Direct imaging of smectic layers in side-chain liquid crystal polymers by high resolution electron microscopy

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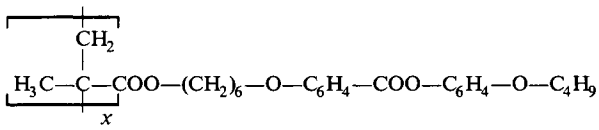
Introduction

X-Ray analysis in the past has been the preferred method of investigation to probe the structure of liquid crystalline side-chain polymers[1-4] in the smectic phase. However, because such polymers do not possess three-dimensional order, and have the structural characteristics of an amorphous material in some directions, X-ray analysis generally shows only a few reflections which cannot be interpreted in a unique way. Recently conventional electron microscopy has been performed on main-chain liquid crystals in order to obtain indirect information about characteristic mesophase texture defects using bright-field and dark-field contrast variations[5,6]. An extension of these investigations is presented in this work, in which high-resolution electron microscopy has been used in order to obtain direct images of the smectic layers in a side-chain liquid crystal polymer.

The liquid crystal polymer used in this work is a polymethacrylate with a mesogenic group in the side-chain. It was synthesized by Zentel and has been described in detail elsewhere[7,8]. The chemical structure of the sample is indicated below:



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Differential scanning calorimetry (DSC) measurements indicate that there are three phase transitions: glass-smectic at 39 °C, smectic-nematic at 107 °C, and nematic-isotropic at 112 °C. X-ray fibre diagrams[4] from these samples showed the typical sharp small-angle spacing and a wide-angle diffuse halo perpendicular to it. In this investigation the smectic spacing was estimated to be 28 Å and the length of the mesogenic group was given as 27 Å. Details regarding the molecular arrangement were not possible on the basis of the X-ray scattering experiment.

For the electron microscopic investigations thin films were pre-oriented by spreading the polymer in solution on a water surface and transferring the films onto a sui-

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tably treated glass slide. Subsequently they were annealed in the smectic phase close to the smectic-nematic transition for several hours. The development of the smectic phase was checked by light microscopy. Some films were prepared by spin-coating and annealing as above.

Experimental technique and results

A structural investigation has been performed on these samples involving the combined techniques of electron diffraction, electron microscopy in bright and dark field, light scattering and light microscopy which will be reported in detail elsewhere[9]. We wish to report here, separately, only the results obtained using high-resolution electron microscopy because this is the first time to our knowledge that this technique has been successfully applied to liquid crystalline polymers. The origin of contrast is phase-contrast. Such images can only be obtained by first calculating the phase contrast transfer function and then employing the correct underfocusing Δf.

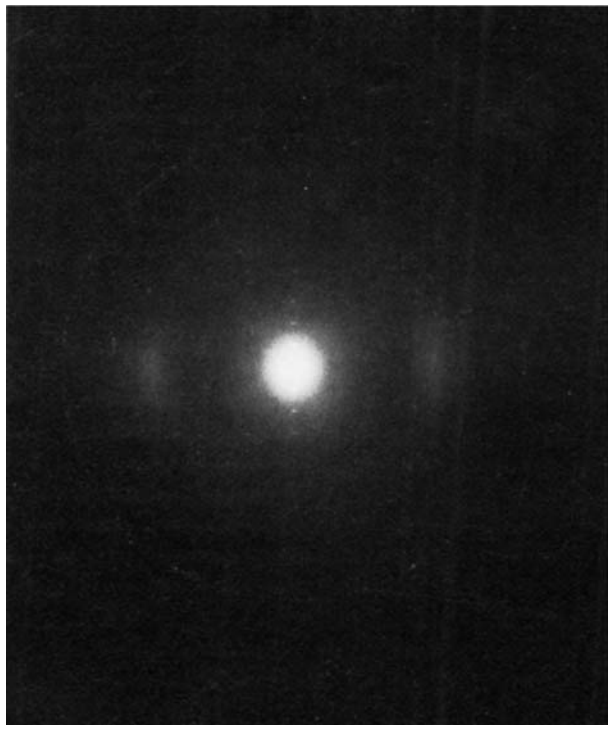

Fig. 1. Electron diffraction pattern obtained from side-chain liquid crystal polymer **1**

Furthermore the images can only be interpreted correctly if it is ensured that dynamical scattering is not involved. This is the case if the film thickness is less than half the extinction distance ξ_g.

It was established by electron diffraction that the thin films were oriented and in the smectic phase (Fig. 1). The smectic layers are clearly well oriented, since 3 orders of diffraction occur corresponding to spacings of 28,48 Å, 14,24 Å, 9,49 Å. Broad wide-angle halos are observed perpendicular to these sharp reflections at values around 5 Å corresponding to the liquid-like arrangement of the side chains.

In order to obtain lattice images from beam-sensitive samples despite of the problems, the optimum criteria in instrumental setting and specimen preparation must be estimated beforehand. This involves calculation of the phase-contrast transfer function, and optimum specimen thickness and orientation[10,11], as well as the use of a low dose unit and suitable cryo-stage. For the Philips 420 scanning transmission electron microscope operating at 100 kV with an objective-lens spherical aberration constant of 2 mm, these criteria were calculated to be optimized at a defocusing value $\Delta f = 100$ nm. The extinction distance ξ_g for carbon in a diamond lattice can easily be calculated from the structure factor and is 40 nm to 100 nm for low-index planes. In the case of these complicated molecules with one-dimensional order, the total atomic scattering is rather complicated and an estimate was made using only the atomic positions of carbon and oxygen, although, for electrons, scattering by hydrogen cannot be neglected. Furthermore, the calculation was performed on the assumption of a smectic E-phase, so that a unit cell and consequently a scattering function could be defined at all. Under these conditions an extinction distance of about 180 nm for the planes corresponding to the smectic planes was estimated. Detailed calculations will be given elsewhere[9]. In this case the films consisted of 2 to 3 layers, each of which had a thickness of about 80 Å, so that dynamical effects need not be taken into consideration. However, chances of obtaining lattice images are only given if the atomic planes involved remain in the correct orientation with respect to the electron beam throughout the layers, since a high-resolution image corresponds to a projection of potential along the beam direction.

A further very important criterion for obtaining lattice images is the correction of astigmatism. To this purpose, the sample was placed on a thin supporting carbon film onto which small carbon particles were deposited. Focusing and astigmatism correction were performed on the carbon particles using the low-dose unit. Astigmatism correction was subsequently checked in a light scattering experiment from the micrograph using the halo from the carbon film[12]. When the optical transform for the carbon film showed optimum underfocus conditions and astigmatism correction, the negative was examined carefully in a light diffractometer in order to detect evidence of sharp reflections from lattice planes.

Discussion of results

An example of the resulting micrographs is shown in Fig. 2a. The smectic planes are clearly visible in well-defined regions marked A. The distance between the planes

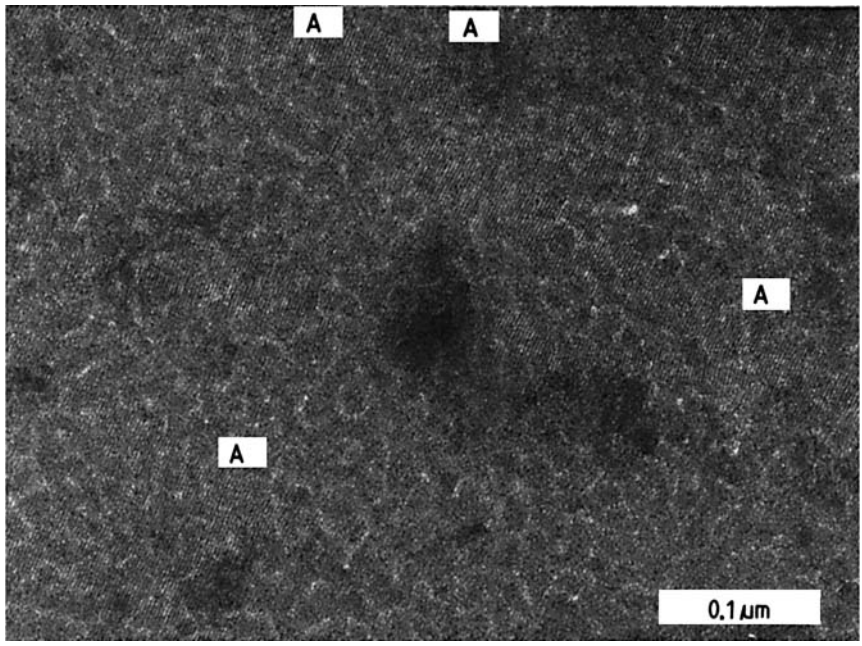

Fig. 2a. Bright-field medium-resolution electron micrograph showing smectic planes of side-chain liquid crystal polymer **1**. A: regions showing smectic planes

can be directly measured and is 28 ± 1 Å, so that these planes can be defined as identical to those which give rise to the 28,48 Å small-angle diffraction maximum. The size of the regions in which the smectic planes are clearly visible is about 600 Å (short dimension) and several µm (long dimension). The smectic planes are approximately perpendicular to the long dimension, as we have shown previously on the basis of diffraction and dark field evidence[13]. However, detailed information about the structure of the smectic planes as observed here can only be obtained by direct imaging and not from diffraction evidence. The side chains lie in the plane of the film. The extended side-chains determine the distance between the planes and are also in the plane of the film. The micrographs show that the smectic planes are curved for this particular polymer. This is emphasized in the transparent overlay (Fig. 2b) obtained from a micrograph of very high magnification. It shows the undulating nature of the smectic layers. The direction of the director in the areas between those showing contrast cannot be determined. Either the orientation of the layers is not in the beam direction or these regions are not oriented.

In principle, this question could be solved by tilting the sample, but in practice, at least for these beam-sensitive specimens, the maximum possible has already been achieved.

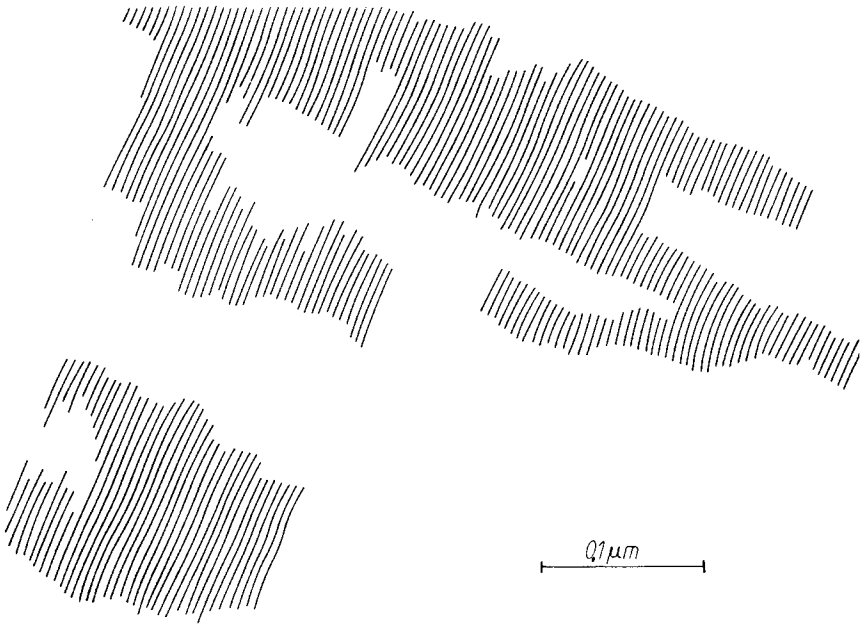

Fig. 2b. Copy of transparent overlay of micrograph in Fig. 2a showing directions of smectic planes (every second plane marked)

Conclusion

It has been possible to obtain detailed structure information from liquid crystal films. This structure information goes beyond the analysis of a diffraction pattern in that it shows details of the perfection of the smectic planes as well as their mutual orientation. Furthermore, the undulating structure of the individual planes has been directly demonstrated for the first time. Previous electron microscopic investigations on smectic layers[14, 15] have not achieved the resolution obtained here. In reference[14] low resolution scanning microscopy indicates the existence of layers, which we have also observed[9] but which are not directly correlated with the smectic planes. The micrographs in reference[15] are obtained from replicas or from stained samples. Replicas are limited in resolution and stained samples have the inherent danger of producing artefacts, particularly if it is uncertain how staining is actually produced. Undoubtedly, there are special features associated with thin films. Furthermore, there is no doubt that the side chains have been orientated in a specific manner due to the nature of the film. Nevertheless, we consider this experiment as having given important fundamental structural information about the two-dimensional arrangement of

macromolecules with mesogenic groups in the side chain which are capable of forming liquid crystals. We are now in the process of applying spatial filtering techniques in order to reduce the background "noise" due to the carbon film.

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