tions $w_{ij}$ and $w_{ii}$ are given by

$$w_{ij} = n_{ij}X_{ij}/X_n = n_i n_j (Y_i + Y_j)/Y_n \qquad \text{(A4)}$$

$$w_{ii} = n_{ii}X_{ii}/X_n = n_{ii}^2 Y_i/Y_n \qquad \text{(A5)}$$

where $Y_i$ and $Y_j$ are the degrees of polymerization of the two molecules of population PY, which couple to give one molecule of population $PX$ with degree of polymerization $X_{ij}$ (or $X_{ii}$ when $i = j$).

If all the possible weight fractions of population PX are written in triangular form as

$$\begin{array}{ccccc} w_{11} & w_{12} & w_{13} & \cdots & w_{1n} \\ & w_{22} & w_{23} & \cdots & w_{2n} \\ & & w_{33} & \cdots & w_{3n} \\ & & & & \vdots \\ & & & & w_{nn} \end{array}$$

the weight average degree of polymerization can be put in the form

$$X_w = \sum_{i=1}^{n} w_{ii}X_{ii} + \sum_{1 \le i < j \le n} w_{ij}X_{ij}$$

and introducing (A4) and (A5)

$$X_w = \frac{1}{Y_n}[2\sum_{i=1}^{n} n_i^2 Y_i^2 + \sum_{1 \le i < j \le n} [n_i n_j (Y_i + Y_j)^2] \qquad \text{(A6)}$$

Since

$$Y_n^2 = (\sum_{i=1}^{n} n_i Y_i)^2 = \sum_{i=1}^{n} n_i^2 Y_i^2 + 2\sum_{1 \le i < j \le n} n_i n_j Y_i Y_j$$

from (A6) one obtains

$$X_w = \frac{1}{Y_n}[Y_n^2 + \sum_{i=1}^{n} n_i^2 Y_i^2 + \sum_{1 \le i < j \le n} n_i n_j Y_i^2 + \sum_{1 \le i < j \le n} n_i n_j Y_j^2] \qquad \text{(A7)}$$

The three summations in (A7) are developed as

$$\begin{aligned} &\sum_{i=1} n_i^2 Y_i^2 + \sum_{1 \le i < j \le n} n_i n_j Y_i^2 + \sum_{1 \le i < j \le n} n_i n_j Y_j^2 = n_1 n_1 Y_1^2 + \\ &n_1 n_2 Y_1^2 + n_1 n_3 Y_1^2 + \ldots + n_1 n_n Y_1^2 + n_1 n_2 Y_2^2 + n_2 n_2 Y_2^2 + \\ &n_2 n_3 Y_2^2 + \ldots + n_2 n_n Y_2^2 + n_1 n_3 Y_3^2 + n_2 n_3 Y_3^2 + n_3 n_3 Y_3^2 + \\ &\ldots + n_3 n_n Y_2^2 + \ldots + n_1 n_n Y_n^2 + n_2 n_n Y_n^2 + \ldots + \\ &n_{n-1} n_n Y_n^2 + n_n n_n Y_n^2 = \sum_{i=1}^{n} n_i Y_i^2 = Y_n Y_w \end{aligned}$$

and from (A7) one obtains

$$X_w = Y_n + Y_w \qquad \text{(A8)}$$

By combination of (A8) with (A1), eq 3 of the text is obtained.

It is of interest to observe that no assumption has been made about the distribution of $PY$, and consequently (A1) and (A8) do not contain any information on the type of the distribution of $PX$. Therefore, $X_w/X_n = 1.5$ for population $PX$ is not typical of the coupling process from population $PY$ to population $PX$, but is only one particular result that is obtained when, for population PY, $Y_w/Y_n = 2$ (a value that does not necessarily correspond to the most probable distribution).

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# Communications to the Editor

## Liquid-Crystalline Polymers Containing Heterocycloalkanediyl Groups as Mesogens. 8.[†] Morphological Evidence for Microphase Separation in Poly(methylsiloxane-*co*-dimethylsiloxane)s Containing 2-[4-(2(*S*)-Methyl-1-butoxy)phenyl]-5-(11-undecanyl)-1,3,2-dioxaborinane Side Groups

Recently, by analogy with the behavior of block and graft copolymers, we have suggested that highly or even completely decoupled side-chain liquid-crystalline polymers would be realizable for systems in which the mesogenic side groups and the polymer backbone are microphase separated.[1-8] Such a morphology is particularly favorable for smectic copolymers based on flexible backbones that contain mesogenic and nonmesogenic structural units. Most probable, a microphase-separated morphology like this is induced by the thermodynamic immiscibility between the random-coil polymer backbone and the rodlike mesogenic units, which in the liquid-crystalline phase tend to segregate into isotropic and anisotropic domains. The tendency toward microsegregation is enhanced when the polymer backbone and the side groups are, due to their chemical dissimilarity, immiscible even within their isotropic phase. Such a microphase-separated morphology can be best observed in copolymers containing about similar weight ratios between the polymer backbone and the mesogenic side groups.

In a previous publication[8] we have presented our investigations on poly(methylsiloxane-*co*-dimethylsiloxane)s containing 2-[4-(2(*S*)-methyl-1-butoxy)phenyl]-5-(11-

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[†] Part 7: ref 8.

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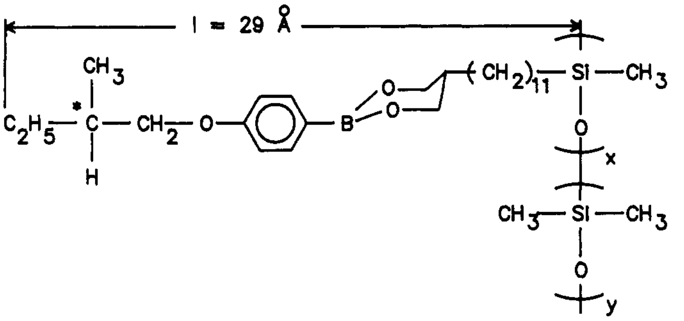
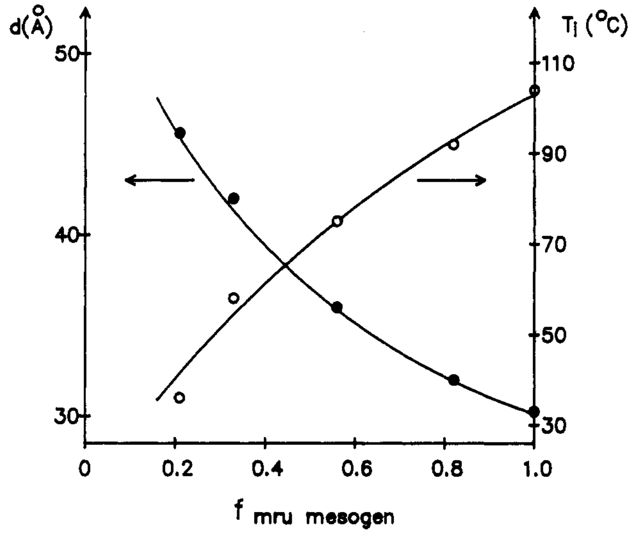
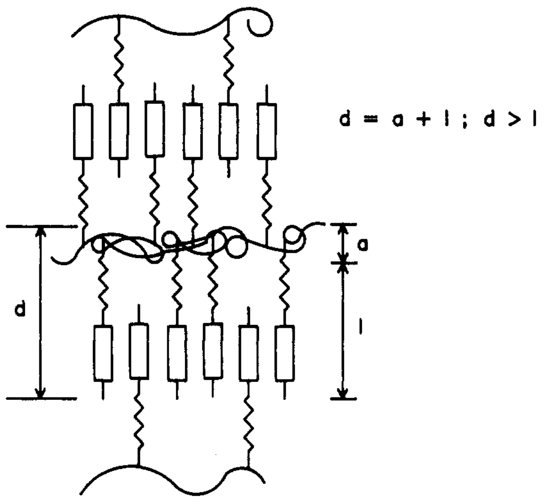
**Chart I**
**Microphase Separated Morphology of Smectic Copolymers**

| mesogen(%) | d(Å) | a(Å) | $T_i$ (°C) |
|---|---|---|---|
| 100 | 30.4 | 1.4 | 104 |
| 82 | 32.0 | 3.0 | 92 |
| 56 | 36.0 | 7.0 | 75 |
| 33 | 42.0 | 13.0 | 58 |
| 21 | 45.6 | 16.6 | 36 |







undecanyl)-1,3,2-dioxaborinane side groups with different molecular weights and compositions. Differential scanning calorimetric (DSC) and dynamic mechanical thermal analysis (DMTA) experiments have suggested a microphase-separated morphology for these copolymers. Both techniques have demonstrated that these copolymers display two glass transition temperatures. They were assigned to the independent motion of the polymer backbone and cooperative (but independent from the polymer backbone) motion of the side groups. The dependence of the width of the isotropization peak observed on the DSC curves on both copolymer composition and molecular weight has also suggested a microphase-separated morphology.

The goal of this paper is to present direct structural evidence for such a microphase-separated morphology obtained from wide-angle (WAXS) and small-angle (SAXS) X-ray scattering experiments.

Poly(methylsiloxane-*co*-dimethylsiloxane)s with number-average molecular weights higher than 18 000 and different contents of 2-[4-(2(*S*)-methyl-1-butoxy)phenyl]-5-(11-undecanyl)-1,3,2-dioxaborinane side groups were synthesized as previously reported.[8] Chart I presents the structure and composition of these copolymers. All copolymers display two phases. The dependence of the parameters of the two-phase transitions on polymer molecular weight and copolymer composition was previously discussed in detail.[8]

X-ray scattering experiments were performed both in the wide-angle[9] and small-angle[10] regions on macroscopically unoriented samples. In addition, flat camera studies were performed on macroscopically oriented samples in glass capillaries. The orientation was induced by surface interaction.

Figure 1a presents a representative WAXS pattern of the high-temperature phase displayed by an oriented copolymer sample containing 56 mol % structural units with mesogenic groups. The X-ray beam was parallel to the polymer flow direction, and both the beam and the flow directions were perpendicular to the equator. The mesogenic side groups are aligned perpendicular to the polymer backbone. WAXS experiments were also performed from the other two directions. This X-ray pattern is characteristic for a $S_A$ mesophase. Figure 1b displays a representative WAXS pattern of the low-temperature phase of an unoriented sample of the same copolymer. This phase is crystalline.

The thickness of the smectic layer, *d*, of the high-temperature phase was determined (from the small-angle region of the WAXS) as a function of copolymer composition and is both tabulated and plotted in Chart I. The calculated thickness of the smectic layer, *l* (assuming an all-trans conformation of the spacer) is 29 Å. The thickness of the smectic layer determined experimentally for homopolymer is 30.4 Å and is in good agreement with the calculated one. When the concentration of the structural units containing mesogenic groups from the copolymer decreases, the thickness of the smectic layer increases (Chart I). This dependence of the thickness of the smectic layer on copolymer composition can be explained only by a microphase-separated copolymer morphology as that described in Chart I. This morphology requires a distortion of the random-coil conformation of the flexible backbone to the extent that it can be squeezed in between the smectic layers. Therefore, the experimentally determined thickness of the smectic layer increases with the decrease of the concentration of structural units containing mesogenic units, since the volume of the flexible backbone which is available to be squeezed between the smectic layers increases. The dependences of the smectic layer

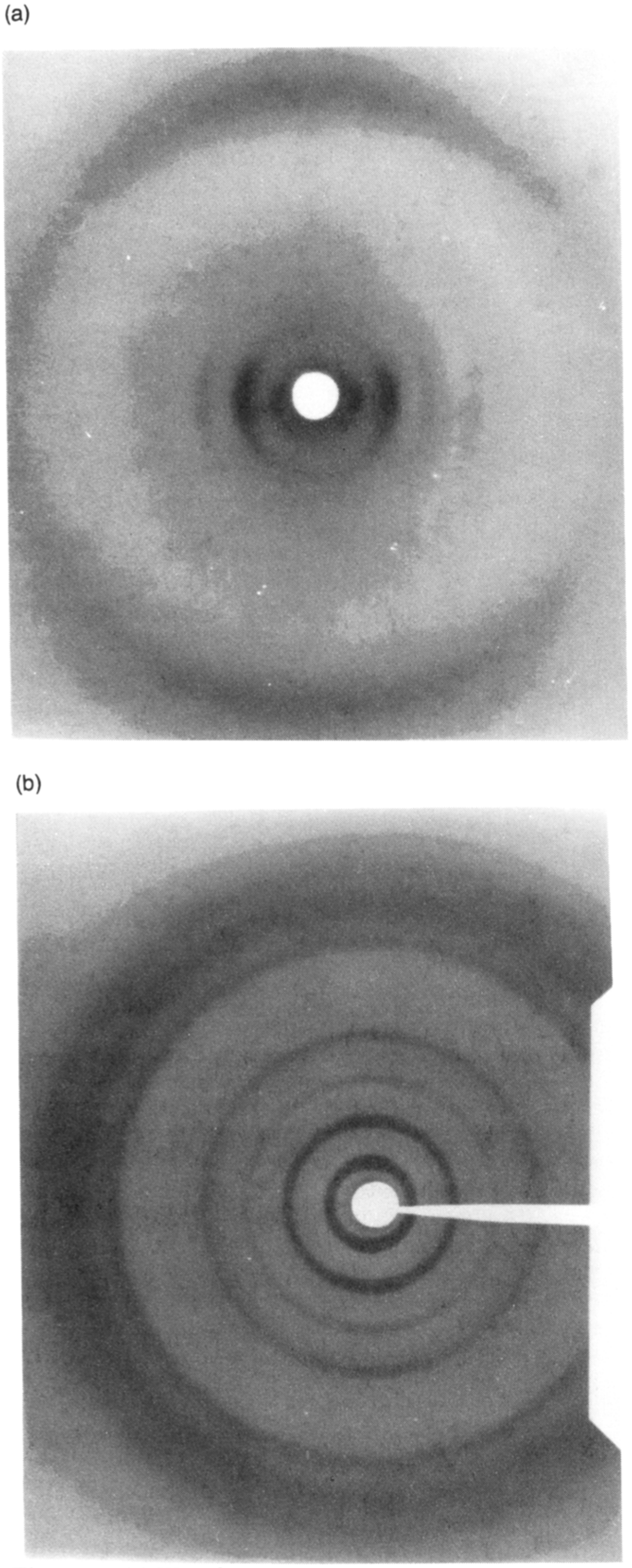


**Figure 1.** (a) WAXS pattern of an oriented sample of copolymer containing 56 mol % structural units with mesogenic groups, within the $S_A$ phase. The beam was parallel to the polymer flow direction, which is parallel to the equator (temperature 75 °C). (b) WAXS pattern of the crystalline phase of an unoriented sample of the same copolymer (temperature 20 °C).

thickness, $d$, and of the isotropization temperature, $T_i$, on copolymer composition are plotted in the left corner of Chart I. Within experimental error both plots display, as expected, almost linear dependences on copolymer composition.

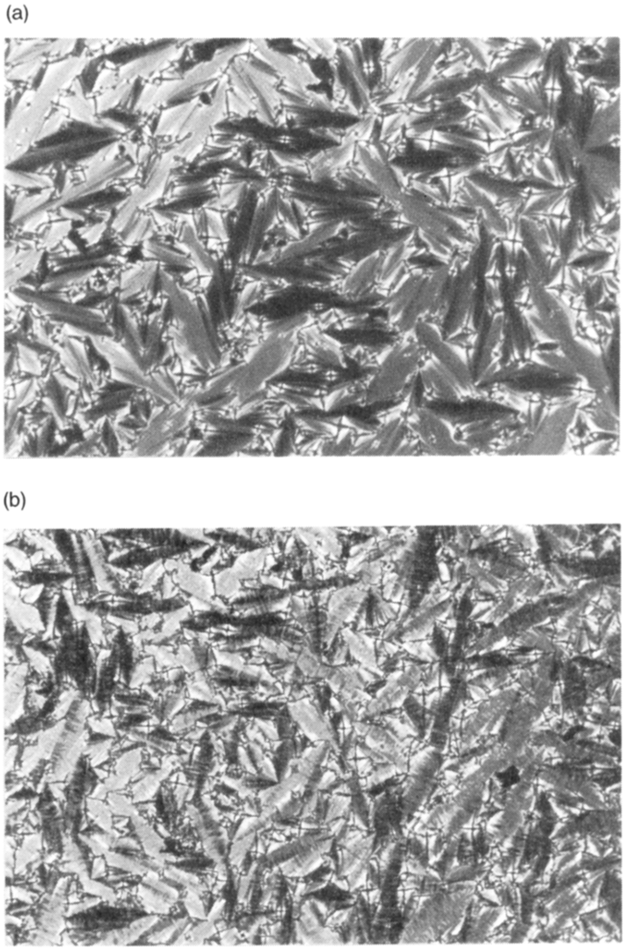


**Figure 2.** (a) Representative optical polarized micrograph (magnification 100×) of the focal conic texture displayed by the $S_A$ phase of cpolymers (copolymer containing 56 mol % structural units with mesogenic groups; temperature 75 °C). (b) Representative optical polarized micrograph (magnification 100×) of the crystalline phase displayed by copolymers (copolymer containing 56 mol % structural units with mesogenic groups; temperature 20 °C).

This microphase-separated morphology is identical with that observed by Ringsdorf et al.[11-13] in copolysiloxanes containing paired mesogens and may represent a general morphology displayed by smectic copolymers containing mesogenic and nonmesogenic structural units and flexible backbones.

A distortion of the random-coil conformation of the polymer backbone within the smectic phase was theoretically predicted[14] and experimentally observed by small-angle neutron scattering experiments,[15,16] even for the case of homopolymers. Smectic polymers based on rigid backbones may display a different morphology, which was discussed in a different publication.[17]

Figure 2a presents a representative focal conic texture displayed by the $S_A$ phase of the copolymer containing 56 mol % mesogenic units. Such a characteristic texture could not be obtained for the parent liquid-crystalline homopolymer even after extensive annealing. Upon cooling into the crystalline phase, the polymer displays the texture presented in Figure 2b. This texture is characteristic for a chiral smectic C ($S_C$*) mesophase. This texture made us assign previously, on the basis of optical polarized microscopy only, this phase to a $S_C$* phase.[4-8] The X-ray scattering experiments described in this paper have definitively demonstrated that this phase is crystalline.

This microphase-separated morphology may be significant for a number of theoretical and practical reasons. First, the dynamics of these copolymers is much faster than that of corresponding homopolymers. Second, this morphology may provide a novel approach to host-guest systems. This two-phase system can selectively dissolve anisotropic and isotropic guests in its different phases.[13] Therefore, we can easily envision systems that can be thermally regulated to capture and release these guests. Third, as we can observe in Chart I, this system provides a unique technique to molecular engineer the thickness, $a$, of a flexible random-coil backbone at will. Combined systems based on more than one immiscible flexible polymer backbone and identical side groups are also of interest.

At least for these reasons it is important to further elucidate the mechanisms by which these microphase-separated systems function, as well as their capabilities for some practical applications which can be considered from the above discussion. Research on these lines is in progress in our laboratory.

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## New Multiphase Architecture from Statistical Copolymers by Cooperative Hydrogen Bond Formation

It is well-known that hydrogen bonds stabilize supramolecular structures in biopolymer systems.[1] Typical structures are helices or $\beta$ sheets. It is a common feature for these complex biological systems that supramolecular structures are formed by cooperative self-organization. In most biological systems each repeating unit is capable of contributing to the three-dimensional structure. The configuration of the covalent backbone has a strong influence on the nature of the supramolecular ordering stabilized by the secondary valence interactions. However, no covalent backbone is necessary to observe a "polymer-like" association and structure formation via hydrogen bonding. Recently Wuest et al. have reported on the crystal structure of a polymer-like association structure of a low molecular weight molecule based on a bipyridone.[2]

We have previously reported on thermoreversible polymer networks based on binary hydrogen bond complexes in an unpolar polymer matrix.[3-5] Temporary junctions between highly polar phenylurazole groups (**1**) attached to polybutadiene chains served as a model system (Figure 1).

In the simple system the complexes are dispersed homogeneously in the unpolar polymer matrix, without indication of cluster formation like in ionomers.

For the formation of a three-dimensional structure it is necessary that each group has two sites for hydrogen bond association. In the case of the phenylurazole groups (**1**), one hydrogen bond donating group (>NH) and two hydrogen bond acceptors (>C=O) are available for complexation. If the phenyl group is substituted by a 4-hydroxy group (**2**), an additional hydrogen bond donor becomes available. In this case the viscoelastic properties indicate the formation of a three-dimensional hydrogen bond network.[7]

In this paper we report on the first successful approach to synthesize a multiphase material by the combination of flexible covalent polymer chains to which an association-type polymer based on hydrogen bonding is connected. Again polybutadiene is used as the base polymer, and the polar groups are introduced by a polymer-analogous reaction using a triazolinedione having two potential sites for hydrogen bonding. This bifunctionality is necessary to form a linear association polymer. It is realized by using the 4′-carboxy derivate of 4-phenylurazole (**3**). Details on the synthesis of the modifying agent and the polymers are reported elsewhere.[9]

In addition to the strong urazole-urazole complexes, dimeric carboxyl hydrogen bond complexes can be formed. Alternatively, urazole-acid H bonds could form the basic units of the association polymer. In Figure 2a the structure of the block-type polymer formed from flexible PB chains and H-bonded complexes is shown schematically.

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