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Anisotropy of non-mesogenic polymer networks dispersed in a liquid crystal matrix

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We report here original results characterizing *in situ* the interactions between a smectic liquid crystal phase and a polymer network dispersed in it. These results have been obtained by neutron scattering on smectic liquid crystal (8CB) samples containing a physical network of 1·5 wt % polymer. The samples were polymerized in the isotropic, or in the smectic A phases. For the first time it is experimentally proved that the polymerization of non-mesogenic monomers in an aligned smectic A matrix induces anisotropy in the resulting network. The network becomes elongated along the liquid crystal director. When the polymerization is carried out in the isotropic phase the polymer network has an isotropic distribution even if a magnetic field, which orients the liquid crystal director, is later applied. On the other hand, studies show that after several thermal cycles, the liquid crystal orientational order still remained. Without other external constraints, the polymer network freezes the alignment of the liquid crystal. It is probably imposed by pendant reticulates on the diffuse liquid crystal–polymer interfaces.

1. Introduction

Based on their morphology, there are two main types of liquid crystal–polymer composites. One is the polymer dispersed liquid crystal (PDLC) material [1], and the other is the liquid crystal dispersed polymer (LCDP) system [2]. PDLCs contain usually more than 40 wt % of polymers and the liquid crystal forms isolated spheres embedded in the continuous polymer matrix. They have been intensively studied from the beginning of the eighties and are already used for electro-optic devices to switch between opaque and transparent states [1].

Recently there has been additionally a great deal of interest in LCDPs [2–11], since they also are promising for the use in electro-optic devices [3–5, 9]. They contain only small amounts of polymers and the liquid crystal forms the continuous matrix. The presence of small amounts of polymer is however sufficient to change the optical properties of the matrix under the influence of external fields [3, 4, 8]. We examine in this paper the interactions which exist between the liquid crystal matrix and the polymer, in order to understand the behaviour of the LCDP in a magnetic field.

The monomers used in these LCDP systems are soluble in the liquid crystal matrix. Since these monomers are also bifunctional molecules, the polymerization gives rise to a broad variety of polymer species from the oligomer state to 3-dimensional networks. Above a certain concentration (1 per cent for non-mesogenic [8] and 10 per cent for mesogenic polymers [7]), the polymers separate from the liquid crystal phase. Similarly to normal polymer solutions [12] (that is to say when the polymer solution is at rest without any external field), this process is usually halted by formation of a physical network and results in a reversible gel. For this reason LCDPs containing a micro-separated polymer network are often called liquid crystal gels [3, 6]. This name, however, can be confusing, since it has been already used for mesomorphic polymers crosslinked into a chemical, irreversible network [13, 14]. Studies of LCDPs have mainly concentrated on systems where the polymerization is induced in the aligned liquid crystal films [2–5]. In the off state, such films are optically transparent, since the liquid crystal remains aligned after polymerization. On applying external fields, the alignment is disturbed in each micro-domain and the sample becomes opaque. When the field is removed, the texture generally relaxes back to the transparent state [3, 4]. In contrast, dispersions prepared in the isotropic phase of the liquid crystal [8–11], present, in the liquid crystal phases, opaque films without an external field, but they can also be switched to transparent states [8]. The optical properties

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of the sample, i.e. the structures of the liquid crystal in external fields, have been broadly described, but little is known about the polymer network itself. X-ray [3, 7], STM [6] and electron microscopic [3] studies give several indications of the morphology of the polymer network, often, however, only after the liquid crystal phase was extracted. It was demonstrated that liquid crystal monomers polymerized in a liquid crystal matrix form anisotropic networks. However, until now there is no information concerning the eventual anisotropy which networks polymerized with non-mesogenic monomers could present. Small-angle neutron scattering (SANS) is a powerful method which allows the study of the network on the scale of the polymer chain and it presents the great advantage of allowing this study *in situ*, without extraction. It is then possible to characterize the interactions between the polymer network and the liquid crystal matrix in order to understand the differences in macroscopic behaviours described above between polymerization in the smectic A phase and in the isotropic phase. In addition the use of a 2-dimensional multidetector and of aligned samples allows the determination of the anisotropy of the interactions.

The first SANS experiments [10] showed that there is effectively enough contrast between the liquid crystal matrix and the polymer network to enable this study to be performed. In this paper, we compare the results on samples obtained by polymerization of a small amount of non-mesogenic monomer in the isotropic phase and in an aligned smectic phase. By small-angle neutron scattering, information on the liquid crystal–polymer interface is provided. It is here demonstrated that the polymerization in the S_A phase induces an orientation of the formed network, whereas the polymerization in the isotropic phase does not produce any anisotropy even by later application of a magnetic field. In addition to the central scattering study, we also examined the alignment of the liquid crystal by observing the 001 smectic reflection and revealed a memory effect of the orientation. These measurements have been carried out as a function of temperature, and with or without a magnetic field.

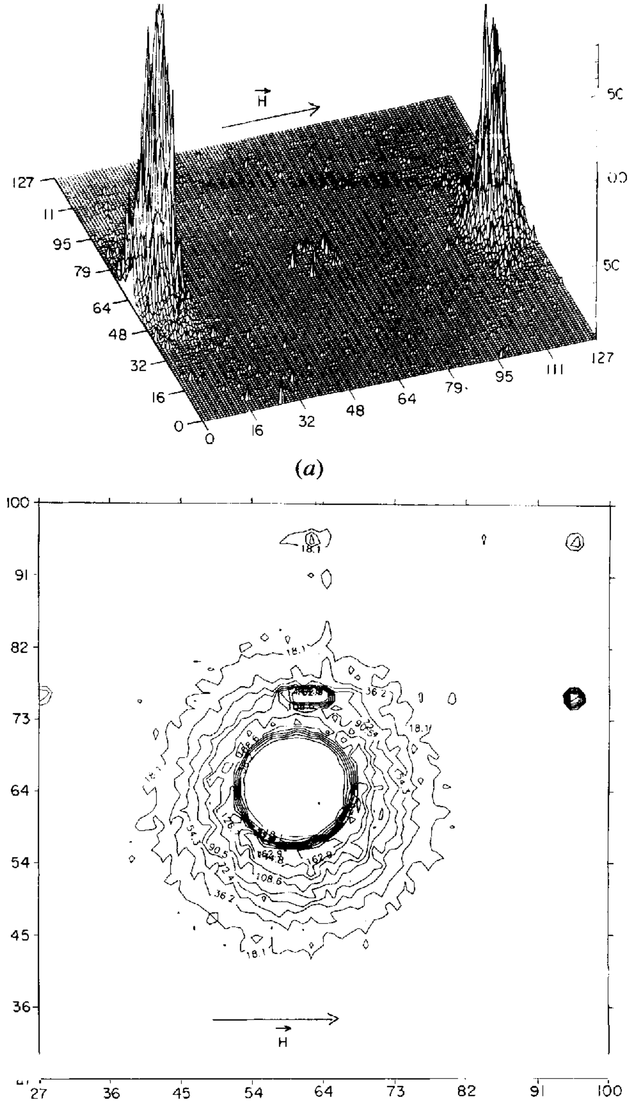
2. Experimental aspects

We have studied a liquid crystal polymer composite system containing 97·7 wt% of 8CB from Merck Ltd (4-cyano-4′-octylbiphenyl) as liquid crystal solvent, 1·5 wt% of 4,4′-bis (2-methylpropenyloxy)biphenyl (BMB) as reactive bifunctional monomer and 0·7 wt% of benzoin methyl ether (BME) as a photoinitiator. Two samples (**A** and **B**) were prepared and placed between two pairs of quartz glass disks each of 15 mm diameter. Both LCDP samples (**A** and **B**) were heated to a high enough temperature to accelerate the homogenization, and were then irradiated for an hour by UV light of flux of 3 mW cm^{-2}. For sample **A**, the polymerization was carried out in the isotropic phase at 50°C, while for sample **B** it was carried out at room temperature in the smectic A phase. In this latter case, the sample was aligned in a magnetic field prior to the polymerization. We also prepared a reference sample of the same size containing only the liquid crystal 8CB. The pure liquid crystal has the phase sequence isotropic–nematic–smectic A–crystal with transition temperatures of 40·4°C, 33·7°C and 21·5°C respectively. The composite samples showed the same sequence with slightly ($\approx 0{\cdot}5$°C) decreased phase transition temperatures.

The samples were placed in an oven standing between the poles of a magnet of maximum field 1·45 T. The trajectory of the neutrons was normal to the magnetic field. The neutrons scattered by the samples were collected by the plane multidetector of the SANS device consisting of 128 × 128 pixels ('PAXY', Lab. Léon Brillouin, CEN-Saclay). At small angles (corresponding to a sample–multidetector distance of 5 m and a wavelength of the neutron beam from 15 Å), the measurements gave us information about the anisotropy of the polymer network in the range 50–300 Å. The error for the small-angle scattering was typically 5 per cent in the range 300 Å, but almost 100 per cent for lengths of 50 Å. At large angles (obtained by switching the sample–multidetector distance from 5 m to 1 m and the wavelength of the neutron beam from 15 Å to 3·5 Å) spatial correlations in the 10–40 Å range could be measured. If the liquid crystal has a smectic phase, it is possible to observe the (001) reflection of the smectic layers. In this way we could check the nature of the phase (nematic or smectic) and probe the quality of layer alignment in the S_A phase.

3. Results

We made the following observations on sample **A**, which was polymerized in the isotropic phase. The texture was black between crossed polarizers, and furthermore, both the small and the large-angle neutron scattering patterns had circular shape (no azimuthal angle dependence). When we cooled the sample in to the liquid crystal phases without external fields, both the liquid crystal and the polymer network showed random orientation. After these observations, we heated the sample to form the isotropic phase and cooled it back in the presence of a magnetic field of $H = 1{\cdot}45$ T. It was found that the liquid crystal was aligned by the magnetic field. At the same time, however, the small-angle scattering pattern still had no noticeable angle dependence (see figures 1 (*a*) and (*b*)). This means only random polymer distributions in the 200–300 Å range. On heating the sample to the nematic phase without a magnetic field, the smectic layer fluctuations remained anisotropic, corresponding to the previous director orientation. On heating further to the



(*a*)

(*b*)

Figure 1. Large and small-angle neutron scattering patterns of sample **A** at $T = 25°C$ after cooling the sample in a magnetic field of $H = 1{\cdot}45\,T$: (*a*) the (001) reflections indicate aligned smectic layers; (*b*) the small-angle scattering from the dispersed polymer network.

isotropic phase, both the small and large-angle scattering had isotropic distributions. After keeping the sample in the isotropic phase at 44°C for an hour, we cooled it back again to the liquid crystal phases, but in the absence of a magnetic field. We observed that the alignment given by the previously applied magnetic field had recovered, although with somewhat decreased quality. Repeating the heating–cooling cycles without the magnetic field, the earlier alignment reappeared, but its quality decreased further. To characterize the quality of the alignment of the smectic layers we plotted the normalized scattering intensity as a function of azimuthal angle. The results at $T = 25°C$ are plotted in figure 2. Figure 2 (*a*) shows the alignment when the sample was first cooled in the magnetic field. Figures 2 (*b*) and (*c*) represent the alignment without a magnetic field after the first and second heating–cooling cycles, respectively. The half width is a measurement of the quality of the alignment: for perfect alignment $\Delta\phi = 0°$, for no alignment $\Delta\phi = 180°$. In the cases illustrated, $\Delta\phi$ is 4·5°, 6° and 11°, respectively. For comparison, we also studied the large-angle neutron scattering of pure 8CB. It was found that the alignment of the above sample was basically as good as that for the pure liquid crystal. The alignment of the pure 8CB was lost however after the sample was heated into the isotropic phase.

For sample **B**, the polymerization was carried out in the prealigned S_A phase a few days before the neutron experiment. After polymerization, the texture seen by polarizing microscopy contained more defects, indicating a somewhat deteriorated alignment. This is also seen by the (001) reflection (see figure 3 (*a*)). Small-angle scattering patterns had an elliptical shape with the aspect ratio 1·6 (see figure 3 (*b*)). This value is relatively constant at different scales of the scattering, indicating that the anisotropy affects a broad range of polymer sizes. The direction of the long axis of the ellipse indicates that the polymer network is elongated along the liquid crystal director. This means that the monomers are not randomly polymerized, but that the smectic field was strong enough to induce an orientation during the polymerization and the

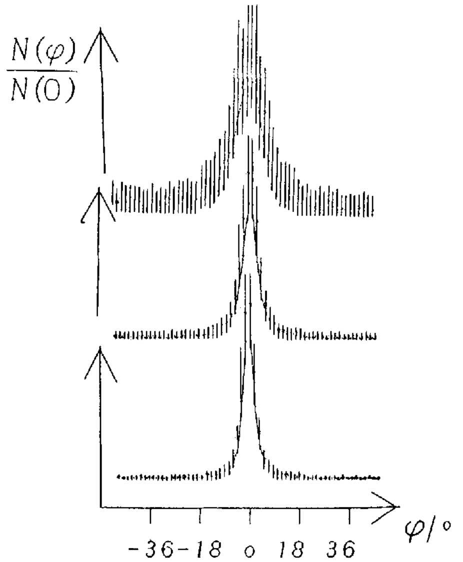


Figure 2. Azimuthal angle distribution of the smectic layers of sample **A**, which was polymerized in the isotropic phase, at $T = 25°C$ when the sample was cooled in a magnetic field (*a*), after the first (*b*) and second (*c*) heating–cooling cycles without a magnetic field.

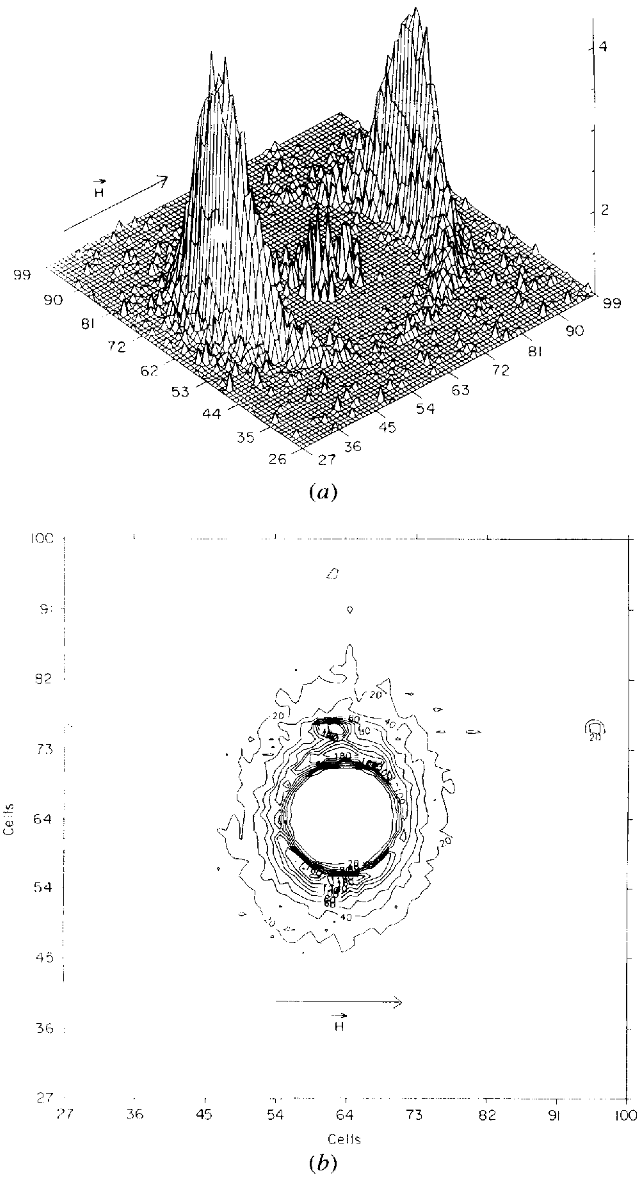


Figure 3. Large and small-angle neutron scattering patterns of sample **B** which was UV cured in the pre-aligned **A** phase at $T = 25°C$: (*a*) the (001) reflections of the smectic layers; (*b*) the small-angle scattering from the dispersed polymer network indicating the anisotropic network distribution.

phase separation process. The sample also showed birefringence in the isotropic phase.

We also measured the smectic layer spacing after the polymerization. We found that the smectic layer distance is $29{\cdot}9 \pm 0{\cdot}1$ Å for all the samples studied, independently of the presence of the polymer network and of the temperature in the S_A phase. The width of the 001 Bragg reflection observed was larger than that obtained by aligning pure 8CB with a field of 1·45 T. It is, however, not possible to conclude that a deterioration of the smectic alignment occurred due to the polymerization, since the sample was not prepared *in situ*.

4. Discussion

Contrary to PDLC systems [1], we observed that the alignment of the liquid crystal is not determined by the average shape of the network. The shape of the polymer aggregates, in contrast, reflects the symmetry of the phase in which the monomers have been polymerized. If the polymerization takes place in the isotropic phase, the separated polymer aggregates randomly [10]. Experiments obtained on different LCDPs containing 1–3 wt % of non-mesogenic polymers formed in the isotropic phase, showed that the polymers were indeed separated from the liquid crystal phase. This result is not in disagreement with a fibre model of separated polymers [8]—(recent STM studies [6] seem to confirm this assumption). The polymer–liquid crystal interface is rough and can be characterized by a surface fractal dimension of about 2·5. The average diameter of the fibres is typically 500 Å. A correlation between the fibre diameter and the surface fractal dimension was found: both slightly increase (by about 20 per cent for $\Delta T = 40°C$) with decreasing temperatures. At a scale of 100–300 Å, an additional magnetic field has no deforming effect on the structure of these non-mesogenic aggregates. In contrast, when the polymerization is carried out in the smectic phase, the liquid crystal molecules provide an orientational direction and this results in fibre network elongated along the director. This is the first time that it has been experimentally demonstrated that an oriented matrix (liquid crystal) induces anisotropy of non-mesogenic polymer networks.

To explain the memory observed macroscopically in the optical properties [3, 4, 11] and microscopically in the 001 smectic reflection after different thermal cycles (see figure 2), we propose the following picture. The chemical cross-linking of the reactive monomers is accompanied by the phase separation of the polymer and the liquid crystal (physical process). The phase separation is halted by formation of a physical network yielding stable structures at constant temperatures. At high temperatures only do larger polymers separate out, and the small chains or reticulates remain dissolved. As the temperature decreases (especially during the isotropic–nematic phase transition), the liquid crystal medium becomes a less good solvent for the polymers. This enhances the phase separation and yields thicker fibres, as was observed by the first SANS experiments [10]. Until this point, the process is similar to that known for normal polymer solution [12]. The main difference is the following. When the polymer is dissolved in an anisotropic solution its shape and orientation reflect the anisotropy and orientation of the solvent molecules [15]. Therefore the isolated polymers which aggregate to form the polymer network after the isotropic–nematic

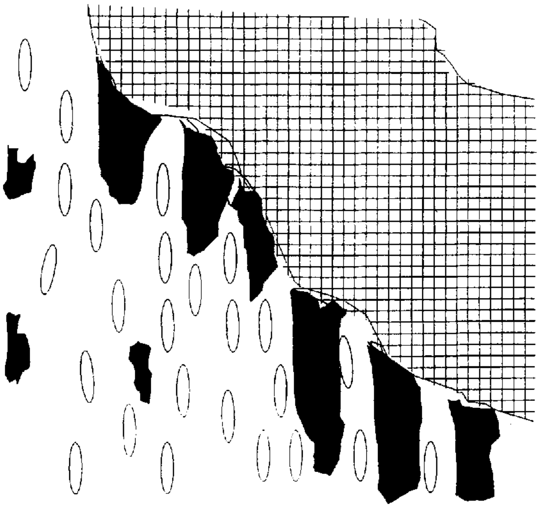


Figure 4. A sketch of a portion of the liquid crystal polymer interface formed after cooling the substance in an external magnetic field. The ellipses represent the liquid crystal molecules, the hatched part is the stem of the polymer network, and the filled parts (fibrillated surfaces) are the smaller polymers segregated in the aligned medium. The relative sizes are intended to approximate to the real situation.

transition must be oriented mostly along the director of the liquid crystal. When the sample is heated to the isotropic phase, the oriented fibrillated surfaces of the network do not dissolve readily and keep the initial orientation. Consequently, when the sample is cooled again to the nematic phase, the polymer network still contains small, aligned attachments and aligned chains. We propose that these fibrillated surfaces induce the memory of the previous alignment. To illustrate this model, we sketched a portion of the liquid crystal polymer interface formed after cooling the substance in an external magnetic field (see figure 4). The memory effect described here has then a completely different origin from anything known about cross-linking polymers [13, 14]. For example, nematogenic polymers cross-linked into a network memorize the cross-linking conditions. In this case, chemically irreversible gelation takes place. In our system, however, the gelation concerns only the non-mesogenic polymer fibres, and it is a reversible phenomenon (physical network).

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