Research News

Polymer Liquid Crystals Forming Biaxial Nematic Phases

The field of polymer liquid crystals has experienced an enormous growth over the last years. It is now established that the different types of molecular ordering (nematic, smectic, cholesteric) can also be realized in polymer liquid crystals.[1] Recently it has been demonstrated by *Finkelmann* et al.[2] that polymer liquid crystals with mesogenic groups in the side chain can form biaxial nematic phases. This type of molecular ordering has not yet been observed in low molecular weight liquid crystals.

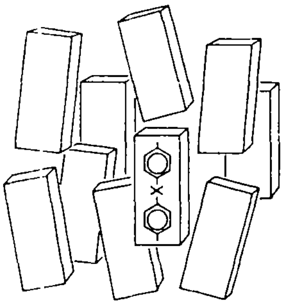

Fig. . Biaxial arrangement of lath-like particles [2b].

In a conventional nematic phase the rod-like mesogenic particles rotate around their long axis leading to an optically uniaxial system. For a system of lath-like particles (Fig. 1) orientational correlation may exist not only for their long axis but also for their short axes. The existence of such a biaxial nematic phase was predicted by *Freiser*[3] in 1970. Since then biaxial nematic phases have been the subject of numerous theoretical investigations (see [2b] for further references). A biaxial nematic phase in lyotropic liquid crystals was first observed by *Yu* and *Saupe*[4] in 1980. For thermotropic systems theory predicts[3] that the uniaxial phase should exhibit a second-order transition to the biaxial state upon lowering the temperature. However, this transition has never been observed experimentally for conventional low molecular weight liquid crystals and polymer liquid crystals with mesogenic groups in the side chain, since usually the onset of crystallization or the transition to a smectic phase or to the glassy state intervenes at lower temperatures. *Finkelmann* et al.[2] succeeded in showing that the stability of the biaxial state can be enhanced significantly if the rotation of lath-like mesogens is hindered by lateral attachment to a polymer main chain (Fig. 2, top).

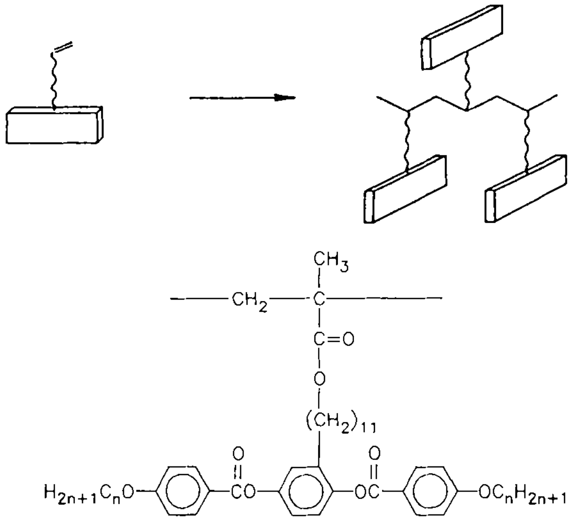

Fig. 2. Polymer liquid crystals with mesogenic groups attached laterally to the polymer backbone [2b]. Top: Schematic drawing; bottom: compounds that exhibit a biaxial nematic phase.

Thus, systems of the type shown in the lower part of Figure 2 exhibit a biaxial nematic phase which transforms into the isotropic state at the clearing temperature. The optical biaxiality was detected directly by conoscopic investigations of aligned samples. This exciting first observation of a thermotropic biaxial nematic phase demonstrates that by means of polymer liquid crystals new types of molecular ordering can be produced which could not be observed in low molecular weight systems. In this context it is important to note that *Ebert* et al.[5] have recently found direct conoscopic evidence for a biaxial nematic phase in a main chain liquid crystal polymer. Here again the stability of the biaxial arrangement was enhanced by long, laterally attached substituents which hinder the rotation around the long axis of the molecule.

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[2] a) F. Hessel, H. Finkelmann, *Polym. Bull. 15* (1986) 349; b) F. Hessel, R.-P. Herr, H. Finkelmann, *Makromol. Chem. 188* (1987) 1597.

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