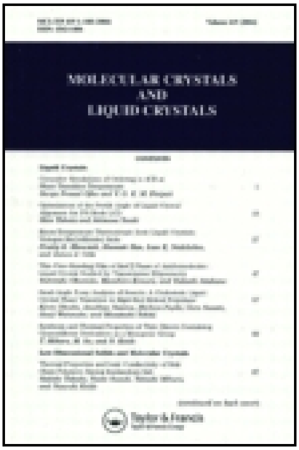

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A Study of Phase Change in Langmuir-Blodgett Films of Mesomorphic Side-Chains Polymers

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A STUDY OF PHASE CHANGE IN LANGMUIR-BLODGETT FILMS OF MESOMORPHIC SIDE-CHAINS POLYMERS.

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ABSTRACT

Langmuir-Blodgett films of mesomorphic side-chain polymethacrylates are investigated from the point of view of their phase change versus temperature via X-ray and neutron reflectivity . Upon heating,"thick" films undergo an irreversible transition towards the well known smectic A1 lamellar phase .In contrast a bilayer deposited onto a solid substrate appears to be very stable upon annealing . Such a behaviour is believed to induce an epitaxial mechanism when cooling "thick" films from the isotropic melt phase.

INTRODUCTION

In a previous work (1) we investigated the phase change in LB films of a mesomorphic side chain selectively deuterated polymer (Figure 1) . In the present work ,we have improved the film quality by choosing more appropriate deposition conditions. This enables the building up of "as prepared " films exhibiting a well defined lamellar structure not observed before. Phase changes are investigated by X-ray and also by neutron reflectivity measurements .

SAMPLE PREPARATION

Differential Scanning Calorimetry (DSC)was performed on the material used in the present study. We obtain:(g-47.7°C-SA_1-105°C-N-113°C-I).

In the present work, films are transferred at an unusually low surface pressure of 5 mN/m. The advantage of such a procedure is to increase the transfer efficiency and to reduce the film viscosity. The average area occupied by a monomer at this surface pressure is found to be 31 to 35 Å^2 ; however the transfer efficiency remains lower than unity (ca 0.8) and decreases slightly with increasing number of superimposed monolayers .In order to reduce this later effect thick films are built by sequences of ten or twelve superimposed monolayers.

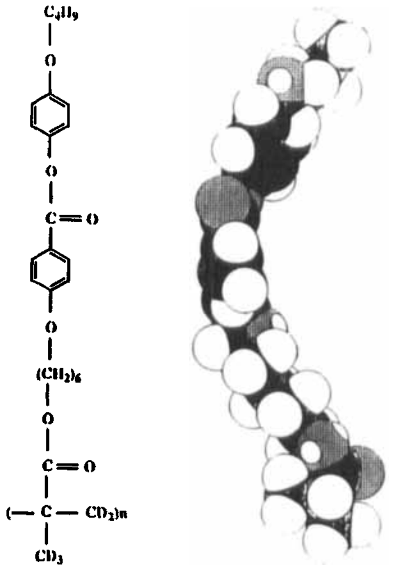

FIGURE 1 Polymers used in the present work.The average number of monomer in a polymeric molecule is estimated to lie between 500 and 1000.

X-RAY TECHNIQUE

LB films are considered as a stratified medium in which the density of the matter vary as a periodic function of the **Z** coordinate measured in the direction of the normal N to the substrate. Variations of the density profile along N produce large modulations of the reflected beam versus the incident angle θ. The reflectivity can be calculated from the standard expression of the classical optics for a stratified medium (2) by substituting the following expression for the complex optical index:

$$n = 1 - \delta - i\,\beta \qquad (1)$$

$$\delta = (\lambda^2 / 2\pi) . r_e . (f + \Delta f') . \rho / M \qquad (2)$$

$$\beta = \mu\lambda / 4\pi \qquad (3)$$

where λ is the X-ray wavelength , r_e the classical radius of electron , $(f + \Delta f')$ the real part of the atomic scattering factor, ρ the density , M the atomic mass and μ the linear absorption coefficient. The most convenient way is to consider the film as a superposition of homogeneous lamellae . For the values of δ and β ascribed to each lamella, one can probe density profiles by comparing the calculated reflectivity to the one measured (3).

.RESULTS

Figure 2 (a,b,c) gives the reflectivity curve versus q=4 π sin θ /λ for a "thick" film made of 31 superimposed bilayers.

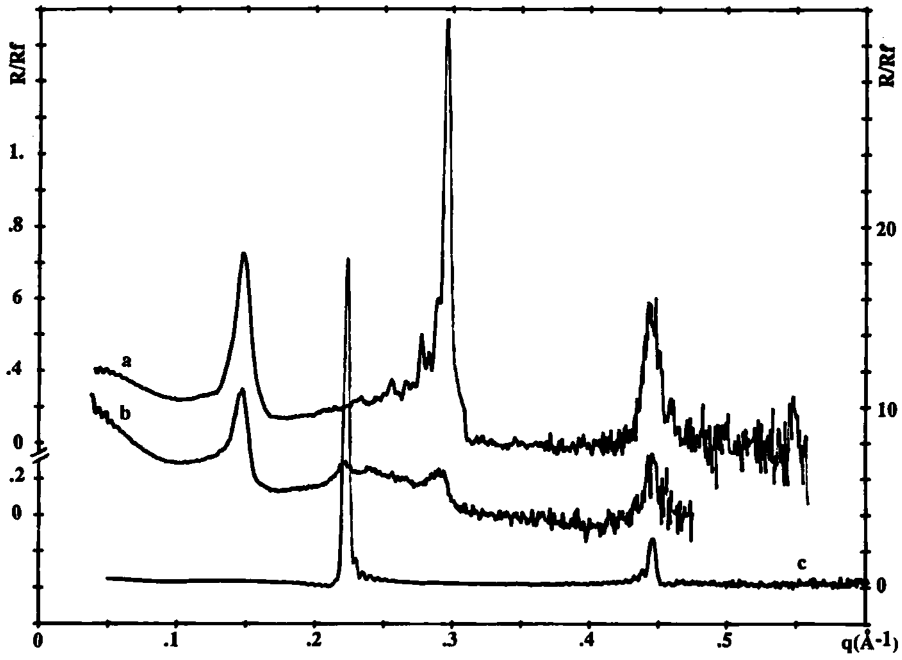

FIGURE 2 X-Ray reflectivity curve versus q=4 π sin θ /λ for a "thick" film made of 31 superimposed bilayers the deuterated backbone polymer. **a** : as prepared sample, **b** : after annealing for one hour at 57°C, **c** : after annealing for one hour at 118°C. Curve **c** refers to the right ordinate scale. .In the bulk material the transition towards the isotropical melt occurs at 113°C.(measurements carried out at room temperature).

Before heating (Fig 2a) ,three main Bragg peaks are visible at q= 0.147, 0.296 and 0.446 Å $^{-1}$ together with Kiessig fringes of weak intensity in the vicinity of q=0.06Å^{-1}.Kiessig fringes result from the interference between X-ray beams reflected at the air-film and film-substrate interfaces and the rapid damping is the signature of some inhomogeneity in the film thickness. However the angular difference between two successive maxima can be measured ; the film thickness is found to be: e = 1350 ± 50Å. Bragg peaks are rather broad hence showing a noticeable dispersion in the interplanar distances. However the 001, 002, and 003 reflections lead to relatively well defined average reticular distances i.e. : 42.5, 21.2, and 14.1 Å (corrected for the refractive index in the Bragg formula) and the corresponding parameter is 42.4 ± 0.1Å. Such a finding is obviously consistent with the presence of an ordered phase , unknown before, built up by the use of the LB method. In the stretched configuration (smectic A for example) the length of a mesogenic side chain is close to 28 Å . The value of 42.4 Å obtained for the interplanar distance necessarily involves couples of adjacent monolayers in a Y type configuration. In addition, this is in complete agreement with the observed behaviour of the meniscus during the transfer which leads to a clear cut conclusion that the transfer is of a Y type. We conclude that 42.4 Å is the thickness of a bilayer, the total thickness of the film being :62 × (42.4 / 2) = 1314 Å in close agreement with the above value e = 1350 ± 50 Å deduced from the Kiessig fringes. The thickness of individual monolayers (21.2 Å) is substantially lower than the length of a stretched side chain (28 Å). This is understood in terms of a pronounced average tilt (ca 40 degrees) or a more or less "coiled" situation for the mesogenic side chains. Such a behaviour is not surprising , keeping in mind that the film has been transferred at an unusually low surface pressure and that, consequently , the molecular array is not expected to be very compact. In the following step, films are heated at a given temperature and subsequently investigated by X-ray in a frozen indefinitely stable state at room temperature. After heating for one hour at 57 °C (Figure 2b) the Bragg peaks strongly decrease but still remain clearly visible while inspection of the Kiessig fringes do not reveal any significant change in the film thickness. In contrast a new Bragg peak can be detected at $q = 0.224$ Å^{-1} which corresponds to the well known interplanar distance of the smectic A_1 phase in the bulk material.

After heating for one hour at 97 °C (fig 2c) the peaks located at q = 0.147, 0.296, and 0.446 Å^{-1} completely disappear while two new ones (001, 002) are observed at q = 0.224 and 0.446 Å^{-1}. As expected these peaks correspond to the reticular distance observed in the bulk material i.e. 28.2 ± 0.1 Å for the smectic A_1 phase. In addition they are very strong (note the change in the ordinate scale) and very sharp hence showing a considerable increase in the molecular order along the normal to the substrate. At the same time inspection of the Kiessig fringes in the vicinity of the 001 Bragg peak reveals a moderate decrease in the film thickness (5 to 10 percent). This is understood in terms of the increase in the film compactness . It is worth noticing that no further change in the reflectivity curve is recorded after the film has been heated for one hour at 118 °C i.e. 5 degrees beyond the transition temperature $N \Rightarrow I$

Investigation of a single bilayer is most interesting and brings out an entirely new result which can be summarised as follows: Reflectivity curves for a single bilayer recorded at room temperature and after successive heating for one hour at 57, 97 and 118°C are basically the same(Figure 3). From the present data we can already conclude that the LB method produces a particular molecular array for which the phase transition $g \Rightarrow SA_1$ does not occur. Moreover for that particular situation an accurate fit can be made. We first investigate the glass coated with the hydrophobic methyl monolayer from dimethyldichlorosilane treatment.

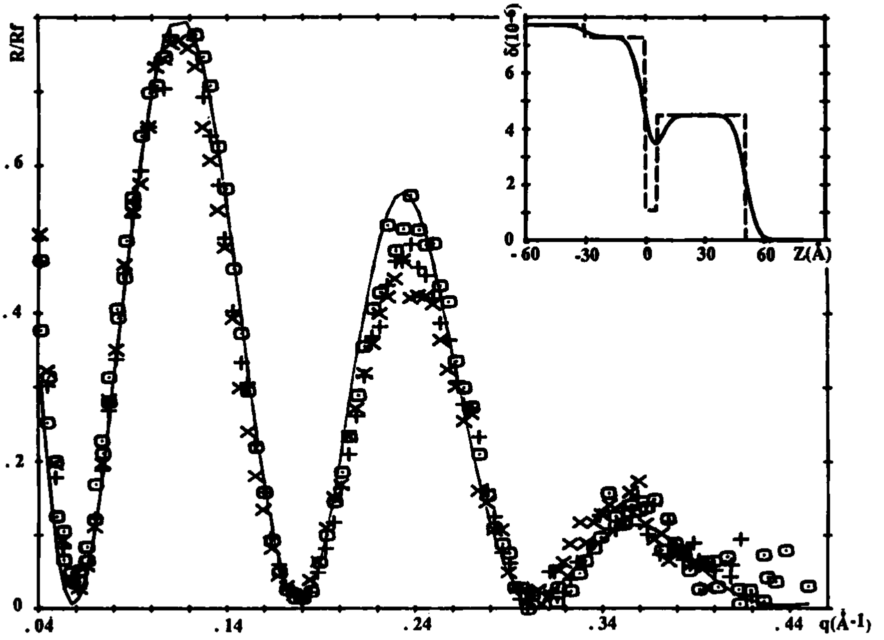

FIGURE 3 X-Ray reflectivity curve versus q=4 π sin θ /λ for a bilayer of the deuterated backbone polymer deposited onto an hydrophobic float glass substrate.✕ :as prepared film .. +after annealing for one hour at 57°C. ⊙ : after annealing for one hour at 118°C (measurements achieved at room temperature). Full line: best fit using the electron density profile given in insert . The film- substrate interface appears as a narrow "dip", 5.9 Å thick ,reflecting the misfit between the methyl groups grafted on the glass substrate by the dimethyldichlorosilane treatment and those belonging to the mesomorphic side chains (measurements carried out at room temperature).

The substrate is constituted of the bulk glass (δ_g =7.74 × 10^{-6} and β_g = 1.3 × 10^{-7}) coated with a surface layer of slightly modified glass, 30 Å thick , as a result of the surface treatment with: δ_l = 7.31 × 10^{-6} and β_l = 1.31 × 10^{-7}. The film- substrate interface appears as a narrow "dip", 5.9 Å thick , reflecting the misfit between the methyl groups grafted on the glass substrate by the dimethyldichlorosilane treatment and those belonging to the mesomorphic side chains. . In order to reduce the number of flexible parameters we postulated that the electron density δ_c is constant within the bilayer . With δ_c = 4.5 × 10^{-6} , a bilayer thickness of 44.4 Å and a roughness equal to 4.9 Å for each interface, we obtain a reasonably good fit (insert in fig 4). Hence we again conclude to a Y type structure.

NEUTRON REFLECTIVITY

Classical optical phenomena such as reflection, refraction, and interference are also observed with neutrons.The neutron refractive index of a medium, neglecting absorption , is defined as (4) :

$$n=1\text{-}Nb\,\lambda^2/2\pi$$

Nb is the average coherent scattering length density of the medium and λ the neutron wavelength. In this study, the reflectivity R is measured as a function of k_z defined as $(2\pi/\lambda)\sin\theta$ where θ is the grazing incident angle. As in the case for X-ray reflectivity described above,the optical matrix is used to analyse the reflectivity data. Figure (4) shows neutron reflectivity data as a function of wave vector k_z for 26 bilayers of polymer deposited at a surface pressure of 5 mN/m on treated float glass. The reflectivity measurements are taken for the sample as prepared (x) , and after annealing at 60°C for 1 hour (squares). There appears to be no difference between the two curves at higher k_z values; at lower k_z values, however , the peaks are more pronounced for the sample which has been annealed. Since the peak position remain more or less unchanged, this indicate that while the overall thickness of the film is unaffected after heat treatment, the interface is better defined.

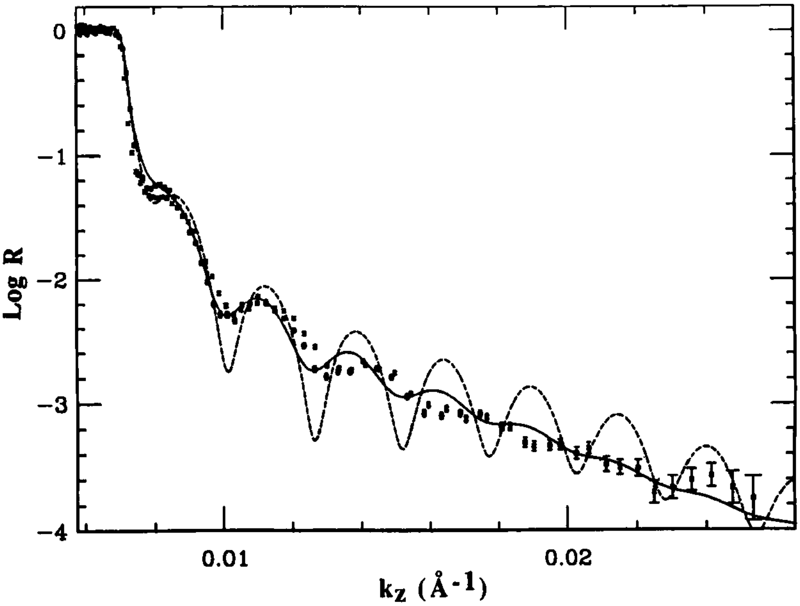

FIGURE 4 Neutron reflectivity versus k_z for a film made of 26 superimposed bilayers of the deuterated backbone polymer deposited onto an hydrophobic float glass . Sample as prepared (x) and sample heated for one hour at 60 °C (squares). Dashed line is calculated using a model of 26 bilayers ; solid line is calculated using a one-layer model of thickness e = 1190 Å with an air -film interface of 250 Å (measurements carried out at room temperature).

In these neutron reflectivity measurement , Bragg peaks are not observed due to the limited range of k_z values.The Kiessig fringes obtained are rapidly dampened, showing a high degree of inhomogeneity in the overall thickness . There is a great difficulty in fitting these data indicating not only inhomogeneity in the overall thickness but also in the composition of the film. It is impossible to fit the data to a model of Y type structure suggested by the X-ray refectivity results, taking into account neutron contrast between the deuterated backbone and protonated side-chain (dashed line: calculated from 26 bilayers with the first monolayer of side chains oriented towards the substrate) The best possible fit using the one layer model solid line) gives an overall thickness e = 1190 Å. This value is smaller than what one would expect if all side chains are completely stretched: 52 × 28.2 = 1466 Å . It is however , not far from the result obtained from X-ray reflectivity : 52 × (42.4 / 2) = 1102 Å. In the model used to fit the data, in order to dampen the oscillations at higher k_z values, a large film-air interface of 250 Å is introduced. These results also suggest the presence of air or water , both of which can render the film inhomogeneous as well as smear out any existing interface between deuterated and protonated zones.

CONCLUSION

The use of an extremely low surface pressure allows the building up of well defined Y type structure never observed before. . This new phase is still present after heating the sample for one hour at ca 60°C . However, as expected, it turns into the classical SA_1 mesophase when the sample is heated at 97°C . The retention of long range lamellar molecular order parallel to the substrate by the same SA_1 phase after heating up to 118°C (i.e. 5 degrees beyond the transition temperature N ⇒ I) is unexpected. The Y structure of a single bilayer (i.e. from the glass toward external air -film interface: side chains--polymeric backbone--polymeric backbone --side chains) is retained even after heating the sample at 118°C . Such a structure is extremely stable because of the long hindering backbones of the polymers. More precisely , side-chains cannot easily cross the molecular planes of the polymethacrylate backbones . In addition , a single bilayer can be stabilized by the substrate as well. In our opinion , this can explain the fact that no mesophase occurs when a single bilayer is heated even beyond the transition temperature . For thick films , the appearance of a smectic A_1 lamellar order parallel to the substrate should involve some epitaxial phenomenon starting from the inner "stable" bilayer . It is worth noticing that a decrease in the film thickness is still observed for films bearing only four superimposed monolayers. Such a finding is indeed a strong argument in favour of interdigitation of side chains

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