

## 4.8. Liquid crystalline phases

For the characterization of liquid crystalline phases there are a couple of methods available, the most oftenly used ones are differential scanning calorimetry (DSC), optical microscopy (OM) with crossed polarizers, and small angle X-ray diffraction (SAXS). The latter method requires relatively large quantities and also materials with a considerable thermal stability as the measurements have to be done over hours at different temperatures. This is why X-ray diffraction is not so prominently used even though it is the only one of the three methods which gives direct insight into the packing behavior including distances and long range order. Several publications describe mesophase behavior just based on the two other methods which in some cases has led to public disputes as to the reliability of the packings proposed. Since X-ray diffractometry was not available during the present thesis this chapter cannot possibly aim at certain structure proposals. It rather aims at the description of some findings with the cycles **E1-E7** by DSC and OM in order to stimulate future work in the direction of the LC behaviour of shape-persistent macrocycles (Figure 107).

The whole matter turned out to be rather complicated. Some of the experiments were even irreproducible. This is why no complete series of transition temperatures and alike is given and, within the time span available for this thesis, not even a near-comprehensive picture could be gained.

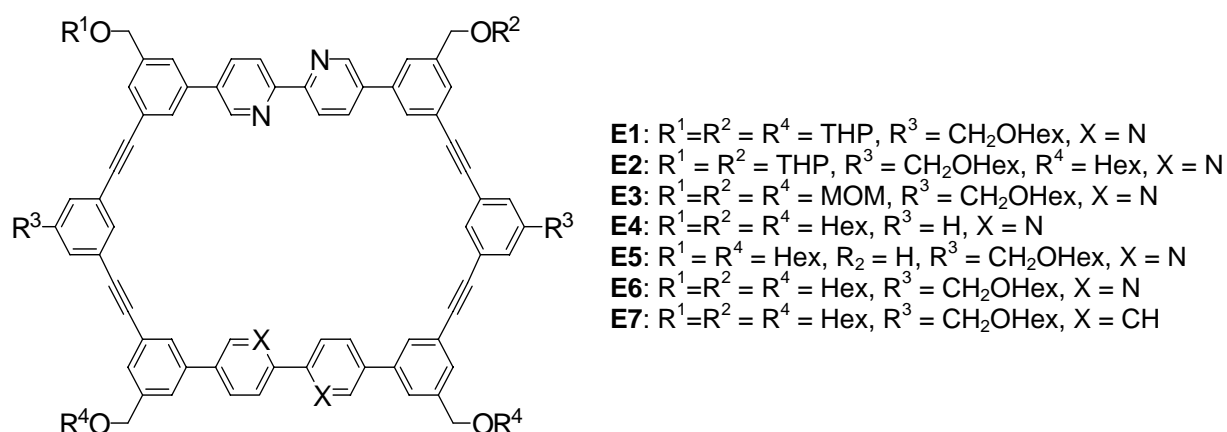


Figure 107. Bipyrididine macrocycles used for investigating LC properties.<sup>[104]</sup>

The mesophase behavior of some shape-persistent macrocycles has already been published in very few cases. Moore et al. observed such behavior for his

phenylacetylene macrocycles which in shape and size, but not in their concrete structure, are similar to the cycles presented in the present work. <sup>[103]</sup> They described their cycles as thermotropic discotic which means the same as what here is referred to as cylindrical stacking with a tube-like interior. Much more closely related to the cycles of this thesis, Henze provided clear evidence for the liquid crystalline behavior of cycle **E4**. As is oftenly encountered in research directed toward liquid crystallinity, lack of sufficient quantity and a too low thermal stability prevented a reliable SAXS analysis to be done and the packing behavior could therefore not be elucidated.

The present work was started with an investigation of the thermal stability of cycle **E6** (Figure 108) in order to evaluate the temperature range in which the cycles **E1-E7** could reasonably be analyzed (Figure 107). The sample was heated at a rate of 20 °C/min from room temperature to 900 °C. This was done in air in order to mimic the conditions to be applied for SAXS measurements (which in the end were not done). The curve shows several sharp steps starting at approximately 335 °C up to 500 °C, where most of the mass is lost. Normally, in mixed aryl/alkyl compounds, in which the alkyl group is directly attached to the aryl, the alkyl substituents are lost at lowest temperature. A preferred cleavage site is the C-C bond between the  $\alpha$ - and the  $\beta$ - carbon atom which in the present cycle obviously does not exist. However, a C-O bond cleavage with loss of hexoxy would produce the same benzylic radical as the above  $\alpha$ -, $\beta$ -splitting. The mass associated with the six hexoxy groups amounts to 38.8%. The mass loss between the first event at approximately 335°C and the last "small" step at 400 °C amounts to 36 % which is in reasonable agreement to the above value and, thus, is supportive of the proposal of a C-O bond cleavage, formally leaving behind a cycle with six *exo*-cyclic methylene radicals. At 450 °C total decomposition starts which is finished when the temperature reaches 650°C. Experiments in which the temperature was kept constant at certain values were not done. In the subsequent DSC and polarizing microscopy studies the temperature was always kept well below 330 °C.

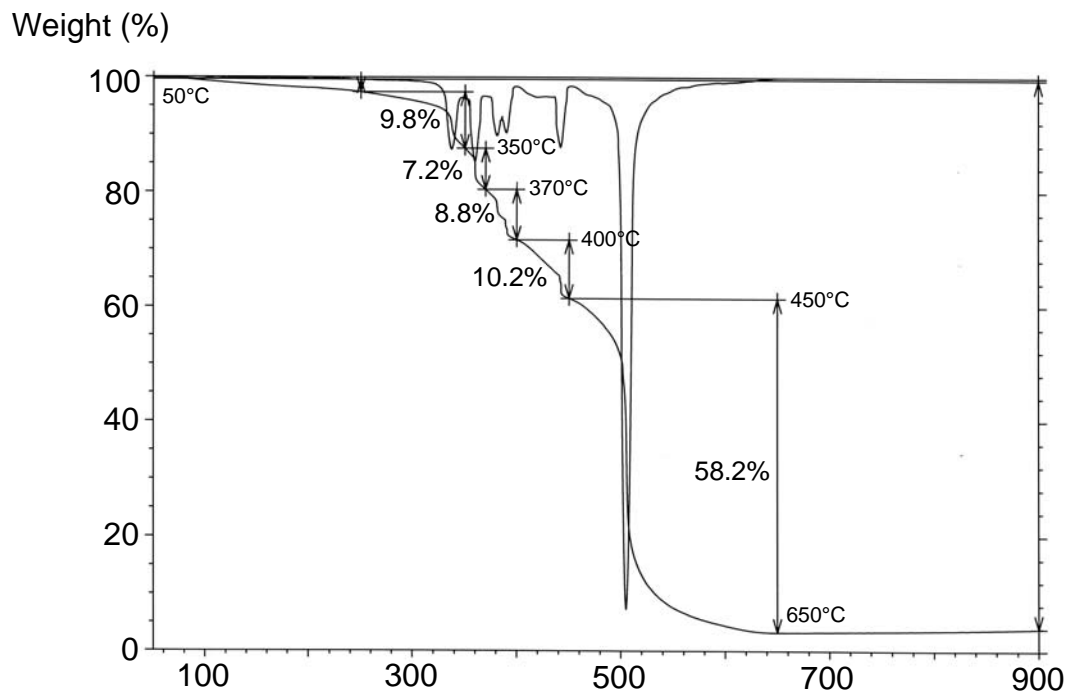


Figure 108. The thermogravimetric analysis of macrocycle **E6**.

Differential scanning calorimetry (DSC) measurements were performed with **E1-7**. The samples were heated at a rate of 10 °C/min from room temperature to about 250 °C, where they were cooled all the way to the starting temperature. Then the DSC heating scan was repeated in order to get reproducible results. It is known that the second heating curve can be quite different from the first one due to residual solvent and water as well as surface-pinning effects. The DSC curves of the cycles show pronounced differences. The two, which are most similar to one another, are those from **E6** and **E7** (Figure 109). As can be seen the heating curves are rather complex and are followed by a cooling curve with just one exothermic transition and a considerable supercooling. The heating curve exhibits several small transitions and two main ones. This may be indicative of the samples consisting as a complex mixture of crystal morphologies and perhaps scattered mesophases which are interconverted into one another. Both second highest transitions do not seem to lead into a mesophase because the endotherms are immediately followed by a sharp exotherm, indicative of a crystallization event. The highest endotherm finally marks the transition into isotropic melt, the isotropization temperature. The isotropization temperatures from the OM studies seem to be lower than that from DSC by approximately 10 °C which could indicate a too fast heating rate in the latter. Why the DSC cooling curves are not reversible to their heating counterparts is not yet

understood. Table 15 contains the isotropization temperatures obtained from OM. Figure 110 contains representative images of the anisotropic phases obtained for all cycles. Schlieren textures can occasionally be observed (for example, see: **E6** at 165.5 °C, Figure 110f). From the very rudimentary data given here it becomes transparent that much more work will be needed before the cycles thermotropic behaviour can be considered understood.

Table 15.

Macrocycle	<b>E1</b>	<b>E2</b>	<b>E3</b>	<b>E4</b>	<b>E5</b>	<b>E5</b>	<b>E7</b>
Isotropization temperature °C	Didn't melt up to 300	265	286	234	230	221	200

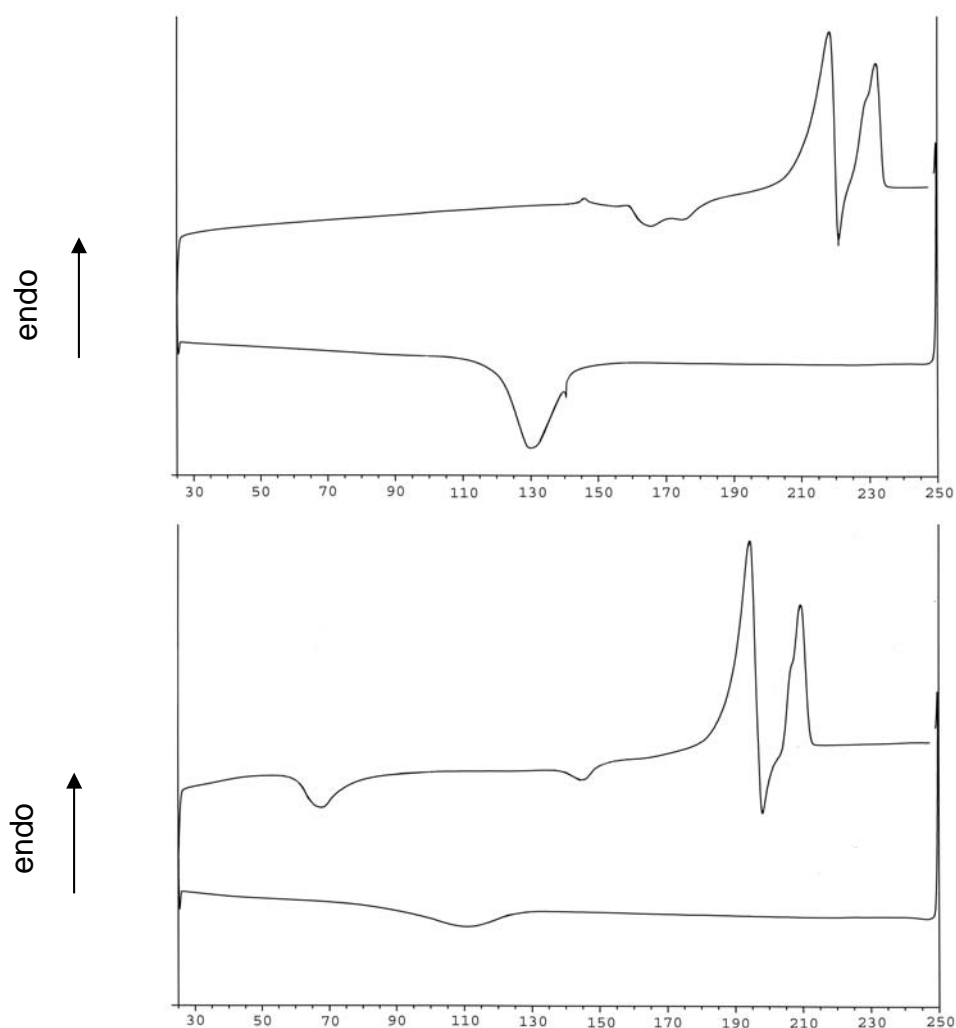
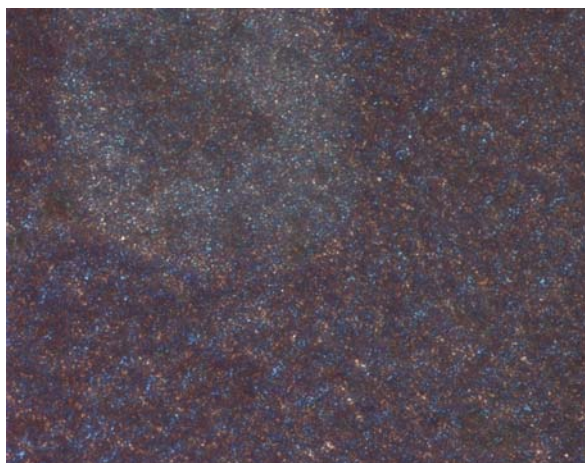
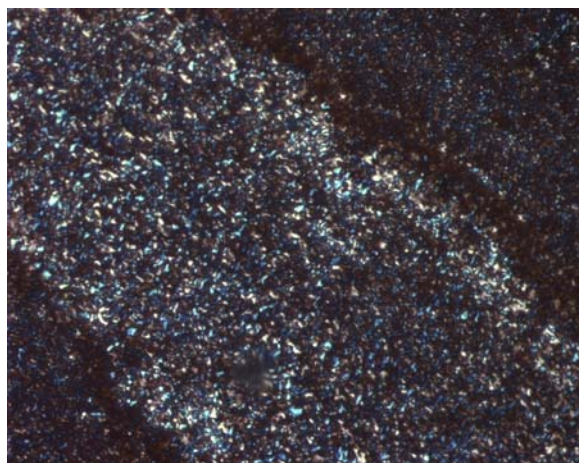


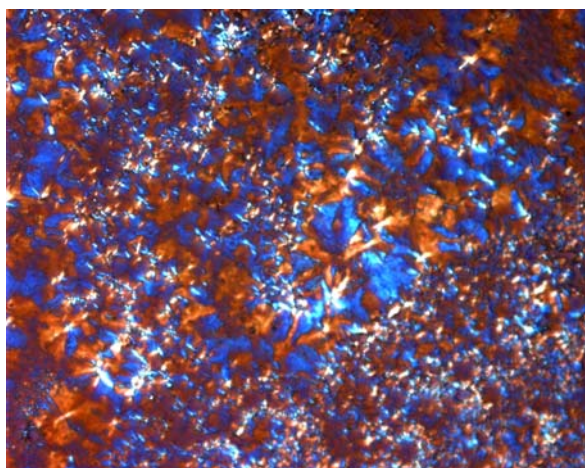
Figure 109. Differential scanning calorimetry traces of macrocycles **E6** (top), and **E7** (bottom) observed on the second heating scan (heating rate: 10 °C/min, under air).



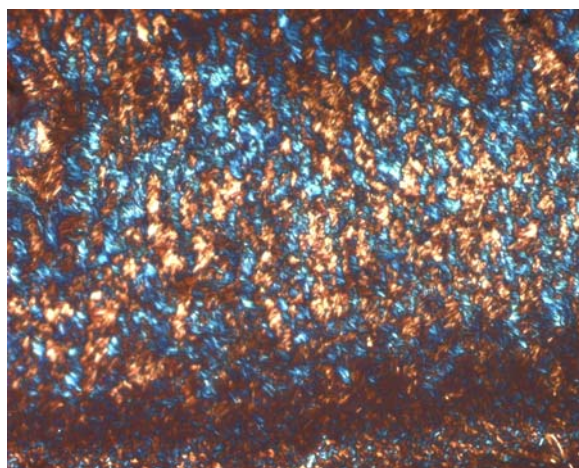
a. **E1** on heating at 277 °C (magnification 50×)



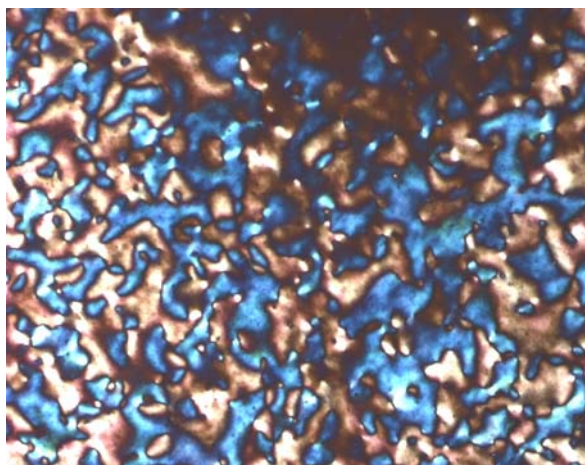
b. **E2** on heating at 234 °C (magnification 50×)



c. **E3** on heating at 140 °C (magnification 50×)



d. **E4** on heating at 230 °C (magnification 50×)



e. **E5** on heating at 230 °C (magnification 50×)



f. **E6** on heating at 165.5 °C (magnification 10×)

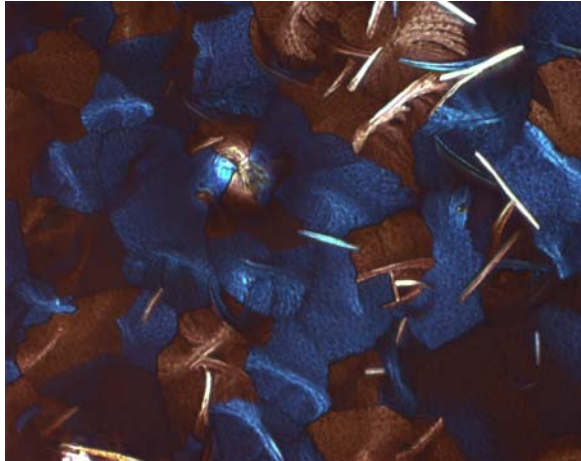
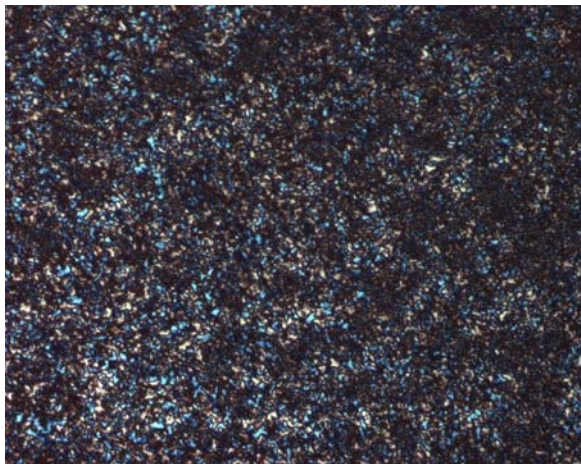
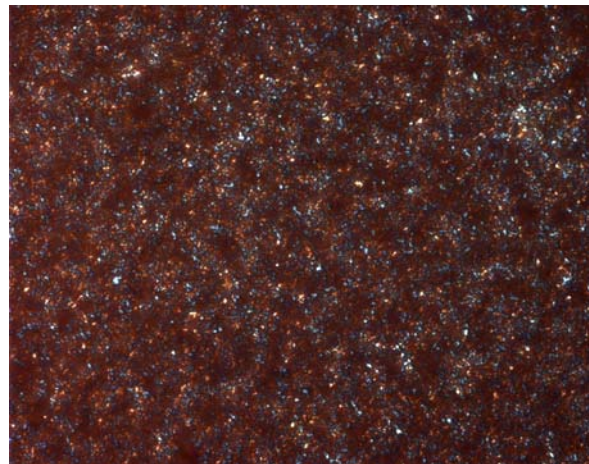
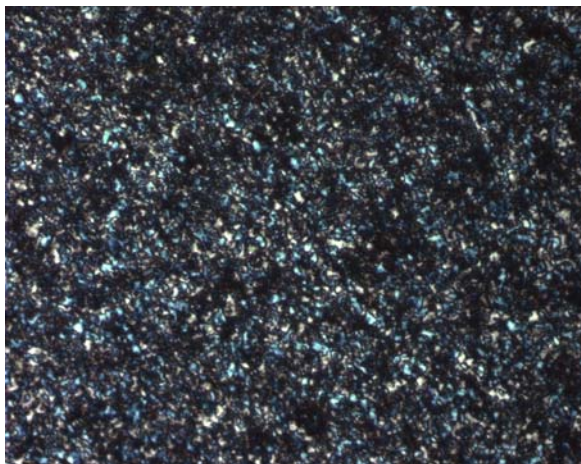
g. **E7** on heating at 195.4 °C (magnification 50×)h. **E7** on heating at 200 °C (magnification 50×)i. **E5** on cooling from i.p. at 194 °C (magnification 50×)j. **E6** on cooling from i.p. at 190 °C (magnification 50×)k. **E7** on cooling from i.p. at 176 °C (magnification 50×)

Figure 110. Texture between crossed polarizers on heating of **E1** (a), **E2** (b), **E3** (c), **E4** (d), **E5** (e), **E6** (f), and **E7** (g); and on cooling of **E5** (i), **E6** (j), and **E7** (k).