Macromol. Symp. **2005**, 229, 93–98 DOI: 10.1002/masy.200551111

Microstructures Based on Thermotropic Liquid-Crystalline Polymers in the Low Molar Mass Nematogenic 5CB

Fabiano V. Pereira,[1] *Rodrigo Zandoná,*[1] *Redouane Borsali,*[2] *Aloir A. Merlo,*[1]
*Nadya P. da Silveira**[1]

Summary: The unique characteristics of two polyacrylates having the same side chain chiral mesogenics groups and different spacer lengths allowed the stabilization of ordered polymer rich-phases in solution with the nematic solvent 5CB. These microstructures are smectic having fibrous-like and rode-like morphologies, in spite of the mesophases of the polymers in bulk. The interactions between the mesogenic groups in the polymer and the solvent 5CB stabilize the microstructures and leads to birefringence at temperatures above the 5CB clearing point. Polarized optical microscopy data are complemented by SAXS to fully describe the mesomorphic behavior of the mixtures.

Keywords: lamellar; liquid-crystalline polymers (LCP); low molar mass nematogenic (LMMN); microstructure; polarized optical microscopy

Introduction

Composite systems comprising polymers and liquid crystal molecules are of great interest due to their important role in technological applications. A great number of polymer/low molar mass nematogenics (LMMN) composites have been already developed,[1] mostly as thin films. Their performance is highly dependent on the structure of the polymer chain in the liquid, which can be enhanced by applying different polymeric architectures, as well as different LMMN as solvent, depending on the organization envisaged. In this way, if the system contains a polymer liquid crystal, different ordered arrangements could be expected. The system known as polymer stabilized liquid crystals can be obtained with a simple mixture of the polymer in a liquid crystal solvent or by first dissolving a small amount of the monomer in an LMMN and then performing thermally or photoinduced polymerization giving rise to a polymer network.[2,3] Theoretical and experimental works focusing such composite systems were performed in the past[4–10] with most papers exploring the different phases in those systems as a function of polymer concentration through phase diagrams.[5–10] In a polymer/LMMN composite, it is known that polymer chains tend to form a network that aligns the liquid crystal.[11] There is also a tendency of the chain to be aligned with the field of the LMMN defining an anisotropic shape for the polymer.[12] The degree of anisotropy depends on the polymer backbone flexibility, molecular weight, spacer length, and if the polymer exhibits nematic or smectic phases. For the mixtures containing a liquid-crystalline polymer, the average nematic axis is defined by the director *n* of the LMMN; and although the polymer chains exhibit a distribution of orientations,

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[1] Instituto de Química, Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves, 9500, CEP 91501-970-Porto Alegre-RS, Brazil
E-mail: nadya@iq.ufrgs.br
[2] LCPO-CNRS-ENSCPB, Université Bordeaux (UMR5629), 16 Avenue Pey Berland, 33607 Pessac, France

the mesogenic groups in the polymer tend to orient parallel to the vector director of the liquid crystal solvent.[12]

The aim of this work is to demonstrate the organization of microstructures formed by two different chiral side chain liquid-crystalline polymers (SCLCP), P_{11M} and P_{4M}, in 4′-*n*-pentyl-4-cyanobiphenyl (5CB) by means of polarized optical microscopy (POM). The POM technique allows a good understanding of the system, describing the mixtures according to the formed textures from the classic morphologies found in neat liquid crystals.[13,14] Small angle X-ray scattering (SAXS) results already obtained are applied to complement the POM data.[15] The polymer P_{11M} contains 11 alkyl carbons as spacer group and presents a chiral smectic A phase (SmA*), whereas P_{4M} has 4 alkyl carbons as spacer group and presents a chiral nematic phase (N*). At room temperature, 5CB is a nematic solvent while P_{4M} and P_{11M} are both glassy materials. General chemical structures are given in Figure 1.

Experimental Part

The chiral SCLCPs were synthesized using radical polymerization of a mesogenic acrylate monomer in solution. Details of the synthesis are described elsewhere.[16–18] The LMMN 5CB was purchased from Aldrich Chemical and used as received. The mesomorphic properties of the neat SCLCP and LMMN are given in Table 1. They were determined using POM, differential scanning calorimetry (DSC), and SAXS. 5CB is nematic at room temperature, until 35 °C, P_{11M} presents a smectic A phase between 60.7 and 110.3 °C, whereas P_{4M} is nematic between 43.8 and 81.2 °C.

The mixtures containing 2 wt.-% of SCLCP were prepared as given elsewhere.[15] A known amount of each SCLCP was mixed with the correspondent LMMN and the samples were heated above the LMMN clearing temperature. They were then ultrasonicated at least 12 h to give a homogeneous and miscible mixture in the isotropic state of the solvent. The mixtures were placed between glass slides, without any previous treatment. Optical textures were observed through a polarizing microscope Olympus BX41 equipped with a programmable Quasar MT300 heating stage. The sample holder was heated with a cartridge heater and the temperature was monitored by a thermocouple. A macroscopic phase separation takes place for concentrations above 5 wt.-% of polymer.

Results and Discussion

Figure 2 shows the polydomain textures of P_{11M}/5CB (a–d) and P_{4M}/5CB (e–h) thin

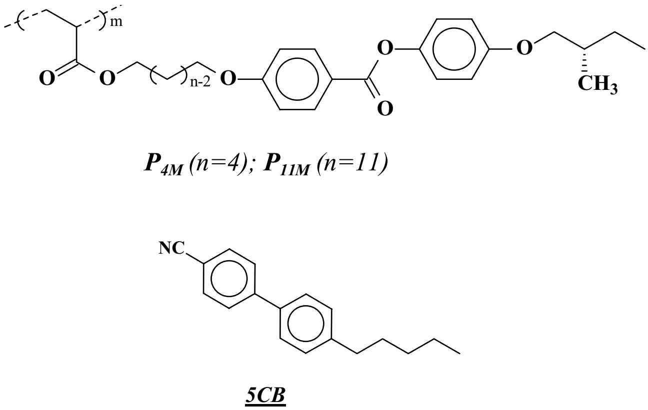

Figure 1.
General chemical structures of the chiral side chain LCP P_{4M} ($n = 4$) and P_{11M} ($n = 11$) and the LMMN 5CB.

Table 1.
Molecular weights (g · mol^{-1}) and mesomorphic properties (°C) of the neat polymers, solvent, and the mixtures.

	M_n	g	SmA		N	I
P_{11M}	25 780	·	60.7	·	110.3	·
P_{4M}	10 570	·	43.8	·	81.2	·
5CB	236	·	21.5	·	35.0	·
P_{11M}/5CB	-		a	·	65	·
P_{4M}/5CB	-		a	·	64	·

g = glassy state; S_m = smectic phase; N = nematic phase; I = isotropic phase. For the polymers, M_n was determined from size exclusion chromatography and transition temperatures were obtained from DSC measurements. Data for the neat 5CB were taken from the literature. a, SmA at room temperature.

films in different temperatures and 45° to the polarizer/analyzer axis. The bars in each micrograph indicate the scale.

The optical texture taken at 27 °C in the Figure 2(a) was obtained in the cooling and exhibits a focal conic fan-shaped texture from a smectic arrangement in the P_{11M}/5CB mixture. When 5CB becomes isotropic, above 37 °C, organized microstructures can be observed. Their appearance is showed in the micrographs taken at 43 and 55 °C [Figure 2(b) and (c), respectively], obtained by heating. The black regions in these micrographs correspond to the 5CB isotropic phase and the fibrous-like microstructures are the polymer-rich phase. Close to the $T_{\text{Sm-I}}$ transition of the polymer-rich phase [59 °C, Figure 2(d)], there is a continuous change in the shape of the fibrous structures and the number of ordered domains is reduced by temperature increase. A focal conic texture [similar to Figure 2(d)] can be observed until 65 °C where the system becomes fully isotropic. At this temperature, thermal agitation is enough to destroy order.

In a recent work, McCormick et al.[4] studied a liquid crystal monomer polymerized in the presence of the 8CB smectic solvent and observed similar optical textures. Their sample could be heated well above the isotropic point of the 8CB with continued birefringence. They have proposed that the liquid crystal molecules interact with the ordered polymer and retain order, inducing a high degree of birefringence at temperatures as high as 90 °C. The mixtures P_{11M}/5CB and P_{4M}/5CB were also studied using SAXS and the results are described elsewhere.[15] The results show that the P_{11M} maintains the smectic arrangement already observed in the bulk in the presence of the nematic 5CB, with a swollen smectic spacing layers in the entire temperature range studied.[15] In this way, there is an interaction between the mesogenic cores of the solvent and the polymer, inducing the formation of the polymer-rich phase microstructures, formed by both polymer and solvent. The swollen layers observed in the mixtures P_{11M}/5CB are a strong evidence that 5CB should be also between the layers formed by the backbone ribbons of the P_{11M} side chain polymer. This interaction between the dissimilar mesogens stabilizes the microstructures until temperatures are well above the isotropic of the solvent, as shown in the Figure 2(c) and (d). All these results suggest an orientational coupling between the polymer and the nematic field of the solvent.

Table 1 gives the temperature transitions (obtained on heating using POM) for the mixtures P_{11M}/5CB and P_{4M}/5CB. Attempts to measure these temperatures using DSC failed due to the relatively low concentration of the polymer. In Table 1, whereas the $T_{\text{Sm-I}}$ transition is related to the smectic-isotropic phase transition of the microstructures, the $T_{\text{N-I}}$ is related to the nematic-isotropic phase transition of the 5CB. The $T_{\text{Sm-I}}$ of the microstructures was found to be 65 and 64 °C for P_{11M}/5CB and P_{4M}/5CB, respectively. These results show that the interaction between the dissimilar mesogens is strong enough to stabilize the microstructures up to temperatures as high as 64 °C, well above the clearing point of the neat 5CB (35 °C). The same $T_{\text{Sm-I}}$ temperature phase transitions were found using SAXS.[15] The $T_{\text{N-I}}$ related to the 5CB in both mixtures is 2 °C higher than in the neat solvent. The increase in the $T_{\text{N-I}}$ temperature is a

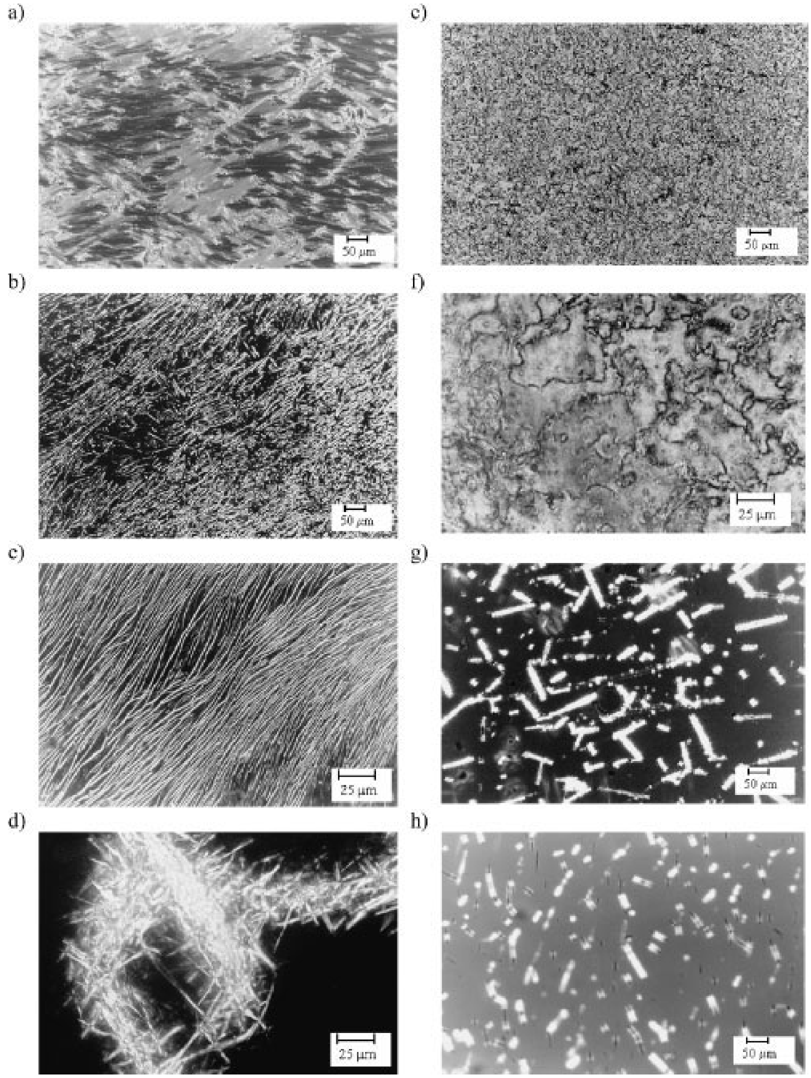

Figure 2.
Textures evolution as a function of temperature for P_{11M}/5CB mixtures (a) 27 °C; (b) 43 °C; (c) 55 °C; (d) 59 °C; and for P_{4M}/5CB mixtures (e) 28 °C; (f) 32 °C; (g) 39 °C; (h) 48 °C.

common phenomenon after adding solutes to an LC solvent.[4]

The appearance of microstructures is also observed in the P_{4M}/5CB sample. Figure 2(e) and (f) show Schlieren textures at 28 and 32 °C obtained on cooling. For higher temperatures, where the solvent becomes isotropic, microstructures like battonets suspended in the isotropic matrix of the solvent can be seen. They are depicted in Figure 2(g) and (h) taken at 39 and 48 °C, respectively, during heating. Structures like battonets are recognized in the literature as characteristic of a layered smectic phase when a liquid crystal is in the neighborhood of the isotropic phase.[13]

A classical smectic focal conic texture was not possible to observe in a higher temperature range ($T > 37$ °C) due to the relatively low concentration of P_{4M} in the mixture (2 wt.-%) if compared to another systems, like PDLCs.[1] In the temperature range where the solvent is nematic [$T < 37$ °C, Figure 2(e) and (f)], the microstructures could not be observed by POM due to the Schlieren nematic texture of the solvent, which represents 98 wt.-% of the mixture. However, our complementary SAXS data[15] showed clearly that the organized microstructures having a layered smectic order are present in the entire temperature range studied, even when the solvent is nematic. The lamellar arrangement in this mixture is, of course, induced by the nematic solvent since the smectic phase is forbidden in the bulk P_{4M}. In this way, combined POM and SAXS results show the coexistence of two mesophases (nematic/smectic) in the temperature range where 5CB is nematic.

It is thus remarkable that the interaction between both polymers and 5CB are of the same type in nature, leading to the formation of microstructures, which remain suspended in the isotropic matrix of the solvent at high temperatures. A similarity in the interaction was expected since P_{4M} and P_{11M} posses the same mesogenic lateral groups. The only difference between them is the number of carbon atoms as spacer group. In this case, we can stand out the influence of the spacer group size in the neat polymers and in the mixtures with the nematic solvent. As it is known,[13] a flexible spacer in SCLCPs decouples the lateral mesogenic group from the backbone and allows the development of positional order in the backbone ribbons. For this reason, the neat P_{11M} polymer has lamellar arrangement (smectic) whereas in the neat P_{4M}, which has only four carbon atoms as spacer, the smectic phase is prohibited. For the mixture P_{11M}/5CB, the smectic phase is maintained and the interaction between the dissimilar mesogens leads to a swell of the lamellae in the polymer-rich phase, forming a fibrillar structure. The same interaction between the 5CB moieties and the lateral mesogenic groups in the P_{4M} induces the formation of rod-like structures (battonets) with an injected smectic phase. This interaction stabilizes the polymer-rich phase microstructures and the smectic ordering induced is retained at temperatures well above the isotropic of the 5CB solvent, as shown in Figure 2(g) and (h).

This interesting phenomenon of induced smectic phase from the mixtures of two nematics components has been described in the literature in some theoretical works[11,19] and only a few experimental works[7,20] involving mainly LCs of low molar mass. This phenomenon is described as a consequence of strong van der Waals interactions[11] between dissimilar mesogens. In this context, the interaction between the mesogens in the P_{4M} and the nematic field of the 5CB solvent is strong enough to modify the backbone conformation of the nematic polymer and allows the development of positional order between the backbone ribbons, creating a smectic phase in the polymer-rich phase.

The difference in morphology observed in the different mixtures suggests a higher degree of order in the P_{11M}/5CB mixture. The morphology of the microstructures in this mixture being fibrous may be due to the presence of more flexible spacer group in the polymer that improves the order in the system.

Conclusion

In this paper, we have shown the texture evolution of mixtures formed by a nematic (P_{4M}) and a smectic (P_{11M}) side chain liquid-crystalline polyacrylates as a function of the temperature. The polymers have the same lateral mesogenic groups but different spacers.

The results show that there is a strong orientational coupling between the lateral mesogenics groups of the polymers and the 5CB moieties. These interactions that are similar in nature for the mixtures, result in a change in the conformation of the backbone for both polymers and the formation of polymer-rich phases (microstructures).

In the temperature range where the solvent is nematic, the P_{11M}/5CB mixture presents a focal conic texture whereas the P_{4M}/5CB mixture shows a shilieren nematic texture. However, complementary SAXS results showed that the nanoscale arrangement for both mixtures is lamellar in the entire temperature range studied.

When the solvent becomes isotropic the microstructures can be easily observed using POM. Both polymer-rich phases are smectic and the morphologies are fibrous-like for P_{11M}/5CB and rod-like for P_{4M}/5CB.

The microstructures in the P_{11M}/5CB are formed by swollen layers of the polymer. In the same way, the microstructures in the P_{4M}/5CB mixture are formed with an interesting induced smectic phase in the backbone ribbons of the P_{4M}. The interactions between dissimilar mesogens stabilize the microstructures until temperatures well above the clearing point of the 5CB.

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