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Competition of Alignment and Aggregation? Phenomena in Constrained Films of LC Poly(Olefin Ulfone)s and Maleic Anhydride Co- and Terpolymers

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Anisotropic films of functionalised polymers such as the liquid crystalline poly(olefin sulfone)s (POS) and maleic anhydride co- and terpolymers (MAC, containing azobenzene side-groups too) are studied. Starting from isotropic spin-coated films annealing results in homeotropically aligned films by spontaneous self-assembling. X-ray specular scattering (XRS) and X-ray grazing incidence diffraction (GIXD) indicate a layered structure across the film parallel to the interface and significant in-plane order in thin films. Polarised UV-VIS spectroscopy investigations show that the homeotropic orientation of the side groups causes the formation of "card packed" or H-aggregates. For azobenzene containing MAC terpolymer an initial UV-irradiation followed by a polarised VIS-irradiation causes a light-induced co-operative reorientation of both types of side-groups and results in a lamellar stacking which is tilted. Orientation and aggregation are therefore driven by the liquid crystallinity and the segregation tendency of POS and MAC in constrained films. This seems to be an important factor for such spontaneous ordering processes.

Keywords: Thin Films; Liquid Crystal Polymers; Aggregation; Alignment

INTRODUCTION

Anisotropic films of functionalised polymers are becoming increasingly desirable for technical applications. For this reason different methods for the

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preparation of macroscopically ordered films characterised by in-plane anisotropy or vertically layered structures are being investigated. The combination of external forces with the amphiphilic or thermotropic self-organisation of these polymers gives the opportunity to produce thin organised films. Optically transparent, but isotropic films of amorphous or liquid crystalline polymers can be prepared easily by spin-coating or casting. Generally, annealing of such film's results in polydomain structures that scatter light.

Recently it was shown that an homeotropic alignment of smectic side and main chain polysiloxanes was established by spontaneous molecular self-assembly starting from spin-coated films or LB multilayers [1-8]. Moreover, the formation of ordered structures caused by the competition between liquid crystallinity and phase separation tendency was shown for some block copolymer's [1]. However, the driving forces and the contribution of various intermolecular interactions to the formation of such ordered structures nearby the interface are not understood so far.

EXPERIMENTAL

In the contribution the spontaneous ordering process of liquid crystalline poly(olefin sulfone)s (POS) and maleic anhydride co- and terpolymers (MAC) characterised by polar backbones and rod-like cyanobiphenyl side groups is studied in thin films by means of ultraviolet spectroscopy as well as X-ray scattering and diffraction methods. Polarised UV-VIS spectra were measured on a Perkin-Elmer Lambda 19 spectrometer containing a self-designed polariser kit to carry out a 360 degree angle scan. The minimum and maximum absorbance yield the dichroitic ratio by $R= A_{max}/A_{min}$. Analogous to the method known from nematic liquid crystals a spectroscopic degree of order $S_{XY}=(R-1)/(R+2)$ was calculated to characterise the orientation. Irradiation's were carried out by a mercury HBO 500 lamp and appropriate filters on a conventional optical desk as well as by an Inova 90 Ar^+ laser system (Coherent) at 357, 457.4 and 488 nm. Angular-dependent XSR was carried out on a STOE Θ-Θ-diffractometer; the energy dispersive XSR measurements were performed at a self designed instrument using a Si(Li) detector and a multichannel analyser (Silena). The resolution amounts to $\Delta d/d=2\%$. The change of lattice parameters under illumination with a HBO 100 lamp was observed in-situ with a time resolution of up to five minutes. Grazing incidence X-ray diffraction (GIXD) was performed at D4 and W1

beam lines (Hasylab, Hamburg (Germany)) in order to evaluate the in-plane lattice parameter.

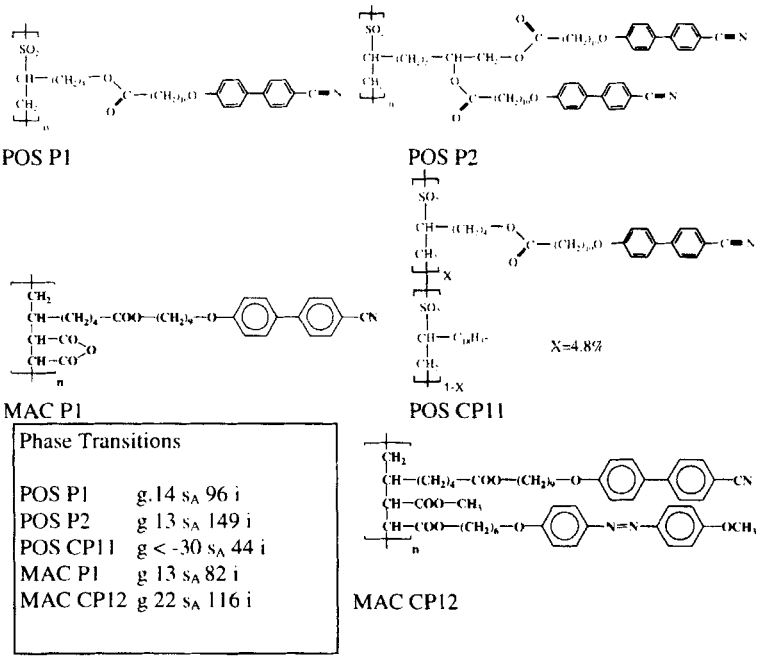


FIGURE 1 Investigated POS and MAC homo-, co- and terpolymers

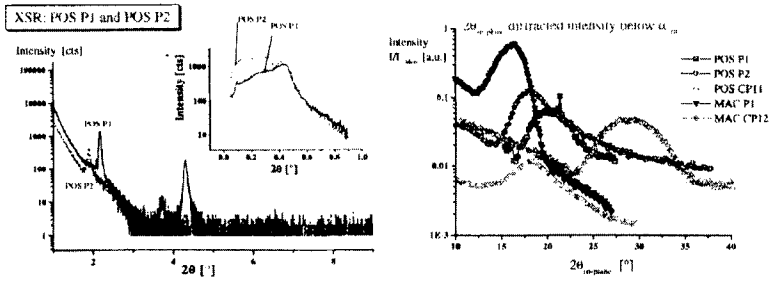
It's shown that thermal treatment and irradiation procedures result in lamellar structures of main and side chains which are parallel aligned to the interface, the homeotropic alignment of the mesogenic side groups as well as molecular aggregation of the aromatic moieties.
Furthermore, the competition of this ordering process and the photoinduced orientation process upon irradiation with linearly light is discussed.

RESULTS

XSR and GIXD

Annealing of the optically isotropic spin-coating films leads to a surprising formation of supramolecular structures within the LC-polymer films and to a

change of the spectroscopic properties [9-11]. The films remain optically clear, i.e. annealing does not cause light scattering. Moreover, the self-organisation process results in a layered structure within these polymer films as measured by X-ray Specular Scattering (XRS) and X-ray Grazing Incidence Diffraction (GIXD). Hereby vertical layer distances (d_{out}) and the vertical correlation lengths L_Z (XRS) as well as in-plane parameters like d_{in} and L_X as the next neighbour distances and lateral correlation factors (GIXD) give access to a description to the overall order of the molecules in thin films.



XSR

	bulk			film	
Polymer	d [nm]			d_{out} [(± 1) Å]	$<L_Z>$ [nm]
POS P1	30°C: 5.0	70°C: 4.81	80°C: 4.65	30°C: 49.0	30°C: 170
POS P2	-	s_A : 4.41	-	35°C: 41.9	35°C: 13
POS CP11	s_B : 4.2	s_A : 4.15	-	30°C: 40.7	30°C: 190
MAC P1	-			30°C: 30.0	30°C: 50
MAC CP12	-			30°C: 30.0	30°C: 300

GIXD

Polymer	L_X [nm]	d_{in} [nm]	L_X/d_{in} [units of lattice constants]
POS P1	1) 1.87 2) 19.6	0.416 0.387	4.5 50.6
POS P2	1.86	0.455	4.1
POS CP11	1.51	0.287	5.3
MAC P1	3.00	0.505	5.9
MAC CP12	1.44	0.441	3.3

FIGURE 2 X-ray scattering and diffraction curves for POS and MAC

The influence of the interfaces and the chemical structure of the investigated POS and MAC on this arranging process is under further investigation.

UV-Vis spectroscopy

The formation of layers is connected with a significant decrease of the absorbance of the cyanobiphenyl side groups. Simultaneously, a hypsochromic shift of the absorbance and a bathochromic shift of the fluorescence maximum are observed. This behaviour suggests the formation of H-aggregates. The chromophores of the side groups undergo a self-association process generating dimers or cluster of molecules with parallel oriented transition moments. The spectroscopic properties are modified by the excitonic splitting according the exciton model introduced by Kasha [6]. Thus, the formation of the layered structure is combined with the homeotropic arrangement of the H-aggregated side groups. This structure model is in agreement with results of polarised UV-Vis spectroscopy. The virgin and the annealed films do not show any in-plane dichroism. However, there is always a significant dichroic ratio in the annealed films if they are tilted with respect to the measuring beam.

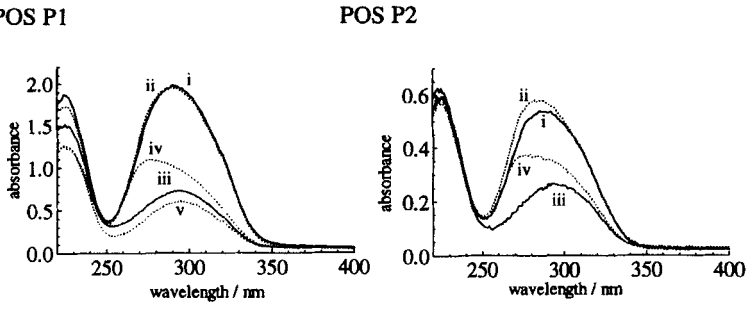


FIGURE 3 Absorbance of polymer POS P1 and POS P2 as virgin (i) and annealed (iii) film in normal position NP and as virgin (ii) and annealed (iv) film in 45° leaning position LP. For polymer I the maximum and the minimum absorbance of the annealed film in LP is monitored for parallel (iv) and perpendicular (v) position of the polariser.

Photoorientation

Upon irradiation the azobenzene moieties undergo E-Z photoisomerization and a wavelength dependent steady state between the rod-like E isomers and the more globular Z isomers is established. The molecular photoreaction causes a change of the electronic structure, the geometrical shape, the polarity as well as the direction of the transition moment. In this way the molecular photoreaction changes of the intermolecular interactions and effects a modification of the supramolecular structure in the annealed films. A sufficient disturbance usually led to a total and irreversible loss of the ordered structure. However, in the case of polymer MAC CP12 there is a competition between the induced lamellar order established by thermotropic self-organisation and the photoinduced orientation by linearly polarised light.

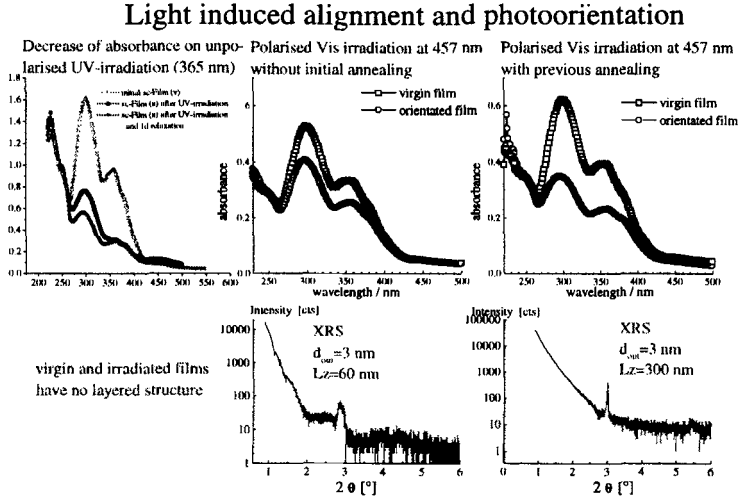


Figure 4 Photoorientation and -alignment of a MAC CP12 thin film

The interaction of photochromic moieties with linearly polarised light offers a principle new way for their photochemically induced orientation.

Conclusions

The liquid crystalline poly(olefin sulfone)s with biphenyl side groups (POS) and maleic anhydride co-and terpolymers (MAC) form layered structures on

annealing. This ordering process also takes place when the light sensitive azobenzene containing MAC terpolymer CP12 is treated with UV and Vis-light. The established layered structure is defined by an almost homeotropic alignment of the side groups. The formation of the structure is accompanied by a significant aggregation of the aromatic side groups changing the intensity and wavelength of absorbance and fluorescence maxima as well as the dichroic ratio. The aggregation leads to a chiral supramolecular structure. The structure-property relationships suggests that the orientation and aggregation phenomena in thin films are driven by the liquid crystallinity of the polymers and the segregation tendency of polar backbone and aromatic side groups of POS and MAC films being under investigation.

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