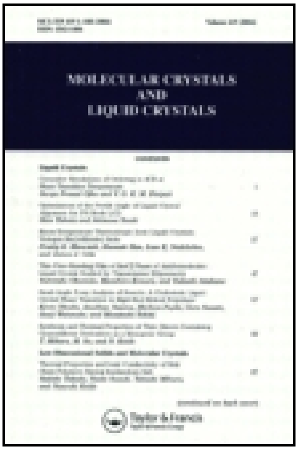

Molecular Crystals and Liquid Crystals

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Liquid Crystalline Networks: Potential uses in Molecular Imprinting Technique

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LIQUID CRYSTALLINE NETWORKS: POTENTIAL USES IN MOLECULAR IMPRINTING TECHNIQUE

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A novel approach to the synthesis of molecularly imprinted polymers via covalent or non-covalent linkages was studied. It relies on the use of thermotropic side-chain liquid-crystal polymer networks. The polysiloxane networks obtained after extraction of the template preserved the mesomorphic organisation set up in the presence of the guest molecule. Batch rebinding analysis were performed: this study revealed that the imprinted polymer has a much greater affinity for the template molecule than the unimprinted one, and a significant selectivity.

Keywords: liquid crystal side-chains networks; molecular imprinting; siloxane

1. INTRODUCTION

The molecular imprinting technique (MIT) is a valuable polymerisation method for preparing synthetic materials able to mimic the molecular recognition phenomena present in living systems [1–3]. In this technique, a molecule (template) is associated with functional monomers to form a ‘complex’. A cross-linker is added and the polymerisation/cross-linking reaction is performed around the complex (Fig. 1). Upon removal of the template species, functionalised cavities that have memorised the spatial features and bonding preferences of the template are left inside the network. These imprinted materials are used as chiral stationary phases in chromatography [4], as sensors in detecting devices [5], as well as materials for stereoselective reactions or as catalysts [6–8].

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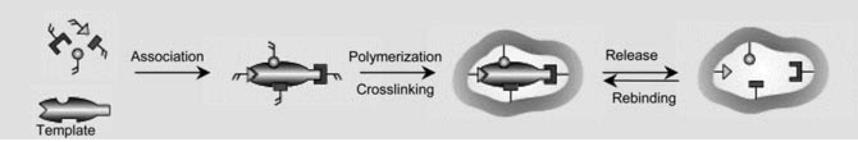

FIGURE 1 Principle of the molecular imprinting technique (MIT).

Most of the drawbacks in MIT have been linked to the need for a large amount of cross-linking agent (usually around 80–90%) to restrict distortion phenomena of the polymer backbones [1,9]. The resulting stiffness of the network hinders the mechanisms of extraction and reinsertion of the template in the imprinted cavities and drastically decreases the capacity of the material.

In order to soften the network while preserving the memory of the template, the use of liquid-crystal networks in MIT appears to be a useful tool. In such systems, the interactions that developed between mesogenic substituents conferred a stiffness on the network through non-covalent reversible interactions [10]. Moreover any manifestations of the interaction between the polymer backbone and the mesogenic side-groups can be transmitted to the macroscopic level providing that chemical cross-links are introduced in the mesomorphic state [11]. The effect of cross-linking biases the structure towards the backbone configuration present at the time of network formation. Any distortion of this configuration is opposed by the elasticity of the network and the material presents some memory effects [12–15].

In such materials used in MIT, larger amounts of template could be introduced and extracted without losing the imprinted information, even with low cross-linking ratios.

2. EXPERIMENTAL

Several liquid crystalline imprinted materials were synthesized (Fig. 2). For that purpose, we chose side-chain liquid-crystal polysiloxanes in which mesogenic units were end-fixed onto the polymer backbone. In some of them acetophenone was chosen as a template and was linked covalently to the mesomorphous network thanks to a ketal link [16]. In the other polysiloxane networks, the templates were in interaction with the mesomorphous polymer via hydrogen bonding. Carbobenzoxy-L-phenylalanine, 1,8-diaminonaphthalene and theophylline were chosen as templates [17]. All the imprinted networks were obtained as circular membranes (diameter 2 cm, thickness 0.3 mm).

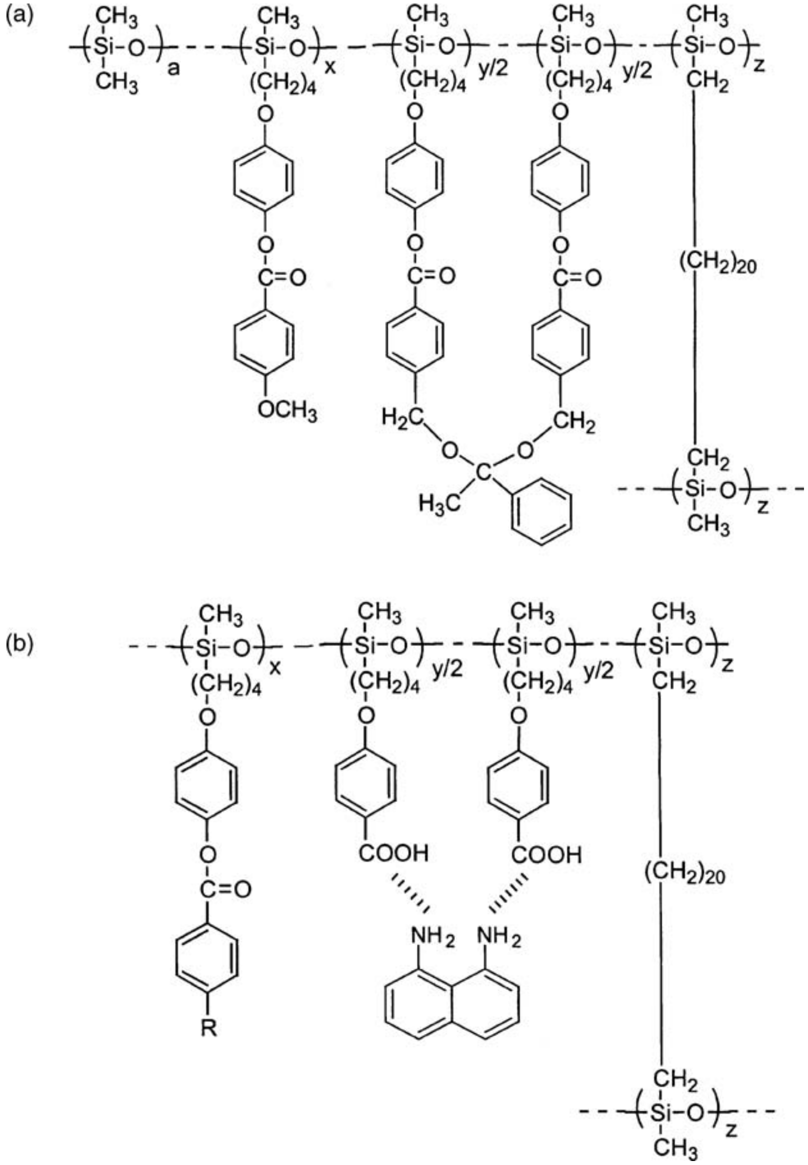

FIGURE 2 Chemical structure of a) a covalent imprinted network (template = acetophenone, a = 50%, x = 26%, y = 14%, z = 10%) b) a non-covalent imprinted network (template = 1,8-diaminonaphtalene, x = 87%, y = 8%, z = 5%).

3. RESULTS AND DISCUSSION

3.1. Morphology of the Imprinted Materials

Scanning electron micrography, microscopy (Fig. 3) and mercury intrusion porosimetry show dense, homogenous materials with no macro or meso porosity. The interactions between mesogenic moieties should explain these observations.

3.2. Polymorphism

Results were obtained from DSC and RX experiments. The mesomorphous properties of the resulting washed imprinted networks and reference non-imprinted materials were analyzed:

- a high amount of template (10%) can be introduced without losing the mesomorphic order [16].
- the polymorphism (transition temperature, enthalpy variations, layer spacing) of the washed imprinted network was quite different from the polymorphism of the washed non-imprinted network. The variations depended on the structure of the template used (the most important variations were observed with theophylline which has a structure far

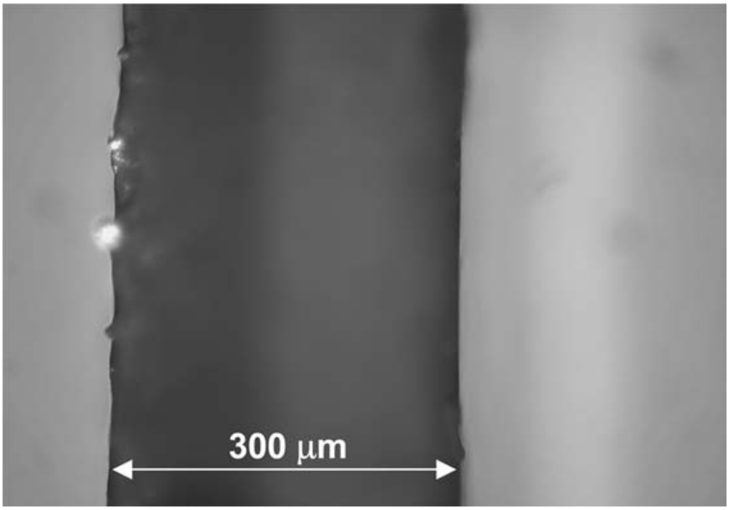

FIGURE 3 Side-view of a mesomorphous membrane obtained by optical microscopy.

removed from that of the mesogenic moieties) and on its concentration [17].

- after heating the samples in the isotropic phase during one hour, the isotropic-mesomorphic phase transition remained the same even after several thermal cycles [16,17].

The differences observed between imprinted and non imprinted materials are the manifestation of a significant memory effect of the template, imprinted inside the mesomorphic structure. This effect arises from the interactions between template and the other parts of the network which can induce conformational constraints inside the networks during cross-linking. It occurs even though the amount of cross-linker is low (5%).

3.3. Molecular Recognition Properties

Experiments of extraction of the template and batch rebinding studies were performed to define the selectivity and the capacity of the prepared networks.

For all the materials synthesised, the imprinted networks exhibit a much more higher affinity than the non-imprinted samples.

For instance, in the case of 1,8-diaminonaphthalene used as the template, the amount of this molecule rebound by the materials in the mesomorphic state, is reported in Figure 4. It is obvious that the non-imprinted network exhibits a significantly lower quantity of template uptaken compared to the imprinted network. These results indicate that, in addition to the hydrogen bonding or electrostatic interactions between the functional groups of the polymers and template, microcavities

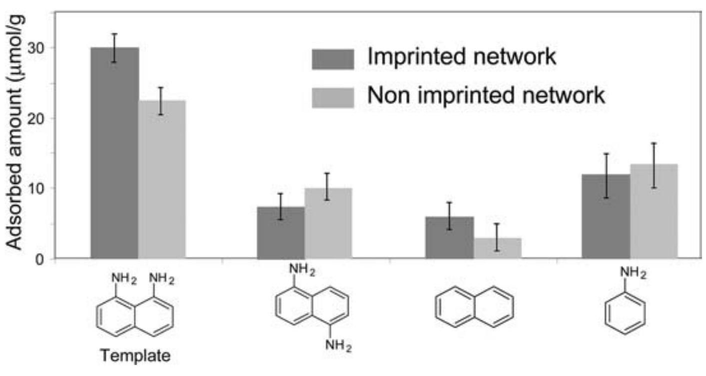

FIGURE 4 Molecular recognition properties of a mesomorphous network imprinted around 1,8-diaminonaphtalene compared to a non imprinted network.

corresponding to the shape of the template are necessary for effective binding. Consequently the polymer gained affinity for the template through the MIT.

Substrate specificity was investigated under the same conditions and the network showed higher selectivity for the template than for a closely related compound (Fig. 4). This demonstrates a specific imprinting effect similar to those usually observed with non mesomorphous networks.

Same other results, obtained when theophylline or carbobenzoxy-L-phenylalanine were used as templates, were shown in Figures 5 and 6.

On the other hand, the molecular trapping capacity of the networks (150 μmol/g of polymer) was shown to be much greater than that of the previously non mesomorphous studied systems (less than 100 μmol/g of polymer). Moreover, the imprinted network showed a high specificity with 40% of the sites able to take up the template molecule [16].

4. CONCLUSION

This study showed the potential of liquid-crystal polymer networks as materials in MIT. Analysis of the mesomorphic order underlined a memory effect of the liquid-crystal structure set up in the presence of the template that was preserved even after heating to the isotropic state. The rebinding studies, performed in the mesogenic phase, showed a significantly higher affinity of the imprinted material towards the template than the

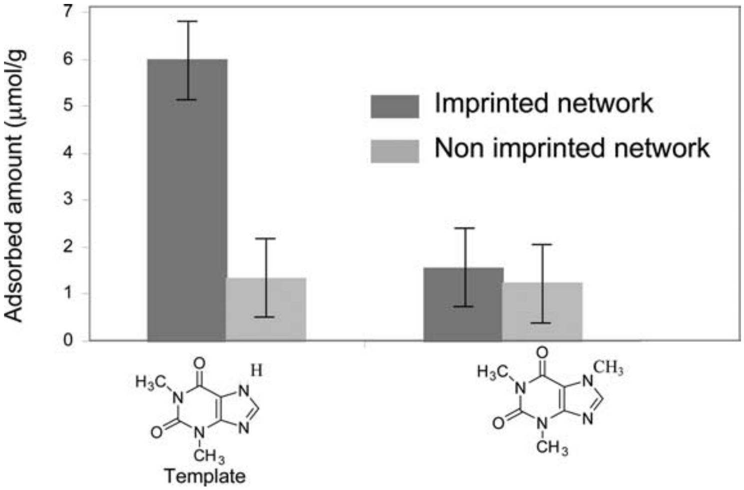

FIGURE 5 Molecular recognition properties of a mesomorphous network imprinted around theophylline compared to a non imprinted network.

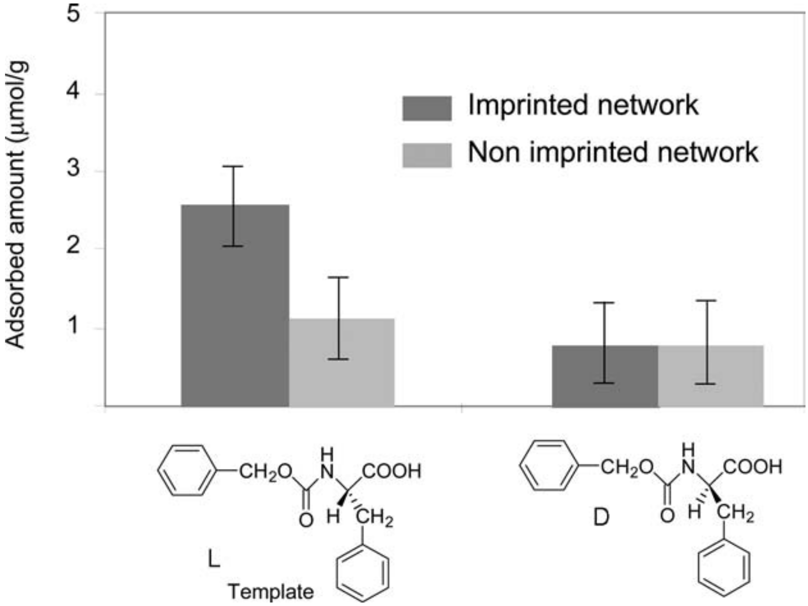

FIGURE 6 Molecular recognition properties of a mesomorphous network imprinted around carbobenzoxy-L-phenylalanine compared to a non imprinted network.

unimprinted material. The liquid-crystal polymer networks kept the memory of the template while preserving the flexibility of the network that consequently increased the capacity of the material. Moreover, these materials exhibited a good selectivity towards the printed molecule.

Some questions arise from these present results, especially the precise role of the pending mesogenic groups. Moreover, It may be possible to benefit specifically from the liquid-crystal character, either to use chiral supramolecular structure or to modify the interactions between the network and the template, by heating to the isotropic state for example.

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