Polymer Bulletin 23, 373–379 (1990)

Polymer Bulletin

Study of the micro-phase separation in LC-polymers with paired mesogens

Frank Kuschel[1,*], Annelore Mädicke[1], Siegmar Diele[1], Hermann Utschick[1], Bernd Hisgen[2], and Helmut Ringsdorf[2]

[1]Martin-Luther-Universität, Sektion Chemie, DDR-4020 Halle, German Democratic Republic
[2]Johannes-Gutenberg-Universität, Institut für Organische Chemie, D-6500 Mainz, Federal Republic of Germany

SUMMARY

Differential scanning calorimetry and miscibility investigations were used to study the micro-phase separation of liquid-crystalline dimesogenic side-group polysiloxanes. Diluted co-polysiloxanes exhibit two glass transition temperatures and an unusual miscibility behavior. The observed biphasic character is compared with that of certain amphiphilic systems.

INTRODUCTION

Micro-phase separation is a widely known phenomenon occuring in polymer mixtures, homo- and co-polymers and amphiphiles. Whereas in polymer mixtures or solutions the micro-phase separation may be considered as an early stage of the unmixing process via spinodal decomposition (1), the chemical connectivity of different building units in certain homo-polymers or of different blocks in co-polymers prevents the usual macroscopic phase separation. A similar situation can be given in lyotropic lamellar mesophases of surfactants or in lipid layers.

The two-phase morphology of certain liquid-crystalline polymers is a consequence of the nearly complete structural independence of the different constituent parts. These polymers consist of relatively rigid mesogenic units incorporated in the main-chain or linked to a backbone as side groups, and non-mesogenic parts represented by soft segments, spacers or tails. The anisotropic behavior of the liquid-crystalline domains, their distinct phase structures and transformations above the glass transition temperature offer additional possibilities to study separation effects.

A particular efficient decoupling of different building units can be realized in LC-co-polymers. To reduce the coupling between the main-chain and mesogenic side groups, co-polymers derived from usual LC side group polymers by incorporation of non-mesogenic dimethylsiloxane groups have been synthesized (2). These co-polymers still show liquid-crystalline behavior up to relatively high contents of non-mesogenic main-chain segments and two distinct glass transitions.

Furthermore, in an attempt to broaden the mesophase region, LC polymers with paired mesogens have been prepared (3). The corresponding co-polysiloxanes are characterized by a definite variation of the concentration of the tuning fork-like

---

[*] To whom offprint requests should be sent

dimesogenic side groups linked to the siloxane chain. Detailed X-ray investigations of these polysiloxanes provided indications for a spatially periodic structure of their smectic phases (4-6). Above a certain dilution degree, that means the number of paired mesogens in relation to the total number of chain segments, a quite distinct biphasic behavior has been observed (7).

The goal of this paper is to present some additional experimental results which support the proposed model of microphase separation in diluted co-polysiloxanes with paired mesogens. These results were obtained by calorimetric and miscibility studies. The properties of such biphasic systems will be compared with those of surfactants and amphiphilic polymers.

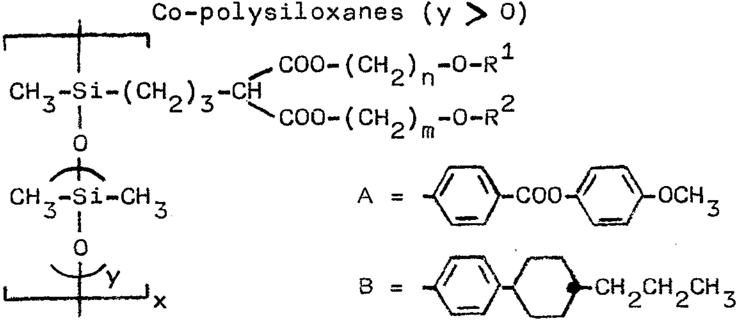
EXPERIMENTAL

Materials

The synthesis of the polymers is described elsewhere (3). They were used without further purification. The chemical structure is given in Table 1. Phases and phase transition temperatures have been summarized in a previous paper (6).

To study the miscibility behavior in binary systems, decamethyltetrasiloxane (MDDM, b.p. 194 °C/1.01·10^5 Pa, n_D^{20} = 1.3895) was kindly supplied to us by K. Rühlmann and U. Scheim (Technische Universität Dresden).

Table 1: Structure of Polysiloxanes (y = 0) and Co-polysiloxanes (y > 0)



No.[a]	Code	n	m	R^1	R^2
1 (y = 0)	I/0	2	2	A	A
2 (y = 10)	I/10	2	2	A	A
3 (y = 0)	II/0	2	2	A	B
4 (y = 10)	II/10	2	2	A	B
5 (y = 0)	III/0	2	6	A	B
6 (y = 10)	III/10	2	6	A	B
7 (y = 0)	IV/0	6	6	A	B
8 (y = 10)	IV/10	6	6	A	B

[a] Numerical values of the dilution degree y are average values

As low-molecular-weight liquid-crystalline component corresponding to one or both of the mesogenic side groups in the polymers, 4-methoxyphenyl-4-ethoxybenzoate (MPEB) (cr 117 °C (n 89 °C) is; cr: crystalline; n: nematic; is: isotropic) was used.

Techniques

All calorimetric measurements were performed on a Perkin-Elmer DSC-2. Since some data on co-polysiloxanes were obtained below room temperature, liquid nitrogen was used as coolant and hydrogen as the purge gas. Polymer samples weighing 7-14 mg were placed in flat aluminium DSC pans. Calibration was done by using mercury and benzene. The samples were heated at 20 $K \cdot min^{-1}$ to 80 °C. After two minutes, they were cooled at 80 $K \cdot min^{-1}$ to -150 °C and the data were collected during reheating at 10 $K \cdot min^{-1}$.

Experimental technique used in the determination of phases and phase transition temperatures of the mixtures is identical to that reported previously (7).

RESULTS AND DISCUSSION

Figure 1 presents representative DSC scans in the low temperature range for the polysiloxane I/0 and the co-polysiloxanes I/10, II/10, III/10, IV/10. Whereas I/0 exhibits

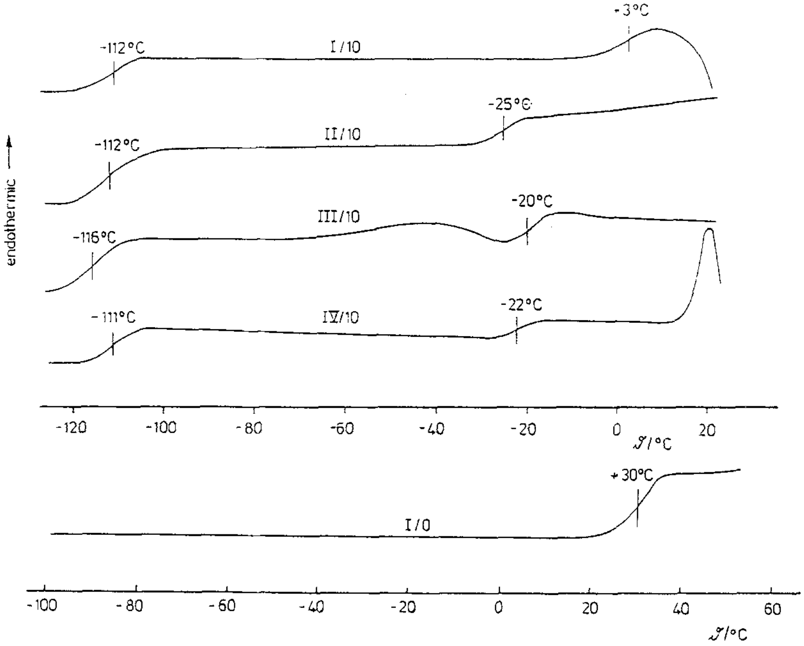
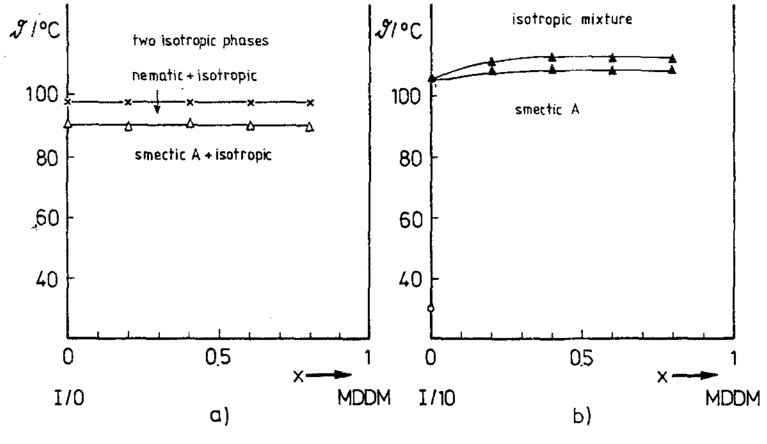


Figure 1: DSC thermograms of the undiluted polysiloxane I/0 and the micro-phase separated co-polysiloxanes I/10 - IV/10

only one Tg at 30 °C, the diluted co-polysiloxanes show two glass transition temperatures. Obviously, the lower one is due to the nearly independent motion of the dimethylsiloxane backbone. Depending on cooling and heating rates poly(dimethylsiloxane) exhibits a glass transition between -120 °C and -130 °C (8). It is interesting to note that slightly elevated Tg's have been found in styrene-dimethylsiloxane diblock copolymers containing $\geqslant$ 34 wt% dimethylsiloxane (8). The weight fraction of the main chains in the four investigated co-polysiloxanes ranged from 0.52 to 0.56. Moreover, one can assume that the dimethylsiloxane repeat units arranged between smectic layers (6) are under a certain mechanical stress and should therefore undergo the glass transition at slightly higher temperatures than the same repeat units as parts of a completely amorphous macro-phase.

It should be reasonable to attribute the higher Tg's to the cooperative motion of the mesogenic side groups.

To investigate the phase separation in LC polymers, simple miscibility studies are useful (7). Using MDDM as a mixing component, complete nonmiscibility with I/0 has been found (Figure 2a). The reason is the lack of a sufficiently extended siloxane sublayer which could be able to include MDDM molecules to a noticable amount. On the contrary, the diluted co-polysiloxane I/10 is miscible with MDDM (Figure 2b). Especially the unusual low dependence of the clearing temperatures on the content of non-mesogenic MDDM demonstrates that the liquid-crystalline order within the smectic sublayers is not altered in the mixture. This is confirmed by X-ray investigations (7). Obviously, the addition of MDDM causes exclusively a swelling of the polysiloxane sublayers leading to increased total layer thickness whereas the lateral distances between the side groups remain unchanged.



a) b)

Figure 2: Phase diagrams for binary mixtures of polysiloxane I/0 (a) and co-polysiloxane I/10 (b) with MDDM

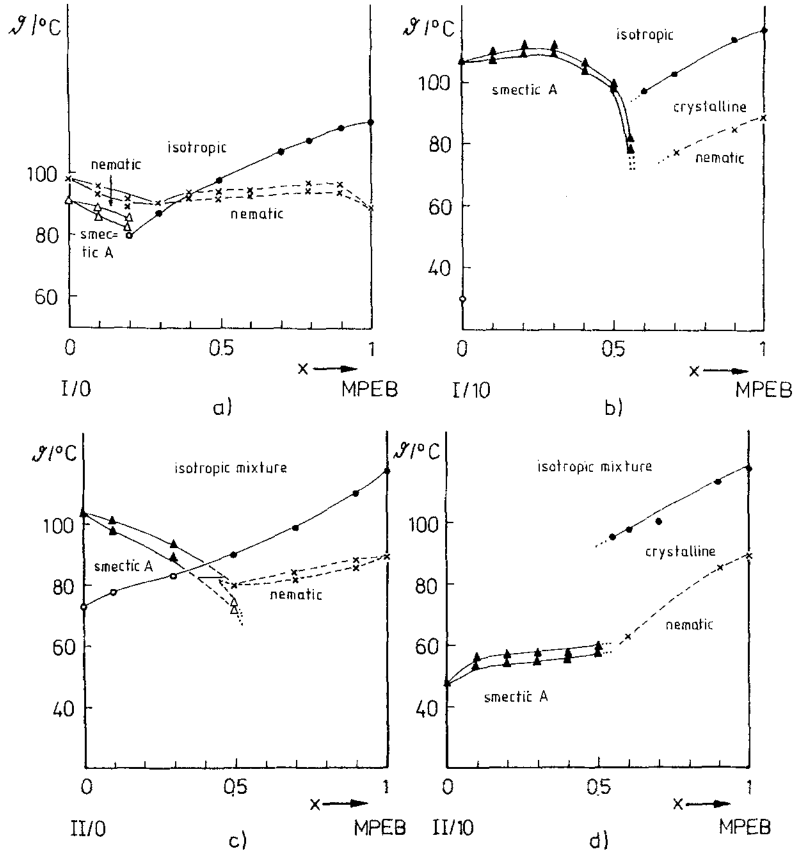


Figure 3: Phase diagrams of binary mixtures of homo-polysiloxanes (a,c) and co-polysiloxanes (b,d) with MPEB. Transition temperatures crystalline - isotropic (●), crystalline - smectic A (○), isotropic - nematic (x), smectic A - isotropic (▲) and nematic - smectic A (△)

The mixing behavior of selected dimesogenic polymers with low-molecular-weight LC-substances structurally related to the constituent parts of the mesogenic sublayers is demonstrated in Figures 3a-d. Apart from unlimited miscibility in the isotropic state, the components were also miscible in the anisotropic phases within relatively wide concentration ranges. Indeed, because of the different polymorphism of the substances, miscibility gaps occur. But the slope of the isotropic - anisotropic transition lines at higher polymer concentrations points to an extended capacity of the co-polysiloxanes to incorporate the low-molecular-weight material without essential alteration of the phase structure. This should be due to the increased lateral mobility of the co-polysiloxane side groups compared with those of homo-polysiloxanes.

The phase structure of the thermotropic co-polymers characterized by a coexistence of two micro-phases differing in the ability for self organization is very similar to that of polymeric lipids containing hydrophilic spacers. The linear relationship between the thickness of bilayers formed by amphiphilic co-polymers (derived from SAXS experiments) and the length of main chain spacers have been explained on the base of a two-phase model (9) of the same kind as proposed for our LC co-polysiloxanes (6).

Depending on the nature of the interaction between ordered aggregates separated by a less ordered subphase, the degree of swelling after addition of a diluent can achieve different extents:

- in block co-polymers consisting of highly decoupled structural elements as realized in the investigated co-polysiloxanes the swelling is limited by the flexibility of the spacers connecting the smectic organized sublayers
- several monomeric or polymeric diols form liquid-crystalline phases with a layered structure. The capability of self-organization arises from hydrogen bonds between diol head groups and from the hydrophobic interaction of alkyl chains. After addition of about two moles water per mole diol the layer spacings as well as the clearing temperatures increase indicating a "lyotropic stabilization" (10). This behavior reminds of findings concerning the improvement of the correlation of lipid bilayers due to the increased length of spacers connecting amphiphilic chain segments (9)
- the swelling of certain lyotropic phases in presence of water leading to lamellar phases with very large spacings (11) may be regarded as a consequence of the biphasic morphology of such systems. It is believed that the large spacings are due to electrostatic forces between the surfactant layers.

The general structural background of these different effects seems to be always the same.

Studies to elucidate further the properties of microphase separated LC polymers are currently in progress.

REFERENCES

1. Nakai, A., Shiwaku, T., Hasegawa, H., Hashimoto, T., Macromolecules, 19, 3008 (1986)
2. Ringsdorf, H., Schneller, A., Br. Polym. J., 13, 43 (1981)
3. Engel, M., Hisgen, B., Keller, R., Kreuder; W., Reck, B., Ringsdorf, H., Schmidt, H.-W., Tschirner, P., Pure Appl. Chem., 57, 1009 (1985)
4. Diele, S., Hisgen, B., Reck, B., Ringsdorf, H., Makromol. Chem., Rapid Commun., 7, 267 (1986)
5. Diele, S., Oelsner, S., Kuschel, F., Hisgen, B., Ringsdorf, H., Zentel, R., Makromol. Chem., 188, 1993 (1987)
6. Diele, S., Oelsner, S., Kuschel, F., Hisgen, B., Ringsdorf, H., Mol. Cryst. Liq. Cryst., 155, 399 (1988)

7. Westphal, S., Diele, S., Mädicke, A., Kuschel, F., Scheim, U., Rühlmann, K., Hisgen, B., Ringsdorf, H., Makromol. Chem., Rapid Commun., 9, 489 (1988)
8. Wang, B., Krause, S., Macromolecules, 20, 2201 (1987)
9. Laschewsky, A., Ringsdorf, H., Schmidt, G., Schneider, J., J. Am. Chem. Soc., 109, 788 (1987)
10. Brezesinski, G., Mädicke, A., Tschierske, C., Zaschke, H., Kuschel, F., Mol. Cryst. Liq. Cryst. Lett., 5(5), 155 (1988)
11. Appell, J., Bassereau, P., Delord, P., Larche, F., Marignan, J., Porte, G., Bull. Soc. Chim. France, 17 (1988)

Accepted January 12, 1990 C