AFM investigations of a glassy cholesteric liquid crystal with hydrophobic aerosil particles

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AFM investigations of a glassy heterogeneous system consisting of an oligomeric cholesteric liquid crystal and the hydrophobic aerosil R812 were carried out. With increasing aerosil concentration, a suppression of the characteristic cholesteric surface pattern was observed. Typical separated aerosil aggregates appear in the samples. Their size and form change from small lumps through bigger rod-like entities to large crystallite-like aggregates of aerosil particles. This matches with observations of light scattering of systems with low molecular mass liquid crystals and of the memory effect. The pitch of the cholesteric fingerprint pattern slightly decreases with increase in the aerosil concentration.

1. Introduction

In the past five years, liquid crystal displays have been developed which contain suspensions of solid particles, especially of aerosil, in a liquid crystalline matrix [1]. In such heterogeneous systems, the solid aerosil particles can give rise to a scattering and to a memory effect [1, 2]. Eidenschink and de Jeu explained the electro-optical behaviour by a model based on a network of aerosil particles [3]. In a previous study we investigated by atomic force microscopy (AFM) the aggregation of hydrophilic aerosil (A300) particles in an oligomeric cholesteric liquid crystalline matrix [4]. Thereby we could detect aerosil aggregates of a diameter between 20 and 250 nm which form rod-like agglomerates of a size 0.4 times 1 μm. As concluded from electro-optical measurements on low molecular mass liquid crystals mixed with aerosil and theoretical considerations, these agglomerates must be responsible for the switching behaviour of these 'filled' liquid crystals [4]. Now the hydrophobic aerosil (R812) in a similar oligomeric cholesteric liquid crystalline matrix has been investigated, to cover a concentration range where the memory effect occurs [2]. We were especially interested in the change of the aerosil structure with concentration in order to understand the maximum of the memory parameter at a certain concentration, as described earlier [2].

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2. Experimental

The liquid crystals used in displays are mostly characterized by a low viscosity and therefore by a low glass transition temperature. AFM experiments need more rigid surfaces. Therefore, we selected the cholesteric oligomeric siloxane C4762L (g 55 N* 216 I, °C) produced by WACKER Chemie as the liquid crystalline matrix. It exhibits a left rotating helix with a reflection wavelength of 619 nm [5] and has been intensively studied, including AFM measurements [6, 7]. We regard the mixture of C4762L and the hydrophobic aerosil R812 with a mean particle diameter of about 7 nm as a model system and expected a correlation with the electro-optical data obtained in the mixture of 4-*n*-pentyl-4′-cyanobiphenyl/R812 [2]. In the last case, a maximum of the memory parameter at between 8 and 14 wt % of aerosil was found. The oligomeric siloxane was mixed with aerosil R812 obtained from DEGUSSA. Samples with 0.85, 1.95, 3.5, 5.1, 7.2 and 10 wt % of aerosil in C4762L were produced. The sample preparation was done by filling the mixture into a 2 μm sandwich cell consisting of ITO-glass, heating to 150°C, cooling and removing the cover plate. After that the substrate with the film was again heated to 150°C and cooled from the cholesteric phase at a rate of about 20 K min^{-1}.

AFM measurements were performed using the TMX 2000 Explorer and Discoverer Scanning Probe Microscope of TOPOMETRIX at room temperature and under

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http://www.taylorandfrancis.com/JNLS/lct.htm

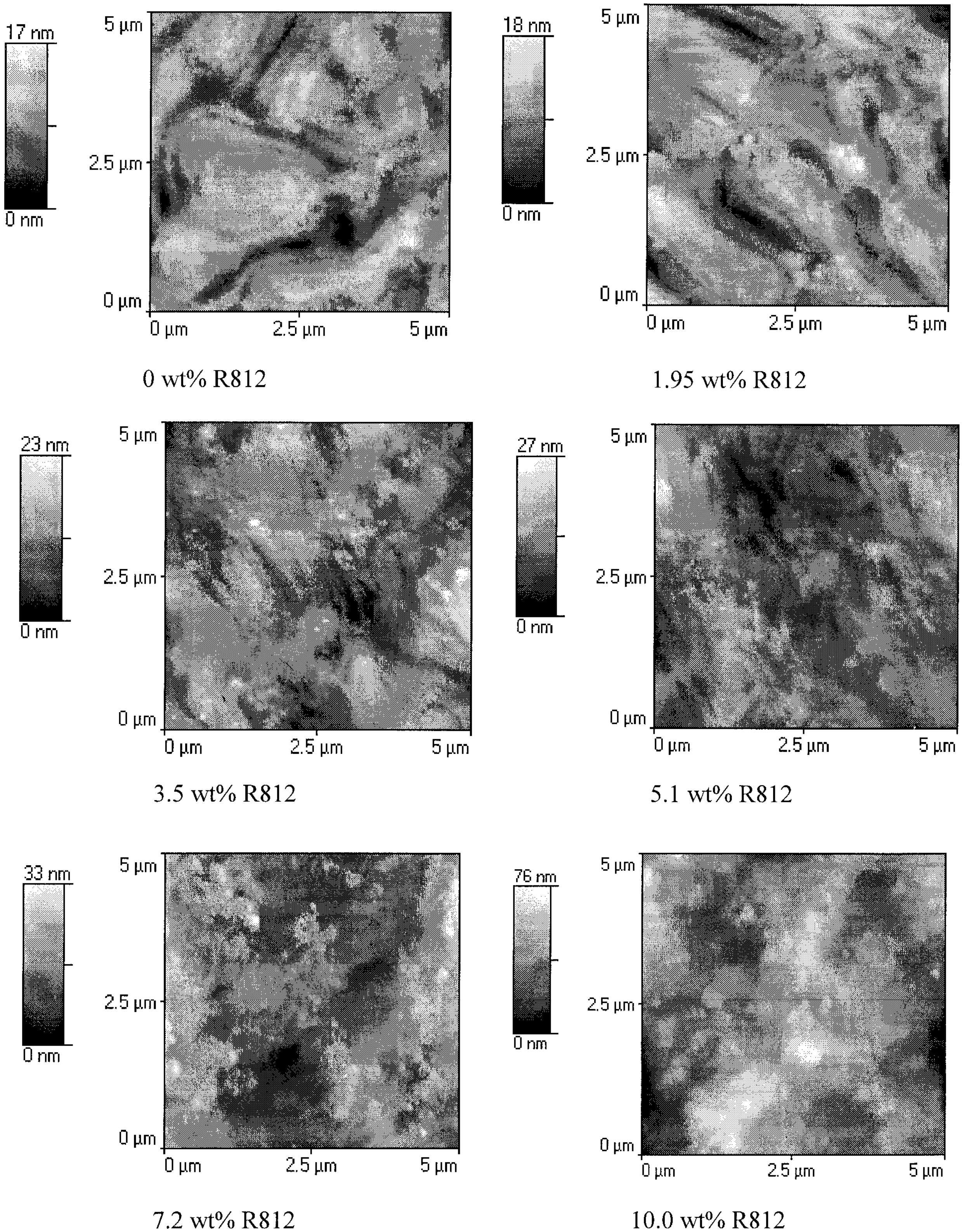

Figure 1. AFM images of the cholesteric liquid crystalline matrix C4762L at different aerosil R812 concentrations.

ambient conditions. The images were obtained by the non-contact method (cantilever resonance frequency: 299 kHz).

3. Results and discussion

3.1. *The aggregation of the aerosil particles*

Figure 1 gives a general overview of the changes of the AFM images with increasing aerosil R812 concentration. The white spots correspond to aerosil aggregates which are phase separated. The cholesteric texture of pure C4762L becomes continuously disturbed by addition of the hydrophobic aerosil. This disturbance can also be well seen in the surface roughness as shown in the RMS values of the given image in figure 2.

More details can be seen in smaller scans and by plotting the surface profiles (line measurements). At 10 wt % the cholesteric surface is covered by aggregates with a crystallite-like structure as seen in the 1.7 μm scan (figure 3). A diameter of about 270 nm was proven by line measurements. Probably these crystallite-like structures are also responsible for the high RMS value at this concentration as given in figure 2. Cholesteric surface patterns are missing in this sample.

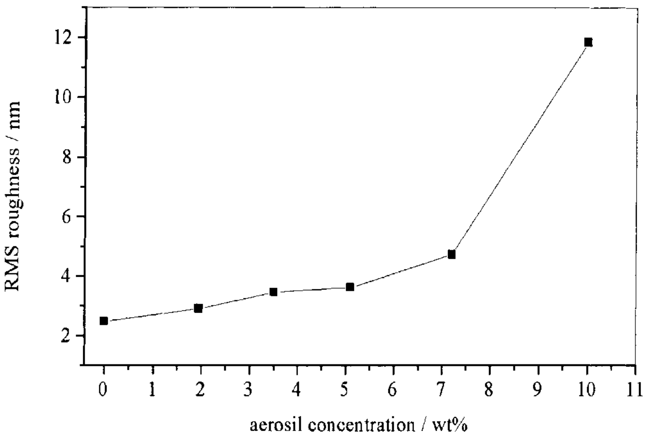

Figure 2. RMS roughness values of the AFM images from figure 1 versus aerosil concentration.

Characteristic aggregates with a length-to-breadth ratio of 150/65 appear at 7.2 wt % of aerosil (figure 4). In this case the line measurement was done only in a small area around one aggregate. These rod-like aggregates are about ten times smaller than the agglomerates found before in a mixture with the hydrophilic aerosil A300 [4]. Probably they are also responsible for the appearance of the high memory parameter in the mixture with the hydrophobic aerosil R812 observed in [2].

Quite different aggregates are observed in a mixture with 3.5 wt % R812 (figure 5). The size of the aggregates decreases to about 50 nm, corresponding to lumps of about 50 aerosil particles in the plane. It was also possible to detect a pattern which corresponds to singular aerosil particles of about 9 nm. Detailed information on the structure of the aggregates and the arrangement of single aerosil particles inside the aggregates could not be obtained.

3.2. *Observation of the fingerprint texture*

A clear fingerprint texture appears if the samples are heated to the clearing temperature and cooled at a rate of 20 K min^{-1}. In figure 6 the fingerprint texture and line measurements at 5.1 wt % aerosil R812 are represented. The distance between two maxima of 160 nm corresponds to the half pitch. At all concentrations the aerosil aggregates are inhomogeneously distributed. We could not detect any preferential distribution of aerosil at the maximum or minimum of the fingerprints which correspond to different molecular orientations [7]. As a result of the disturbances the lines are only equidistant in a small area. Furthermore one has to consider that the cooling regime down to the glassy state may influence the defect structure which was not in equilibrium.

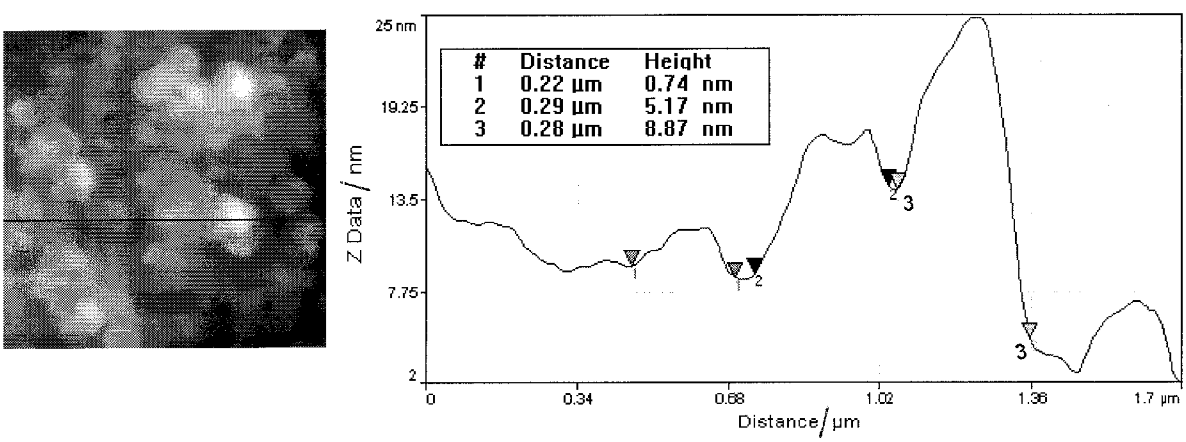

Figure 3. AFM image and line measurement (cross section) of the sample with 10 wt % R812. Inset data relate to the distance and height differences between points on the line indicated by the differently numbered pairs of inverted triangles.

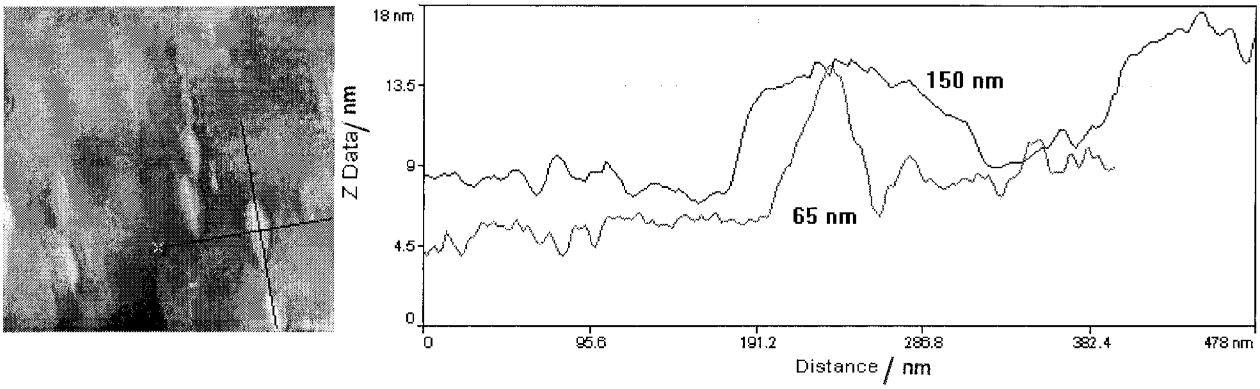

Figure4. Cross-sections of an aggregate at the surface of a sample with 7.2 wt % of R812.

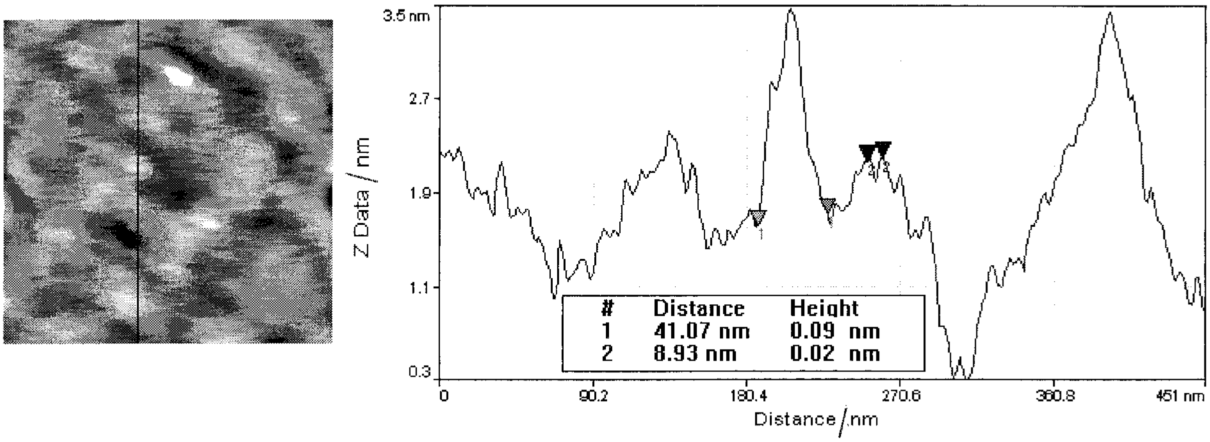

Figure 5. Line profile in the AFM image of the sample with 3.5 wt % R812. Inset data as described in the legend to figure 3.

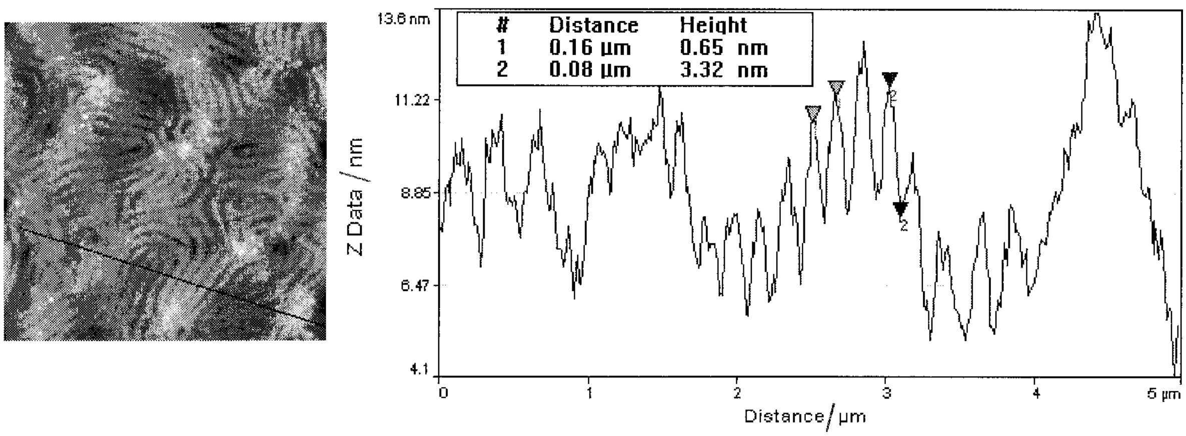

Figure 6. Line measurement of the AFM image of the sample with 5.1 wt % R812. Inset data as described in the legend to figure 3.

Therefore, the error of the line measurements is bigger than in well oriented liquid samples. For the sample containing 10 wt % aerosil we could not obtain a fingerprint texture. The results are summarized in figure 7. There is a slight decrease of the pitch with increasing aerosil content.

4. Conclusions

The presented data prove the existence of phase separated aerosil aggregates in the model system investigated. These aggregates disturb the orientation of the liquid crystal. The aggregation of the hydrophobic aerosil particles in the cholesteric phase changes with increasing

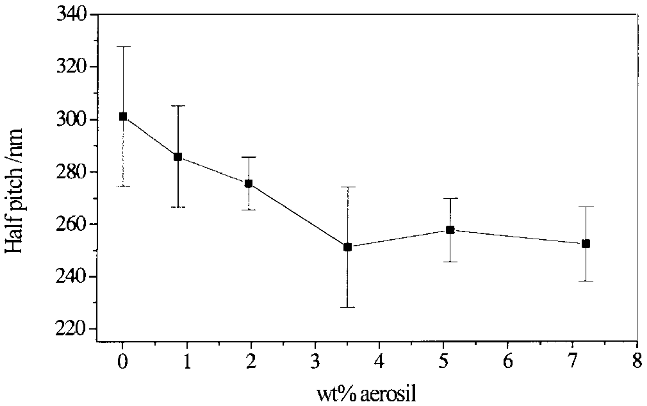

Figure 7. Half pitch from line measurements of the AFM images.

aerosil concentration from small lumps through rod-like to bigger crystallite-like aggregates. The rod-like aggregates at intermediate concentrations seem to be responsible for the memory effect observed before. At low concentrations, a distance in an AFM image was seen which corresponds to single aerosil particles. After heating into the isotropic phase, a better phase separation was obtained. In this way, it was possible to detect distorted areas with a fingerprint texture. Astonishingly the measured pitch decreases slightly with increasing aerosil content.

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