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Introduction of unusual properties into polymers by the use of liquid-crystalline moieties

G Palaprat, M Weyland, T Phou, C Binet, JD Marty, AF Mingotaud and M Mauzac*

Laboratoire Interactions Moléculaires et Réactivité Chimique et Photochimique, UMR CNRS 5623, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse, France

Abstract: The introduction of mesogenic substituents on polymer backbones facilitates the formation of materials with anisotropic properties. At the same time the polymer chains are connected each other through these substituents in a transient network. The properties of the polymer material, such as the mechanical response or conductivity, are modified by the presence of the liquid-crystalline groups and can be tuned by changing the organisation of the mesogenic groups. Crosslinking the polymer in the liquid-crystalline state induces the manifestation of some memory effect. These phenomena were used for improving the mechanisms of recognition in molecular imprinted materials.

Keywords: liquid-crystal polymers; conductivity; mechanical properties; molecular imprinting technique

INTRODUCTION

The design of so-called intelligent materials, the properties of which can be controlled by the operator, has been and is still now the subject of many studies. To reach such a goal, one way is to combine the specific characteristics of the polymers with the orientational behaviour of the liquid-crystalline state.

Numerous structures, divided into two families, are conceivable for developing mesogenic polymer materials: main-chain liquid-crystalline polymers, in which the mesogenic moieties are located in the backbone, and side-chain liquid-crystalline polymers (Fig. 1a), in which they are linked to the polymer support via a flexible spacer, allowing the mesomorphic organisation to set up.^{1,2} In the latter family, the specific properties of the polymer chain are preserved and can be combined with the liquid-crystalline order. In such polymers, the different chains are in interactions through their mesogenic substituents, which are trapped in mesomorphic domains. The mesogenic groups can either be macroscopically disoriented in the liquid crystalline state (so-called poly-domain samples) or macroscopically ordered (so-called mono-domain samples). If the mesogenic groups are macroscopically oriented, any manifestations of the interaction between the polymer backbone and the mesogenic side-chains can be transmitted to the macroscopic level. On the molecular

scale, an anisotropy of the global conformation of the polymer chain can be induced and the intrinsic properties of the chain can be modified. The architecture of the material allows one to predict the sign of this anisotropy:³⁻⁸

- ‘Side-end’ materials, in which mesogens are linked to the backbone by one of their end-groups, essentially exhibit smectic lamellar structure. It has clearly been shown by neutron-scattering experiments that in the oriented mesophase the backbone is rather well confined, as flat discs, between the smectic layers.³⁻⁵
- ‘Side-on’ materials, in which mesogens are laterally attached, essentially form nematic phases. The backbone in the oriented nematic state appears in this case to be strongly elongated in the direction of the mesogens.⁶⁻⁸

In side-chain liquid-crystalline networks (Fig. 1b), the polymer chains bearing the mesogenic groups are covalently linked by flexible or mesogenic-like crosslinkers.⁹⁻¹³ If the cross-linking density is low enough, these networks preserve the mesomorphic order of the liquid crystalline phases. In such networks, a memory function is introduced which relates to the conformation of the polymer chains at the points of crosslinking.^{13,14} The crosslinking biases the structure

* Correspondence to: M Mauzac, Laboratoire Interactions Moléculaires et Réactivité Chimique et Photochimique, UMR CNRS 5623, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse, France
E-mail: mauzac@chimie.ups-tlse.fr

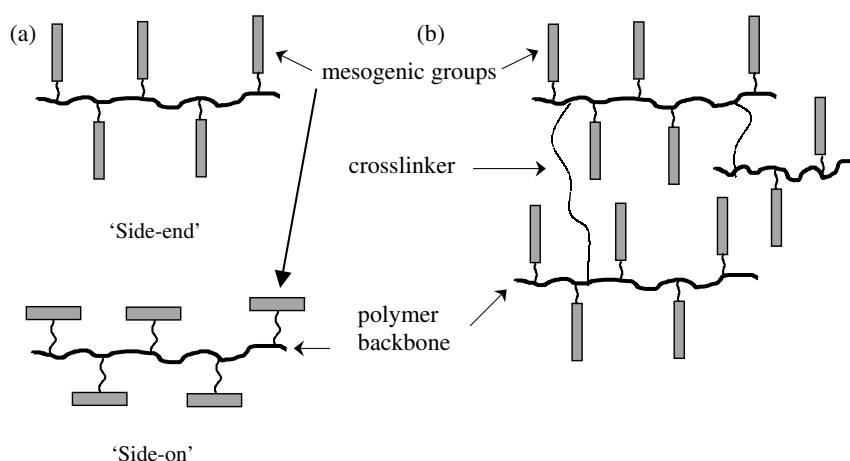


Figure 1. (a) 'Side-end' and 'side-on' architectures of liquid-crystalline polymers. (b) Example of side-chain liquid-crystalline networks.

towards the backbone conformation present at the time of network formation. Any distortion of this conformation is opposed by the elasticity of the network. Consequently, a number of phenomena have been observed, including reversible electrically induced shape changes,¹⁵ strain-induced switching,¹⁶ transfer of chirality¹⁷ and memory effects.^{18–23}

This article presents the unusual behaviour of mesogenic polymers on three examples that are developed in our laboratory. They demonstrate how the introduction of mesogens could be taken into account to modify some physical properties (conductivity, mechanical characteristics) of polymer materials or to improve the efficiency of materials used for molecular recognition.

ANISOTROPY OF CONDUCTIVITY IN LIQUID-CRYSTALLINE CONDUCTING POLYMERS

Orientation techniques (polymerisation in an oriented nematic solvent, mechanical stretching of the polymer, deposition of the material on oriented surfaces) are commonly used on conducting polymers to improve the conductivity and/or to induce an anisotropy of this property. Grafting mesogenic groups onto conducting polymers is of special interest because of the potential for intrinsic combination of the electrical properties and the orientational behaviour. We illustrated this point on two different (side-end and side-on) mesomorphous polypyrroles.

The liquid-crystalline monomers (Fig. 2a) were first spread on a metallic support used as electrode, oriented in the mesomorphous phase by a magnetic field of 1 tesla and then polymerised *in situ* by exposing the monomer to iodine vapour^{24,25} (at the end of the reaction, the excess of iodine was removed under dynamic vacuum). By varying the direction of the magnetic field, two orientations of the mesogenic moieties were obtained: the samples in which the mesogenic groups were oriented in one of the directions of the plane of the electrodes are called 'planar'; and those in which the mesogens were

perpendicular to this plane are called 'homeotropic'. The obtained polymers exhibited molar masses around $5 \times 10^4 \text{ g mol}^{-1}$. They were shown to contain the I_3^- species at a ratio of one I_3^- for every three monomer units,^{24,25} without possible location of these species inside the polymer material.

Static conductivity (DC conductivities) measurements were carried out using the four-probe technique (Fig. 2b). The obtained values were low, probably due to the fact that in such hindered and ordered structures the doping phenomena have trouble in setting up.

On the other hand, regardless of the architecture of polymers ('side-end' or 'side-on'), a large anisotropy of conductivity was observed when comparing planar and homeotropic alignment measurements.²⁵ In the case of 'side-end' polypyrroles, which presented a smectic A mesophase, the conductivity obtained in the planar configuration was about seven times greater than that of non-oriented or homeotropic samples. In the oriented mesophase, the chains are well confined between smectic layers: the gyration radius of the main chain, determined by neutron-scattering experiments, was found to be four times higher in the plane perpendicular to the axis of the mesogens than in the direction of the mesogens.²⁶ Thus the orientation process induced a strong anisotropy of the backbone and as a result the chains were globally present in the planes perpendicular to the electrodes, which favours conductivity. 'Side-on' polypyrroles exhibited the opposite behaviour: the best conductivity was obtained for the sample in a homeotropic configuration. This sample is nematic and the main chain is strongly stretched in the direction of the mesogens, which means parallel to the electrodes. In all cases, the anisotropy of conductivity, which is due to the coupling between the mesogenic order and the polymer backbone, disappeared in the isotropic state.

This study of liquid-crystalline conducting polypyrroles pointed out that the lateral substitution of a conductive polymer with mesogenic groups is an effective way to create an anisotropy of conductivity. This anisotropy could be controlled by the architecture of the side-chain polymer.

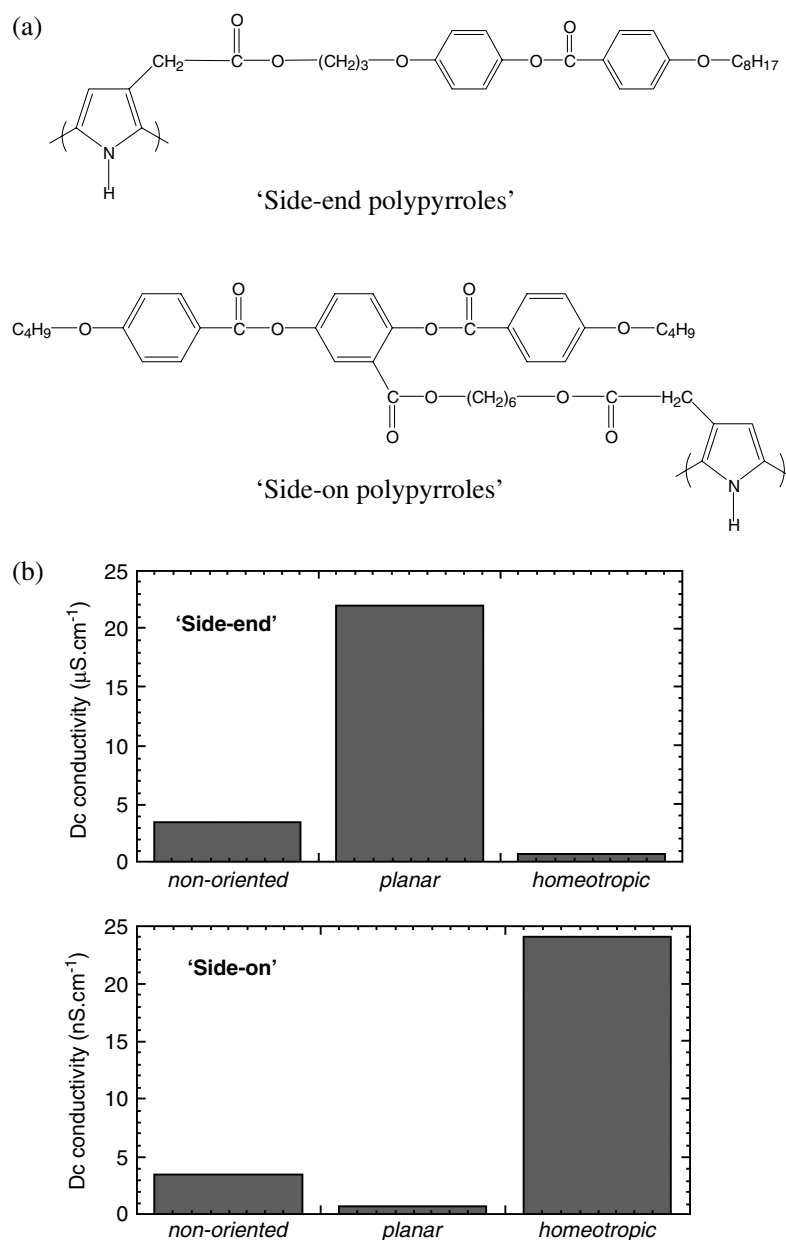


Figure 2. (a) Chemical structure of the side-end and side-on polypyrroles. (b) Static conductivities for different orientations of 'side-end' and 'side-on' mesomorphous polypyrroles.

MECHANICAL PROPERTIES OF LIQUID-CRYSTALLINE POLYMERS

In mesogenic polymers, it has been shown that the interactions between liquid-crystalline side-chain groups induced significant modifications of the mechanical behaviour when compared to 'classical' polymers. The side-chain mesogenic polymers appeared to behave like gels below their gelation point.^{27,28}

If crosslinks are introduced (example in Fig. 3a), the liquid-crystalline networks display remarkable elastic properties^{29–31} due to the mesomorphic order. For example, a transition from a poly-domain to a mono-domain can be induced by a strain field, which couples itself directly to the mesomorphic order. Rheological experiments made in a wide frequency range with nematic samples showed that the mono-domain

samples presented marked anisotropy of the shear modulus.^{32–35} This anisotropy stems from the fact that the director is coupled to the local shear flow when the sample is sheared in a direction parallel to the director, and not when the sample is sheared in a direction perpendicular to the director.

Whether the networks were poly-domain or mono-domain samples, the results obtained by rheological experiments in the isotropic and nematic phases showed that the real part of the shear modulus is the sum of two terms:^{32–34,36} one is frequency-independent and reflects the permanent network; the other depends on the frequency and gives rise to scaling behaviour ($G' \sim G'' \sim \omega^{0.5}$). The dynamic behaviour of the smectic A phase was completely different and characterised by a $\omega^{0.3}$ scaling law. It is governed by the transient smectic network

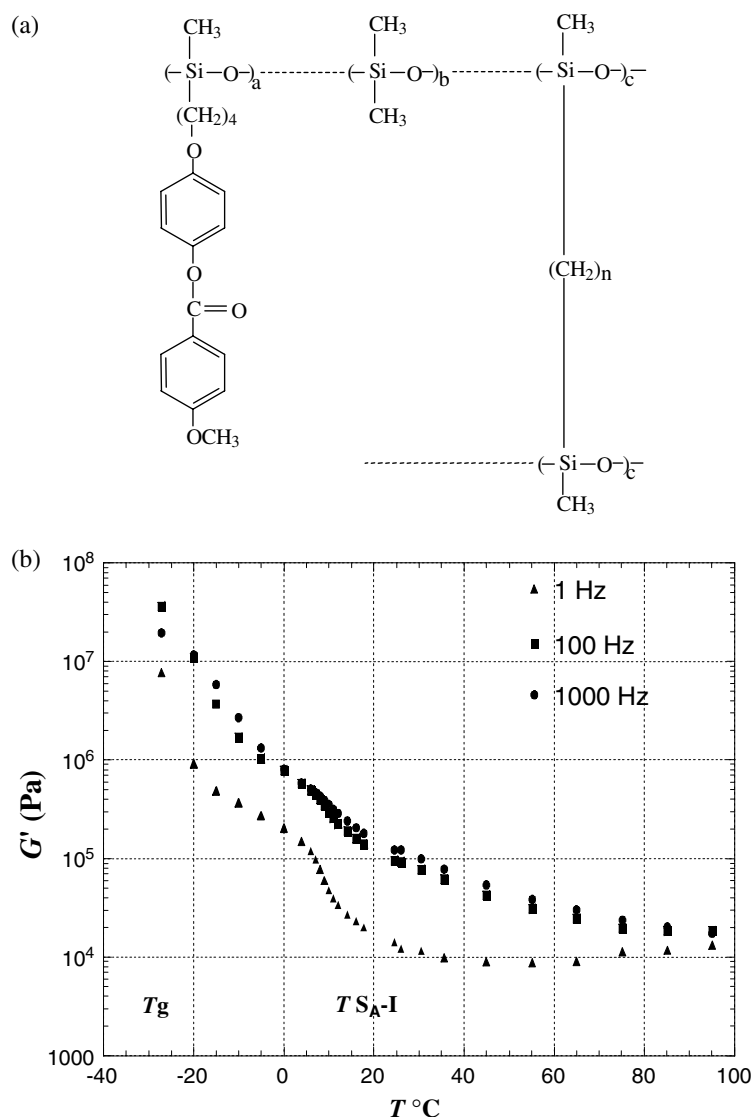


Figure 3. (a) Chemical structure of the studied liquid-crystalline network. (b) Temperature dependence of the elastic modulus G' for the liquid-crystalline polysiloxane network taken at various frequencies.

with a very long lifetime. The contribution of this transient network to the shear modulus is greater than that of the permanent network. This network stems from the fact that different polymeric backbones are connected through their mesogenic groups, which are trapped in different smectic layers or smectic domains.³²

The effect of the mesomorphous order is clearly visible on the thermal evolution of the mechanical response. For example, Fig. 3(b) shows the temperature dependence of the real part G' of the shear modulus observed at different frequencies from a liquid-crystalline polysiloxane network; G' is controlled by the dynamics of the glass transition on the whole temperature range under study, with an anomaly near the smectic A/isotropic transition for the lowest frequency. This anomaly, which is not observed near the nematic–isotropic transition,^{34,36} reflects the disappearance of the lamellar structure associated with the smectic A phase. It has also been observed at the nematic–smectic A transition on samples exhibiting a

nematic phase.³⁶ The anomaly in G' is only observed at 1 Hz because at the other frequencies it becomes almost hidden by the dynamic glass transition.

This study of mechanical properties of liquid-crystalline polymers shows the influence of the mesomorphic order, especially the smectic order, on the response of the material. Moreover a strong anisotropy of the shear modulus was observed in macroscopically ordered networks.

MOLECULAR IMPRINTED LIQUID-CRYSTALLINE POLYMERS

The molecular imprinting technique allows the preparation of synthetic materials mimicking the natural processes of molecular recognition (Fig. 4). The principle consists of polymerising and crosslinking functional monomers, previously positioned by low-energy or covalent interactions around a molecule—the template molecule—so as to ‘freeze’ the imprint. Following extraction of the template molecule, the

side-chain orientation. As a result, in such liquid-crystalline imprinted materials the template can be extracted without losing the imprinted information even with low crosslinking ratios (5–10 mol%).

Such liquid-crystalline imprinted materials were synthesised (Fig. 5) from polysiloxanes with mesogenic side-end groups. In some of them, the template (acetophenone) was covalently linked to the mesomorphous network.⁴² In the others, the templates (carbobenzoxy-L-phenylalanine, 1,8-diaminonaphthalene or theophylline) were in interaction with the mesomorphous polymer via hydrogen bonding.⁴³ All the imprinted networks were obtained as dense membranes. It was observed that a high proportion of template (10 mol%) can be introduced without losing the mesomorphic order. Moreover, after template extraction, the polymorphism was quite different from that of the non-imprinted material, the variations depending on the structure of the template used and on its concentration. This is the manifestation of a significant memory effect of the template imprinted inside the mesomorphic structure. It arises from the interactions between the template and the other parts of the network which induce conformational constraints inside the networks during crosslinking.

Capacity and selectivity of the mesogenic imprinted materials

For all the synthesised materials, the molecular trapping capacity (up to $150 \mu\text{mol g}^{-1}$ of polymer) was shown to be much greater than that of most of the previously studied non-mesomorphous systems.^{44–47}

Concerning their selectivity, imprinted mesomorphous networks exhibited a much higher affinity towards the template than non-imprinted networks. Moreover, the networks showed higher selectivity for the template than for a closely related compound. For example, a liquid-crystalline network imprinted by theophylline (Fig. 6) exhibited a much higher affinity for theophylline than the non-imprinted sample

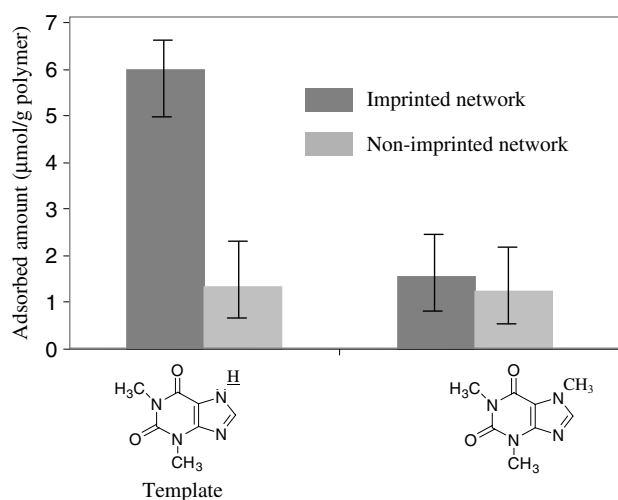


Figure 6. Molecular recognition properties of the network imprinted around theophylline compared to the non-imprinted one.

and a good specificity for theophylline towards structurally analogous caffeine. These results indicate that, in addition to the hydrogen bonding or electrostatic interactions between the functional groups and the template, microcavities corresponding to the shape of the template are necessary for effective binding. Consequently the polymer gained affinity for the template through the molecular imprinting technique. On the other hand, the molecular-trapping capacity of the networks ($6 \mu\text{mol g}^{-1}$ of polymer) was much greater than that of the previously non-mesomorphous studied systems ($1 \mu\text{mol g}^{-1}$ of polymer studied by Wang *et al.*^{48,49} and $0.057 \mu\text{mol g}^{-1}$ of polymer reported by Ye *et al.*⁵⁰).

Special case of chiral template

If the template has a chiral structure, it can induce a helical structure inside a nematic liquid-crystalline network, like a chiral dopant. Indeed it had been previously shown that a helical symmetry can be introduced by simply generating the liquid-crystalline network in an oriented chiral solvent.^{20–23} Mao and Warner⁵¹ discussed the ‘robustness’ of the imprinted phase chirality as a function of the helical twisting power of the dopant: the imprinting would be successful in the case of low helical twisting power, or equivalently, a large pitch. Using this type of macroscopically oriented cholesteric elastomer, Courty *et al.*⁵² recently presented a study of separation of chiral isomers. They demonstrated the capacity of the material to preferentially absorb and retain the ‘correct’ chirality molecule from a racemic solvent.

Combining molecular imprinting and chiral induction, a cholesteric imprinted elastomer with a large helical pitch was obtained by crosslinking a nematic side-chain polysiloxane around the chiral *N*-(carbobenzyloxy)-L-phenylalanine template.⁵³ The sample was macroscopically oriented during the synthesis. Thus, both a molecular chirality and a supramolecular phase chirality were topologically imprinted inside the network.

Batchwise adsorption tests, performed by putting the polymer sample in a solution containing the template or the other enantiomer, showed that the imprinted polymer has a pronounced stereoselectivity towards the template enantiomer (Fig. 7). The rebinding capacity (around $2.5 \mu\text{mol g}^{-1}$ of polymer) appeared to be greater than that of a non-imprinted mesogenic network ($1 \mu\text{mol g}^{-1}$ of polymer) as well as that of an imprinted non-mesogenic one (at best around $1 \mu\text{mol g}^{-1}$ of polymer⁵⁴). Moreover, in this case of liquid-crystalline imprinted material, the amount of imprinted sites was low and could easily be increased.

In imprinted materials, molecular separation occurs by recognition phenomenon inside the molecular imprinted cavities as well as by diffusion mechanism through the polymer matrix. The first mechanism is provided by steric interactions between the ligand and the functional groups inside the pre-formed imprinted

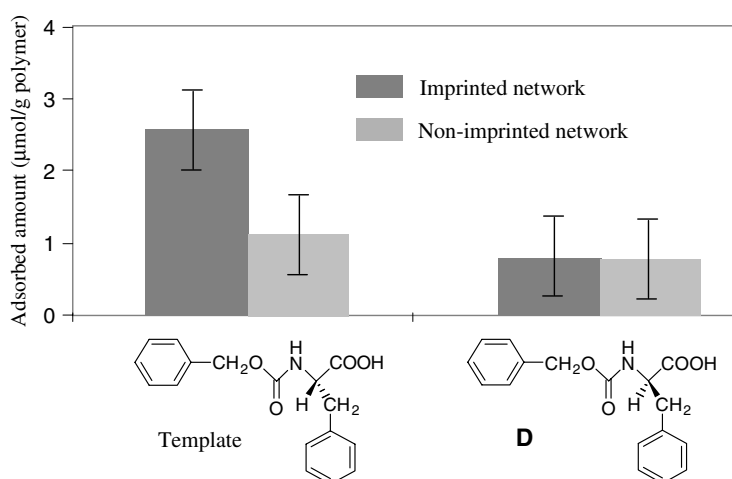


Figure 7. Adsorbed amount of the L and D enantiomers of *N*-(carbobenzyloxy)-phenylalanine by the mesomorphous network imprinted around L-form compared to the non-imprinted network.

micropores. Relative to the second mechanism, the liquid-crystalline environment should have several effects: the interactions between the mesogens act as physical crosslinkers, allowing a decrease of the amount of chemical cross-linkers and consequently an increase of the capacity of the material. Moreover, the template would be easily extracted by use of a solvent that swells the network or by heating the network above the liquid-crystal/isotropic transition. In the case of chiral template, liquid-crystalline organisation should induce a specific supramolecular structure in the polymer matrix that should participate in the selectivity of the imprinted material.

CONCLUSION

Liquid-crystalline polymers appeared as macromolecular organised systems in which the mesomorphic supramolecular structure can be macroscopically ordered or not. This internal organisation allows the tuning of the intrinsic properties of the polymer material or the inducement of new behaviours.

Via interactions between the mesogens, the polymer backbones are connected together as in physical networks and, at the same time, are trapped in nematic or smectic domains. This internal organisation depends on temperature and can be reversible. The anisotropic behaviour can be extended to the macroscopic level and induce a large modification of the conformation of the main chain. The intrinsic properties of the polymer material, such as the mechanical response or the conductivity, appear to be significantly modified. Moreover, due to the coupling between the mesogens and the backbone, some memory effects can be introduced by crosslinking the material in the liquid-crystalline state. We have shown in this paper that these effects are beneficial to the molecular imprinting technique.

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