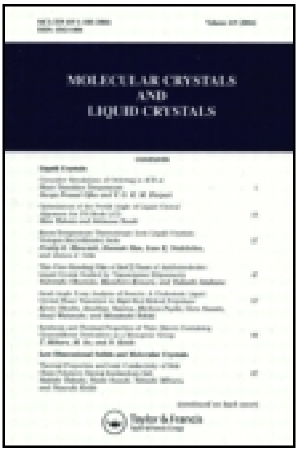

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Side Chain Polymer Liquid Crystals in High Magnetic Fields

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Side Chain Polymer Liquid Crystals in High Magnetic Fields

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We report an optical study of Side Chain Polymer Liquid Crystals (SCPLCs) in magnetic fields up to 20T. A novel sensitive set-up, which allows simultaneous birefringence and static light scattering measurements, was used to study polynorborene and polyacrylate based SCPLCs. We find that only magnetic fields bigger than a threshold value B_{min} are able to induce orientation effects and this only at the crossing of the Isotropic-Nematic (IN) transition when cooling from the melt. The existence of a minimum field B_{min} proves to be general, while its value is strongly dependent on the polymeric backbone elasticity, polymerization degree and spacer length. We have produced bulk and thin film aligned samples, stable at room temperature, characterized by an optical uniaxial anisotropy, with a director order parameter $S_D \sim 0.9999$.

Keywords: Side Chain Polymer Liquid Crystals; Magnetic Fields; Induced Orientation.

INTRODUCTION

Side chain polymer liquid crystals [1] are made of polymeric backbone chains to which rigid mesogenic units are laterally attached, see fig1. The connection is done via flexible spacers, which gives the mesogenes enough freedom to form liquid crystalline mesophases. Combining the versatile properties of polymers with the intrinsic self-organization of liquid crystals, the SCPLCs are of interest for advanced technological applications such as nonlinear optical devices, displays and optical data storage[2,3]. Their current limiting factor is the lack of a reliable method to drive the SCPLCs systems from microscopic self-organized mesophases to macroscopic order, in the general context that although liquid crystals and polymers are fairly well understood, their combined properties in SCPLCs are not.

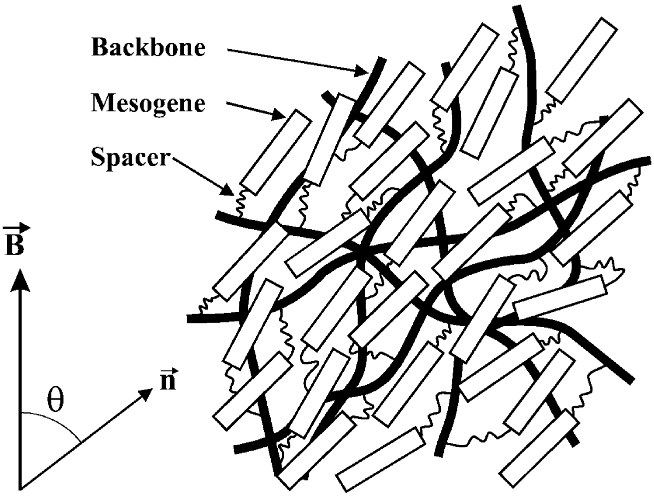


FIGURE 1 Schematic representation of SCPLCs.

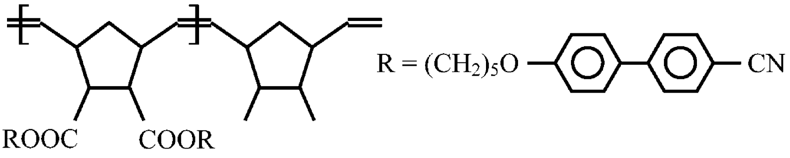
In the present work, we investigate the interaction of SCPLCs with high magnetic fields, via an optical study, in the search for a suitable SCPLCs processing method.

EXPERIMENTAL

A polynorborene based and a polyacrylate-derivative SCPLCs, both with cyanobiphenyl groups as mesogenes and methylene units as spacers were investigated.

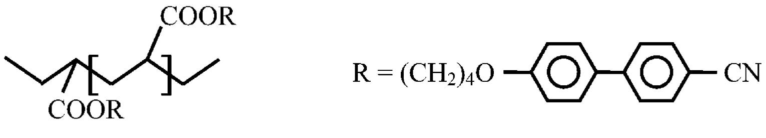
We studied the polynorborene SCPLC in two distinct conformations, with a spacer length of 5 methylene units respectively 3:

Poly[(±)-*exo,endo*-bis{5-[(4′-cyanobiphenyl-4-yl)oxy]pentyl}norborn-5-ene-2,3-dicarboxylate], later referred as C5 and Poly[(±)-*exo,endo*-bis{3-[(4′-cyanobiphenyl-4-yl)oxy]pentyl}norborn-5-ene-2,3-dicarboxylate], C3.



The C3 and C5 polymers are both thermotropic SCPLCs with a glass-nematic-isotropic phase space. Their backbone is relatively stiff due to the double bonds that connect the cyclo-pentyl units. Synthesized by Ring Opening Methahesis Polymerization (ROMP) with a living character, C3 and C5 feature a relative low degree of polydispersity, PDI~1.2.

The polyacrylate-derivative is also a thermotropic nematic SCPLC, but its backbone chain is more flexible in comparison with the polynorborene one. The spacer is 4 methylene units long and the mesogenic unit is the same cyanobiphenyl group:



Poly-{4-[(4′-cyanobiphenyl-4-yl)oxy]butyl}acrylate, later referred as B4. Synthesized by free radical polymerization the polydispersity of B4 is higher, PDI ~2.

Film samples were prepared on optical glass support by spin coating from solution and subsequent solvent removal by thermal annealing. Bulk samples were prepared poring molten isotropic phase solution in a 2mm optical path “precision cuvette”. For experimental investigation, the samples are placed in a temperature-controlled chamber (±0.01°C stability), within the bore of a 20T resistive Bitter magnet. The sample is passed by a polarization-intensity double modulated green He-Ne laser beam, with the optical path perpendicular to the magnetic field, which allows simultaneous measurement of the magnetic field induced birefringence and of the optical transmission. The field induced birefringence signal is proportional to the macroscopic order parameter of the sample, $S(B)=b(B)/b_{max}$ [4], with b the magnetic field induced birefringence and b_{max} the birefringence of a perfectly oriented sample. The optical transmission signal is proportional only to the amount of scattered light, which is directly related to the sample domain morphology because the SCPLCs used in the present work do not absorb at the laser wavelength used for the experiments ($\lambda = 543.5$nm). Intrinsically, the SCPLCs mesophase consists in locally ordered domains, whose directors are randomly oriented to each other. The total order parameter S describing such a morphology is given by $S = S_N \cdot S_D$ [5,6], a convolution of the local order parameter S_N, describing the local strength of the ordered mesophase, and the director order parameter S_D, which represents a measure of the macroscopic induced alignment. Out of field optical measurements allowed accurate determination of the director order parameter as well as the type of ordering, such as e.g. uniaxial or biaxial.

RESULTS AND DISCUSSION

Fig.2 shows the field induced birefringence recorded as the sample is cooled down in different magnetic fields, from the isotropic phase, across the IN transition, down through the nematic phase until the Nematic-Glass (NG) transition is crossed. In the isotropic phase there is no response due to the applied magnetic field. As the IN transition is reached a birefringence signal is recorded, which strongly depends on the applied field. After the NG transition is crossed the signal becomes constant and no changes take place upon further cooling. The order is preserved after the magnetic field is removed. Visual and polarized microscopy inspection of the ordered specimen shows a monodomain uniaxial alignment. In the vicinity of the IN transition, the birefringence signal follows a $b \sim (T_{IN} - T)^{\beta}$ scaling law, see the inset of fig.2. The critical exponent β has different values for the C3, B4 and C5 families but, within a family, β does not depend on the polymerization degree or the applied magnetic field value, (see table 1).

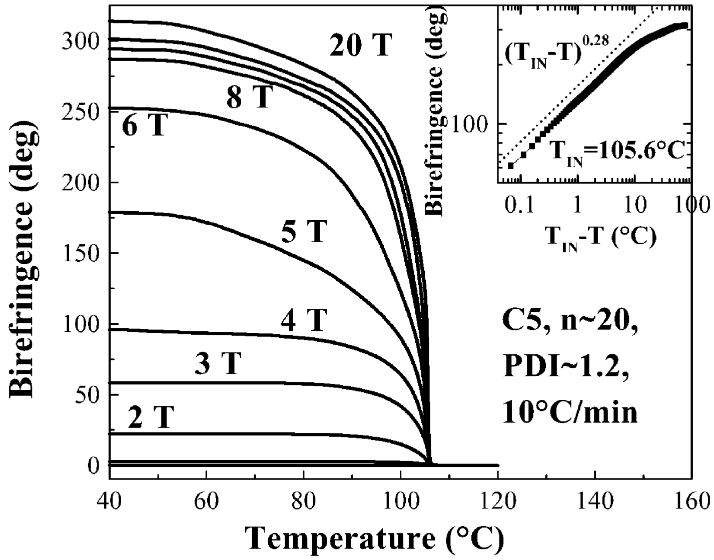


FIGURE 2 Magnetic field induced birefringence recorded for a C5, 20μm thick sample, n~20, PDI~1.2, cooled in various magnetic fields. Inset: $(T_{IN}-T)^{\beta}$ scaling of the 12T curve.

Fig.3 presents the optical transmission data recorded simultaneously with the birefringence data from fig.2. In zero magnetic field, from high transmission in the isotropic phase the sample starts to scatter light as it undergoes the IN transition, the transmission is constantly decreasing during the biphasic region and the sample ends up completely opaque deep in the nematic phase. For low applied magnetic fields, the induced changes are small and the sample follows almost the same path as cooled in zero magnetic field.

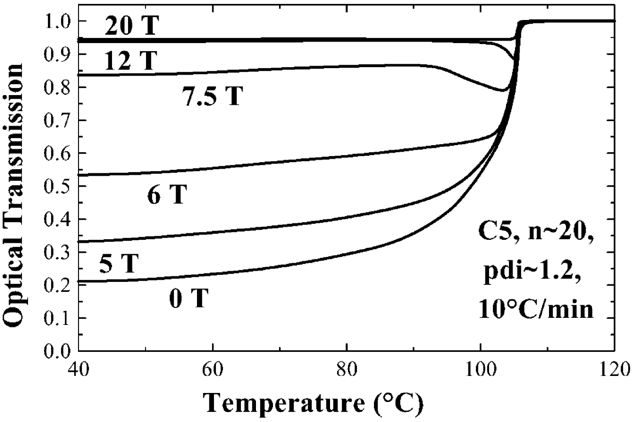


FIGURE 3 Optical transmission recorded for a C5, 20 μm thick sample, n~20, PDI~1.2, cooled in various magnetic fields.

When the experiments are performed in stronger magnetic fields, the transmission signal deviates from the above behavior. At some point in the biphasic region the transmission completely changes its trend, showing a sharp increase, followed by saturation at some intermediate value in the nematic phase. Higher applied magnetic fields move the transmission turning point toward the beginning of the IN transition, while the transmission saturates at higher values. For fields above 15T the biphasic region completely disappears, the transition itself taking place in a very narrow (0.5°C) temperature interval. The saturation value of the induced birefringence, trapped in the glass phase, is presented in fig.4a. Every point of the graph is the result of a cooling experiment in a different magnetic field. For low magnetic field values the signal is relatively small, followed by an increase and saturation with increasing fields. The onset happens over a finite field range, characterized by B_{min}, which is taken as the middle point of the abrupt region. Fig.4b shows the final optical transmission of the same sample, indicating as well that a minimum field is needed to induce an effect. For the same system (C5 SCPLCs) but with a higher degree of polymerization the value of B_{min} tends to shift to higher values, from B_{min}~6T (n~20), to B_{min}~10T (n~30). As the polymerization degree increases further, the value needed to trigger alignment at T_{IN} increases, but upon further cooling the sample orientation starts to decline and is only partially preserved at T_{NG}.

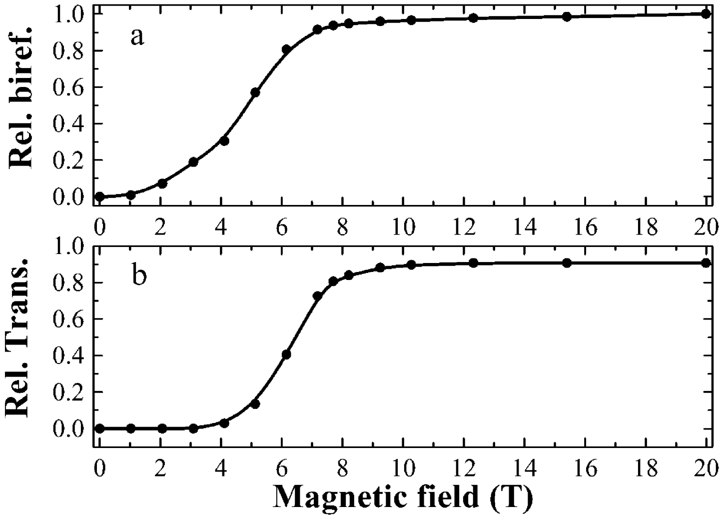


FIGURE 4 Magnetic field induced birefringence (a) and optical transmission (b) measured at 40°C, for a C5 20 μm thick sample, n~20, PDI~1.2, after being cooled in different magnetic fields.

For example, for n~40, B_{min}~19T at T_{IN}, but around 70°C the sample starts loosing its induced order and at T_{NG} the alignment is completely washed out. The experiments in the case of the polyacrylate-derivative samples show a similar behavior. In this case B_{min} is lower, i.e. B_{min}~2T, for n~20, while for n~30 B_{min}~3.5T. The main results are summarized in table 1. A cooling rate of 10°C/min was used for all the above experiments. Lower cooling rates give rise to identical values, while for very high cooling rates the results are no longer accurate, since the system is not able to follow such fast changes.

Sample	B_{min}	Alignment preserved upon cooling	β	Transition temperatures T_{IN} and T_{NG}
C5, n~20, PDI~1.2	6T	Yes	0.28	105.6°C 43°C
C5, n~30, PDI~1.2	10T	Yes	0.28	109.2°C 43°C
C5, n~40, PDI~1.2	19T	No, Decays below 70°C	0.28	112.5°C 45°C
C3, n~20, PDI~1.2	Over 20T	No induced effect	0.10	92.6°C 57°C
B4, n~20, PDI~2	2T	Yes	0.40	94.0°C 43°C
B4, n~30, PDI~2	3.5T	Yes	0.40	96.7°C 43°C

TABLE 1 Summary data of the studied SCPLCs

The behavior of 2mm thick bulk samples is found to be completely similar to the one of 20-40μm thick film samples.

When the samples were exposed to magnetic fields at a fixed temperature, no alignment was induced, regardless the time scale and the temperature of the experiment or the sample chemical details.

Out of field optical characterization of the aligned samples revealed that the order is uniaxial, with the mesogenes moieties along the magnetic field direction. The anisotropy of the birefringence (see fig5) was $b_{0^\circ}/b_{\pm 45^\circ} \approx 10^4$, corresponding to an anisotropy of the refractive index $\Delta n \approx 0.1$, leading to a director order parameter as high as $S_D \approx 0.999 \div 0.9999$.

In magnetic field a diamagnetic molecule acquires an extra energy $E = -\chi \cdot B^2$, where B is the magnetic field induction and χ is the molecular diamagnetic susceptibility. The energy represents the interaction energy between the molecular induced magnetic moment and the magnetic field. For almost all molecules, the susceptibility χ exhibits anisotropy, $\Delta\chi = \chi_{//} - \chi_{\perp}$, where the indices "||" and "⊥"denote the susceptibilities parallel and perpendicular to the molecular axis. This anisotropy gives rise to an orientation dependent energy and therefore, in magnetic field, molecules try to orient such that the magnetic energy is minimized. For individual molecules $\Delta E = \Delta\chi \cdot B^2 << kT$ and therefore the induced effect is very small. However, in the case of collective molecular behavior, like in liquid crystalline mesophases, the ΔE added up for all molecules within an average correlation volume, can become comparable with the thermal fluctuations, kT, thus allowing an important degree of induced orientation [4].

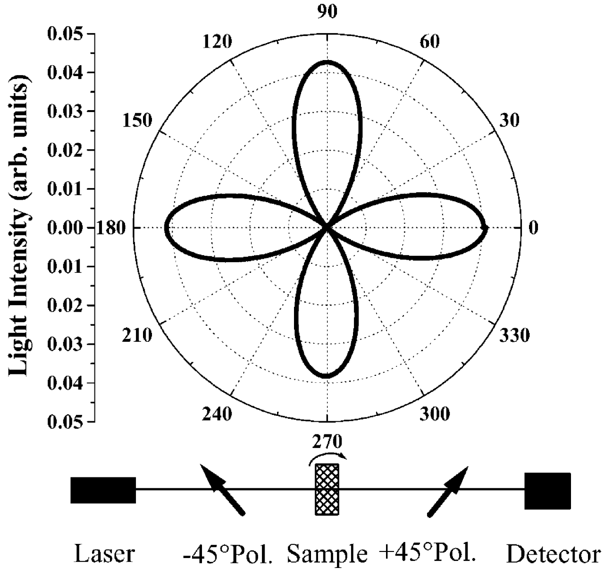


FIGURE 5 Out of field optical analysis of a C5, n~20, PDI~1.2, 20μm thick sample, aligned in 17T. The sample correspond to a uniaxially monodomain with $S_D \sim 0.999$.

In the nematic phase of SCPLCs, the mesogene moieties are orientation correlated within an average correlation volume, the strength of this local order being described by the nematic or local order parameter S_N. Because $\Delta\chi \cdot B^2 << k \cdot T$ it is generally accepted that the magnetic field leaves the local order unchanged, $S_N \neq S_N(B)$, but changes the orientation of an entire correlation volume, affecting the director order parameter, $S_D = S_D(B)$, the total order parameter being a convolution between the local order parameter and the director order parameter: $S(B) = S_N \cdot S_D(B)$ [5,6]. The polymeric backbone does not contribute actively to the mesophase and is not directly influenced by the magnetic field. Its presence will rather hinder the mesogene degrees of freedom. Because the free volume per molecule in the mesophase does not allow a free molecular rotation, any change of mesogene orientation needs to be accompanied by local rearrangement of the surrounding polymer chains.

In the absence of an external magnetic field, the IN transition of SCPLCs is a two step process [7]. A volume fraction of the sample undergoes a sharp first order jump at a fixed temperature, T_{IN}, via nucleation of nematic islands at equilibrium with the surrounding isotropic phase. The rest volume fraction of the sample changes continuously from isotropic to nematic over a large temperature range, via a growth mechanism on the already existing nematic nuclei. The isotropic and nematic components have different refractive indices, causing incoherent light scattering on the interfaces. Toward the end of the biphasic region the sample volume is mostly covered by nematic islands, which have different orientations relative to each other. Light propagating through such media suffers massive scattering due to spatial variation of the refractive index. Investigated via scattered light, the IN transition appears as a monotonic decrease of transmitted light throughout the biphasic region, while no birefringence signal is produced due to the spatial average over the randomly oriented nematic director in different domains.

In the presence of a magnetic field the IN transition is modified. Due to a finite correlation length, induced order of the mesogene moieties develops already in the pre-transitional region. As T_{IN} is reached nematic islands nucleate and in the same time undergo orientation along the magnetic field lines. This results in a strong suppression of the local order parameter fluctuations and a larger volume fraction of the sample turns nematic at the T_{IN} temperature. The biphasic region shrinks accordingly in the absence of fluctuations and because there is less isotropic volume fraction left to turn nematic via the continuous growth process. As seen via optical measurements, the IN transition in magnetic field still shows an initial transmission decrease. But at the point where the nematic fraction becomes equal with the isotropic one, due to the fact that the nematic islands are oriented along a common director, a turn in transition occurs. From this point on, the transmission increases, corresponding to the second part of the biphasic region where the nematic component gets dominant, the sample has less scattering interfaces and the refractive index becomes uniform. At the end of the biphasic region, when the nematic islands meet each other, the sample becomes a monodomain with a uniaxial alignment along the magnetic field direction and the transmission saturates. In the presence of an applied magnetic field the birefringence signal is no longer zero due to a macroscopic orientation of the nematic director. Close to the T_{IN} the birefringence signal clearly reveals the pretransitional ordering followed by a sharp increase, corresponding to the ordering of the nucleating nematic islands. Away from the IN transition, the birefringence increase corresponds only to the strengthening of the nematic order, as revealed by fig.2 (inset) scaling law.

In comparison with the case of the low molecular weight liquid crystals or main chain polymer liquid crystals when an alignment via magnetic field is possible at any fixed temperature within the mesophase [6], our SCPLCs shows the need to be cooled over the IN transition to achieve magnetic field induced ordering. This indicates the existence of conformational barriers that mesogenes have to overcome, any mesogene rotation dictating a local rearrangement of the surrounding polymer chains. At the collective behavior of the mesogenes is partly developed, so they can respond to the magnetic field influence, while the conformational barriers are small due to a low persistence length of polymer chain entanglements.

CONCLUSIONS

The present results propose the possibility of SCPLCs processing via magnetic field ordering. Versus other traditional methods used to study and process liquid crystalline mesophases [4,5,6] such as surface fields, flow fields, electric fields or mechanical fields, the magnetic field features a unique combination of advantages: a clean, contact free method, which does not dissipate kinetic energy into the samples, it does not create electrodynamic instabilities and it makes no difference if the sample is a thin film or a bulk material.

We have shown that with a suitable choice of the chemical structure, namely flexible polymeric backbones, long enough spacer and low polymerization degree, ordered samples can be produced at industrial available magnetic fields. Such highly ordered samples are ideally suited for X-ray and neutron scattering experiments as well as for optical applications in the field of nonlinear optics, retardation-polarizer plates and alignment layers for low molecular weight liquid crystals.

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