0{\cdot}33$ with indices $(n,m)$, $(8,\text{CN})$ indicating the nature of the mesogenic group.

## 3. Results

### 3.1. *Mesomorphic properties*

The mesomorphic properties were characterized by the usual methods: optical microscopy (with a polarizing microscope and a Mettler F 52 hot stage), differential scanning calorimetry (Perkin–Elmer DSC 7), and X-ray diffraction on powder samples (Hüber Guinier camera, monochromatic Co–$K_{\alpha 1}$ radiation).

The transition temperatures are listed in table 1 for precursor mesogens, in table 2 for twin dimeric compounds and table 3 for homopolymers and copolymers.

The following comments can be made on these results:

(i) The precursor alkenes are all nematics (see table 1). Their fixation in a siloxane compound, either twin or polymer, promotes smectic phases instead of the nematic phase (see tables 2 and 3). This first analogy underlines the prominent role of the siloxane segments in determining the appearance of smectic structures, whatever the molar mass.

(ii) In each twin series, the lengthening of the siloxane segment, which corresponds to a dilution of the mesogenic parts ($x'\searrow$) leads to a decrease of the clearing temperature and thus to the destabilization of the mesomorphic properties (see table 2). Nevertheless in all cases studied here, the mesomorphic character is preserved even at high dilution ($x'=0{\cdot}3$). These tendencies observed in the twin compounds duplicate very well the influence of the proportion of mesogenic groups on the mesomorphic properties of LC side chain polymers (see table 3 and [14, 16, 17]).

(iii) The influence of the increase in the dilution (i.e. $x'$ or $x\searrow$) on the polymorphism also deserves some remarks: the clearing temperatures are depressed and the nematic phase disappears first in the twin series (see table 2). The same behaviour is observed in the polymers (see table 3 and [16, 17]).

Thus a parallel between the mesomorphic properties of dimeric compounds with a siloxane containing spacer and those of side chain polymers is clearly drawn. Moreover, increase in the proportion of siloxane segments has the same effect upon the thermodynamic behaviour of twin systems and of side chain polymers.

Table 1. Transition temperatures for the mesogenic precursors.

| | Transition temperatures °C | | | | |
|---|---|---|---|---|---|
| Mesogen | C | | N | | I |
| V$_{4,4}$ | ● | 67·8 | ● | 69·4 | ● |
| V$_{6,1}$ | ● | 50·1 | ● | 58·7 | ● |
| V$_{8,\mathrm{CN}}$ | ● | 84 | ● | 233 | ● |

Table 2. Polymorphism and transition temperatures for the twin dimeric compounds. [ ] indicates a monotropic transition.

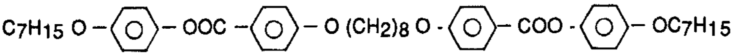
| | | Transition temperatures °C | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Twin | $x'$ | C | | $S_A$ | | N | | I |
| DI$_{4,4}$ | 1 | ● | 99·5 | ● | [68·4] | ● | [80·5] | ● |
| TRI$_{4,4}$ | 0·66 | ● | 69 | ● | | | 74·8 | ● |
| TETRA$_{4,4}$ | 0·5 | ● | 71·3 | ● | | | 71·6 | ● |
| HEXA$_{4,4}$ | 0·33 | ● | 52 | ● | | | 59 | ● |
| DI$_{6,1}$ | 1 | ● | 70 | ● | [51·5] | ● | [59·4] | ● |
| TRI$_{6,1}$ | 0·66 | ● | 57 | ● | | | [51·8] | ● |
| TETRA$_{6,1}$ | 0·5 | ● | 48 | ● | | | [45] | ● |
| DI$_{8,\mathrm{CN}}$ | 1 | ● | 100 | ● | | | 270 | ● |
| TRI$_{8,\mathrm{CN}}$ | 0·66 | ● | 58 | ● | | | 260 | ● |
| TETRA$_{8,\mathrm{CN}}$ | 0·5 | ● | 58 | ● | | | 248·5 | ● |
| HEXA$_{8,\mathrm{CN}}$ | 0·33 | ● | 50 | ● | | | 230 | ● |

Table 3. Polymorphism and transition temperatures for the homopolymers and copolymers.

| | | Transitions temperatures °C | | |
|---|---|---|---|---|
| Polymer | $x$ | $S_A$ | | I |
| P$_{4,4\ 100\%}$<br>from [13] | 1 | ● | 141 | ● |
| P$_{4,4\ 50\%}$ | 0·5 | ● | 127 | ● |
| P$_{4,4\ 30\%}$ | 0·3 | ● | 65 | ● |
| P$_{6,1\ 100\%}$<br>from [13] | 1 | ● | 109 | ● |
| P$_{6,1\ 50\%}$ | 0·5 | ● | 70 | ● |
| P$_{6,1\ 30\%}$<br>from [16] | 0·3 | ● | 38 | ● |
| P$_{8,\mathrm{CN}\ 50\%}$ | 0·5 | ● | >270 | ● |
| P$_{8,\mathrm{CN}\ 30\%}$<br>from [14] | 0·3 | ● | 260 | ● |
| P$_{8,\mathrm{CN}\ 9\%}$<br>from [14] | 0·09 | ● | 170 | ● |

### 3.2. *Structural properties*

The X-ray diffraction experiments on powder samples enabled us to determine the thermal variation of the layer spacing $d$ in the smectic phases. For homopolymers, this experimental value can be directly compared to the length $l$ of the side group (in its most extended conformation and including one Si atom, see table 4). As for low molar mass polar compounds, the $S_A$ phases of polymers bearing mesogenic groups with a strong polar head (CN) are partially bilayer ($S_{Ad}$). For the homopolymers with an aliphatic tail, the layer spacing can be significantly larger than the molecular length for short tails ($P_{6,1}$) or practically equal to $l$ for longer ones ($d=l$ for $P_{4,4}: S_{A1}$ phase). Thus at the microscopic level two kinds of $S_A$ organizations have to be distinguished here: either associated mesogenic groups (8, CN and 6, 1) or unassociated ones (4, 4). Concerning the twin compounds, we first notice in table 5 that in all cases the experimental layer spacing $d$ strongly differs from the length of the extended dimeric molecule. These results are obviously different from those obtained for twins with an aliphatic spacer. For example the following compound:



exhibits a smectic A phase with the layer spacing $d=51$ Å close to the length of the extended dimer $l_{\text{extended}}=57$ Å.

Now, if the $d$ values of the siloxane dimers are compared to the length of the mesogenic unit $l$, we observe striking similarities to the similar analysis of the layer spacing in polymers and diluted polymers. If we focus first on the DI compounds, which have to be compared to homopolymers ($x'$ and $x=1$), we remark that, depending on the nature of the mesogen, two kinds of $S_A$ phase can be distinguished, as for homopolymers: a partially bilayer $S_{Ad}$ for $DI_{8,CN}$ and $DI_{6,1}$ and a monolayer $S_{A1}$ for $DI_{4,4}$. These strong similarities observed for the same mesogenic groups between the homopolysiloxanes (see table 4) and the twins with a disiloxane segment in the spacer (see table 5) are consistent with a comparable organization of the mesogenic groups inside the layers. Moreover, this structural analogy underlines a common influence of the siloxane moieties in the smectic structures of both polymers and twins. Besides, on the basis of the $DI_{6,1}$ compound, we note that a partial bilayer $S_{Ad}$ arrangement can also be obtained in a low molar mass system without a strong polar head.

We will now describe the influence of dilution by dimethylsiloxane segments on the structural properties of polymeric and dimeric systems. Concerning the polymers, the

Table 4. Layer spacing $d$ in the $S_A$ phase for polymers. Length $l$ of the mesogenic unit in its most extended conformation (SASM stereomodel) including one Si atom.

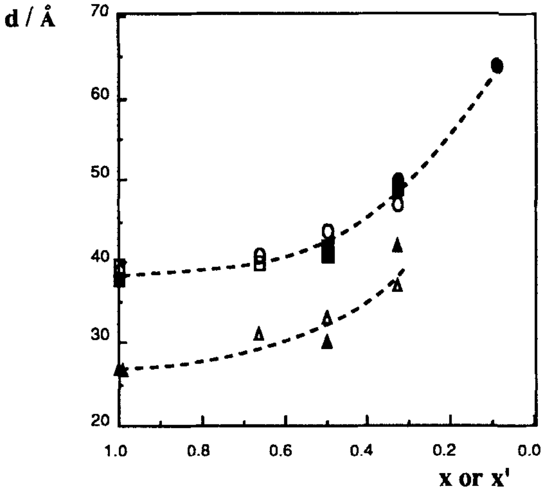
| Polymer | $x$ | $d$ Å | $l$ Å |
|---|---|---|---|
| $P_{6,1\ 100\%}$ | 1 | 38 | 26·7 |
| $P_{6,1\ 50\%}$ | 0·5 | 41 | |
| $P_{6,1\ 30\%}$ | 0·3 | 49 | |
| $P_{4,4\ 100\%}$ | 1 | 27 | 27 |
| $P_{4,4\ 50\%}$ | 0·5 | 30 | |
| $P_{4,4\ 30\%}$ | 0·3 | 42 | |
| $P_{8,CN\ 50\%}$ | 0·5 | 42 | 32 |
| $P_{8,CN\ 30\%}$ | 0·3 | 50 | |
| $P_{8,CN\ 9\%}$ | 0·09 | 64 | |

Table 5. Layer spacing $d$ in the $S_A$ phase for the twin series. Length $l$ of the mesogenic unit in its most extended conformation (SASM stereomodel) including one Si atom. $l_{\text{extended}}$ length of the dimeric molecule in the all-*trans* conformation.

| Twin | $x'$ | $d$/Å | $l_{\text{extended}}$ | $l$/Å | $d/l$ |
|---|---|---|---|---|---|
| $DI_{4,4}$ | 1 | 27 | 54 | 27 | 1·00 |
| $TRI_{4,4}$ | 0·66 | 31 | 57 | | |
| $TETRA_{4,4}$ | 0·5 | 33 | 61 | | |
| $HEXA_{4,4}$ | 0·33 | 37 | 68 | | |
| $DI_{6,1}$ | 1 | 39·5 | 51 | 26·7 | 1·48 |
| $TRI_{6,1}$ | 0·66 | 40 | 55 | | |
| $TETRA_{6,1}$ | 0·5 | 42 | 58·5 | | |
| $DI_{8,CN}$ | 1 | 39 | 64 | 32 | 1·22 |
| $TRI_{8,CN}$ | 0·66 | 41 | 67 | | |
| $TETRA_{8,CN}$ | 0·5 | 44 | 70·5 | | |
| $HEXA_{8,CN}$ | 0·33 | 47 | 77 | | |

evolution of the layer spacing in the smectic A phase as a function of the concentration of mesogenic groups shows an increase of $d$ with decreasing $x$ (see table 4). This effect is commonly considered as the result of a swelling of a sublayer containing the backbone by the dimethylsiloxane units [18, 19]. However as shown in table 4, the magnitude of this effect depends on the nature of the mesogenic side groups [14, 17].

Concerning the twins, the dilution by dimethylsiloxane segments ($x' \searrow$) induces a similar increase in the layer spacing for the different mesogenic systems. If we plot together the layer spacings $d$ as a function of the dilution parameters, $x$ for polymers and $x'$ for dimers, it is clear from the figure that, whatever the nature of the mesogenic groups, these two parameters play the same role. So the comparison of the structural results shows a striking relation between dimers and side chain polymers, not only from a qualitative point of view, but also on a quantitative basis. This figure preserves a distinction between associated systems (8, CN and 6, 1) and unassociated ones (4, 4), but



Trends in the layer spacing $d$ as a function of the parameters $x$ for polymers and $x'$ for dimers. The dotted lines are only guides for the eye. T = twins and P = polymers. □, $T_{6,1}$; ■, $P_{6,1}$; ○, $T_{8,CN}$; ●, $P_{8,CN}$; △, $T_{4,4}$; ▲, $P_{4,4}$.

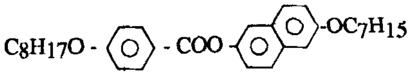
shows no difference between dimers and polymers in each category. In other words, the layer spacing of the $S_A$ phase is strongly dependent upon the kind of associations between the mesogenic groups, even in diluted systems. On the other hand, the layer spacing appears poorly correlated (i) to long range or statistical effects specific to the nature of the polymers and (ii) to the difference (polarity and length) between the two associated systems (8, CN and 6, 1).

### 3.3. *Properties of the solutions with low molar mass liquid crystals*

Phase diagrams for binary mixtures between a low molar mass liquid crystal (LMM) and a liquid crystalline polymer are remarkable through the occurrence of two kinds of non-ideal behaviours: phase separation may occur in the nematic domain [20–22], and enhanced or induced smectic A phases can be observed [16, 23].

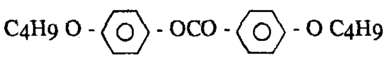
In this part, we try to extend the analogy between siloxane twins and side chain polysiloxanes to the behaviour of binary mixtures. These properties were investigated by means of the contact method.

As expected, phase separation is not characteristic only of mesogens with a siloxane moiety: for example, the homopolymers $P_{6,1}$ and $P_{4,4}$ exhibit a phase separation in the nematic state [22] when mixed with the compound



while the corresponding twins $DI_{6,1}$ and $DI_{4,4}$ are completely miscible with the same LMM liquid crystal. This result shows that the large difference in molecular weight compared with the LMM compound is the leading parameter determining phase separation with a polymer.

At the opposite extreme, enhanced (or induced) smectic A phases appear in dimer–LMM liquid crystal systems as in LC polymer–LMM liquid crystal systems. This enhancement or induction of $S_A$ phases is characterized by the maximum temperature of existence of the smectic A phase in the diagram: $T_{S_{A\max}}$. With the non-polar conventional liquid crystal



($M_{4,4}$ for short)

the homopolymer $P_{4,4,100\ \text{per cent}}$, as well as the twin $DI_{4,4}$, does not exhibit any enhanced smectic A phase. Nevertheless, on increasing the content of dimethylsiloxane segments, the smectic A phase is stabilized by mixing the M4, 4 compound with either the twin $HEXA_{4,4}$ or the polymer $P_{4,4,30\,\text{per cent}}$ (see table 6). These preliminary miscibility experiments therefore confirm the correlation between the behaviour of $S_A$ phases of dimers and side chain polymers.

Table 6. Smectic A enhancement by mixing a twin or a copolysiloxane with a non-polar conventional liquid crystal.

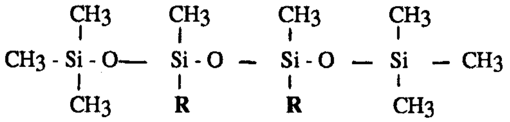
| | I–$S_A$ transition temperatures | |
|---|---|---|
| | Pure compound | By mixing with M4, 4 ($T_{S_{A\max}}$) |
| $P_{4,4,30\,\%}$ | 65°C | 70°C |
| $HEXA_{4,4}$ | 59°C | 71°C |

## 4. Conclusion

In conclusion, this systematic analysis of twins with a highly flexible siloxane spacer and side chain polysiloxanes reveals the strong analogy between their behaviours with respect to:

(i) the thermal properties of the mesomorphic state;
(ii) the structural properties of the smectic phases,
(iii) the behaviours of the $S_A$ phases in mixtures.

These conclusions strongly diverge from those obtained up to now for twins with an aliphatic spacer, which serve as models for mesomorphic main chain polymers. This point emphasizes the specific role of the flexible siloxane part in the mesomorphic organizations at a microscopic level. To support this view we give additional information relating to a comparison of the structures of TETRA$_{6,1}$ and its corresponding isomer:



$$CH_3-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{R}{\overset{CH_3}{Si}}-O-\underset{R}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-CH_3$$

The smectic A layer spacing is not modified ($d=42$ Å) by the position on the tetrasiloxane moiety of the two mesogenic groups ($R$). This underlines that the layering arrangement is influenced by the amount of siloxane and not at all by the size of the siloxane spacer. Consequently, we confirm that the smectic A layer spacing is not correlated to the dimeric size.

Finally, preliminary structural studies of dimers show an additional diffuse scattering around 7·5 Å as in diluted polysiloxanes. This diffuse scattering which can be interpreted as the average distance between dimethylsiloxane groups is a signature of their microsegregation in the $S_A$ structure. These X-ray results will be published elsewhere.

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