Study of Hydrogen Bonding in Liquid Crystalline Solvent by Fourier Transform Infrared Spectroscopy

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A hydrogen-bonded complex between an aromatic acid and an enantiopure chiral amine has been dissolved in a nematic solvent, giving rise to a cholesteric medium. Fourier transform infrared (FT-IR) experiments have been performed at various temperatures on both sides of the cholesteric−isotropic transition. Liquid crystalline order provides significant enhancement to the strength of interaction, inducing a discontinuous jump in concentration of the complex at the cholesteric−isotropic transition.

1. Introduction

Various systems have been already described exhibiting at the same time mesomorphous behavior and hydrogen interaction self-assembly properties. In such systems, the relative weakness of the hydrogen bonding (on the order of 9−40 kJ/mol compared to 200−400 kJ/mol for that of a covalent bond) allows the mesogenic interactions to play a large part in the mechanism for assembly. Some "living" low molar mass liquid crystals or "living" liquid crystal polymers were created so by hydrogen-bonding from smaller fragments.[1−7] Bladon and Griffin[4] analyzed these systems by the use of simple mean field models, balancing the competition between rotational and translational entropies, hydrogen-bonding energy, and nematic interactions. They predicted that nematic order provides significant enhancement to the strength of the hydrogen bond.

Furthermore, molecular recognition in natural or synthetic systems is often based on noncovalent interactions such as hydrogen bonding. For example, in molecular imprinting techniques, most of the systems use hydrogen-bonding interactions between the template molecule and the polymer network.[8−13] In such systems, we proposed in previous papers[13,14] to introduce liquid crystalline groups as substituents on the polymer backbone (Figure 1).

Inside mesomorphous networks, the integrity of the structure is ensured, not only by covalent chemical bonding like in standard network, but also by the so-called "weak interactions" between the mesogens. As a result, the template can be extracted without losing the imprinted information even with low cross-linking ratios (5−10 mol %). As a result, the molecular trapping capacity was shown to be much greater than that of the previously studied nonmesomorphous systems.[15] Moreover, in the case of nematic materials, a chiral template acts as a chiral dopant. It induces a helical cholesteric structure inside the liquid crystalline network that can participate in the molecular recognition. Such a cholesteric-imprinted elastomer was obtained by cross-linking a nematic side-chain polysiloxane around a chiral template. This imprinted network showed a pronounced enantioselectivity.[15]

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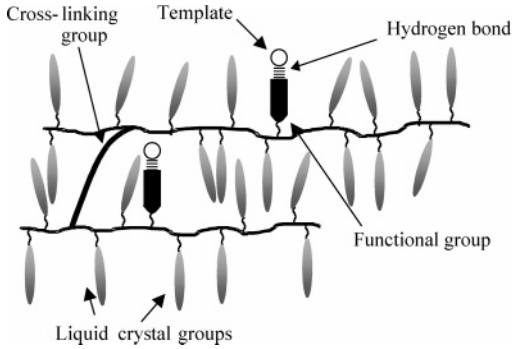

Figure 1. Scheme of liquid crystalline network imprinted via hydrogen-bond interactions.

In connection with this previous study, the aim of the present work was to analyze how the mesomorphic order can contribute to the bonding interactions between the template and the network. For that, the complex formed by hydrogen bonds between the template [(*R*)-α-methylbenzylamine] and the corresponding functional groups [4-(3-butenyloxy)benzoic acid] was introduced in a mesogenic solvent [4-methoxy-4′-(3-butenyloxy)phenylbenzoate]. It was analyzed by infrared spectroscopy, either in the mesogenic phase (cholesteric phase) or in the isotropic state.

2. Experimental Section

2.1. Reactants and Materials. The (*R*)-α-methylbenzylamine was purchased from Aldrich Fine Chemicals. It interacts, via a hydrogen bond, with 4-(3-butenyloxy)benzoic acid synthesized as previously described.[13] The 4-(methoxy)-4′-(3-butenyloxy)-phenylbenzoate mesogen was synthesized as previously described.[16]

To form the complex, (*R*)-α-methylbenzylamine and 4-(3-butenyloxy)benzoic acid were mixed together in toluene at 70 °C for 4 h in stoichiometric proportions (Figure 2). The 4-(methoxy)-4′-(3-butenyloxy)phenylbenzoate mesogenic group was added to the complex solution in 10/1 molar proportion.

2.2 Polymorphism Analysis. The nature of the mesophases and the corresponding transition temperatures were determined by polarized-light optical microscopy (Olympus microscope

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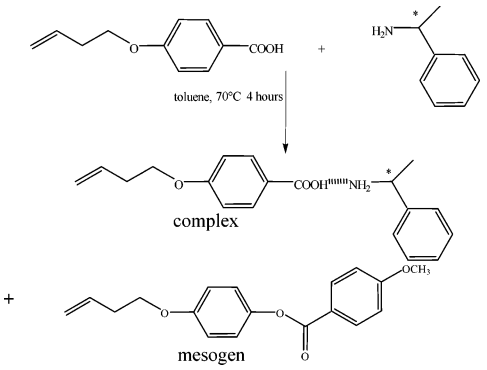

Figure 2. Complex between (*R*)-α-methylbenzylamine and 4-(3-butenyloxy)benzoic acid and liquid crystalline groups used as solvent.

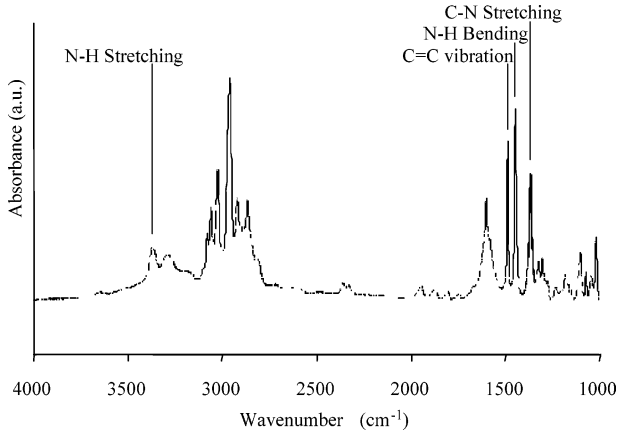

Figure 3. FT-IR spectrum of (*R*)-α-methylbenzylamine.

equipped with a Mettler FP82HT hot stage) and differential scanning calorimetry (DSC) using a Perkin-Elmer PYRIS 1 calorimeter.

2.3. Spectroscopic Measurements. Transmission infrared spectra were recorded on a Perkin-Elmer 1760-X FTIR spectrometer and analyzed with the Perkin-Elmer Spectrum 2.00 program. Samples were studied as thin films obtained from toluene solutions and placed between CaF_2 plates. The measurements were performed at various temperatures, by use of a thermostat linked with a thermocouple, in the 4000−1000 cm^{-1} frequency range. For each spectrum, the stabilization of the temperature was checked before 10 scans were run.

3. Results and Discussion

To assess each compound's effect, both components of the complex, that is, (*R*)-α-methylbenzylamine and 4-(3-butenyloxy)benzoic acid, as well as the mesogenic group were successively studied as references. The complex was then analyzed alone or in the presence of the mesogenic solvent. To mimic the expected liquid crystalline network, the (*R*)-α-methylbenzylamine/4-(3-butenyloxy)benzoic acid complex was studied in the presence of the mesogens taken at the same concentration conditions (0.1 molar ratio) as those of the final imprinted network.

3.1. (*R*)-α-Methylbenzylamine. The FT-IR spectrum (Figure 3) presented the characteristic peaks of the amine group (for example, C−N deformation at 1368 cm^{-1}, N−H stretching at 3364 cm^{-1}, and N−H bending at 1451 cm^{-1}) and of the phenyl group (for example, C═C vibration at 1492 cm^{-1}). As expected, all peak intensities exhibited linear evolution with increasing temperature (Figure 4).

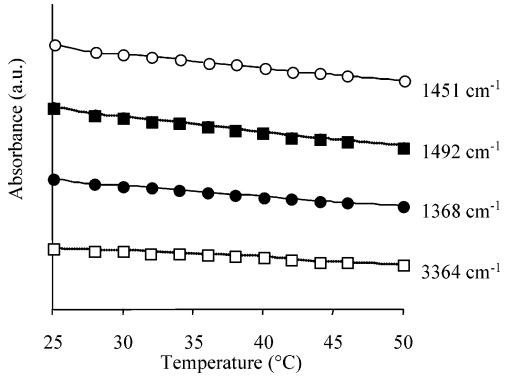

Figure 4. Thermal evolution of (*R*)-α-methylbenzylamine bands (1368 cm^{-1}, C−N stretching; 1451 cm^{-1}, N−H bending; 1492 cm^{-1}, C═C vibration of phenyl; 3364 cm^{-1}, N−H stretching).

3.2. 4-(3-Butenyloxy)benzoic acid. 4-(3-Butenyloxy)benzoic acid exhibits a nematic phase, from the melting point at 121.8 °C and the isotropic state up to 140.5 °C, as a result of dimer formation (Figure 5) in a process that involves homointermolecular hydrogen bonds.[6] It is well-known in the literature[17] that such compound presents two peaks in the C═O region in its IR spectrum: the first one, typically over 1700 cm^{-1}, is attributed to the free carboxylic group, and the other one, generally lower than 1700 cm^{-1}, is due to the associated form. In our case, these bands were observed, respectively, at 1730 and 1687 cm^{-1} (Figure 6), The thermal evolution of these two absorbance peaks was studied and is presented in Figure 7. The evolution of the absorbance of the asymmetric in-plane C═C vibrations of the phenyl rings at 1606 cm^{-1} is also reported.

Since the dipole moment corresponding to C═C vibrations is directed along the axis of the mesogen, any change of orientation is visible on this band[19−21] and this leads to the nonlinear evolution in the absorbance observed near the nematic−isotropic transition temperature. A similar but much weaker effect, due to different dichroic ratios,[20] could also appear on the 1687 cm^{-1} absorption band. However, the intensity of this band is essentially linked to the concentration of dimers formed by hydrogen bonds. In agreement with previous studies,[1,4,7,18] a discontinuous decrease was clearly shown (Figure 7) at the clearing temperature, connected with hydrogen-bonding dissociation. At the same time, an increase in the intensity of the signal corresponding to the monomer form (1730 cm^{-1}) was observed.

3.3. 4-Methoxy-4′-(3-butenyloxy)phenylbenzoate. The mesogen exhibits a monotropic nematic phase at 52.2 °C, observed when the temperature is decreased from the isotropic state. The intensity of the signal relative to the asymmetric in-plane C═C vibrations of the phenyl rings at 1606 cm^{-1} was analyzed (Figure 8) as a function of temperature. A significant jump was observed around 53 °C, proving that the sample had been partially oriented before the experiments. A decrease of the orientation down to zero occurred in the vicinity of the liquid crystalline−isotropic transition.

3.4. (*R*)-α-Methylbenzylamine/4-(3-butenyloxy)benzoic Acid Complex. The FT-IR spectrum of the complex is superimposed in Figure 9 with those of the acid and the amine. Two signals proved the formation of the complex: first, a new band was clearly visible at 1550 cm^{-1}, linked to the associated amine function, and second, the signal corresponding to C−N stretching in the (*R*)-α-methylbenzylamine was shifted from 1368 to 1378 cm^{-1}. At the same time, two bands relative to the 4-(3-butenyloxy)benzoic acid disappeared at 1281 and 1423 cm^{-1}.

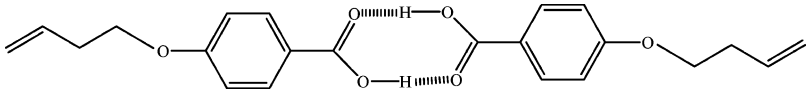

Figure 5. Dimer of 4-(3-butenyloxy)benzoic acid.

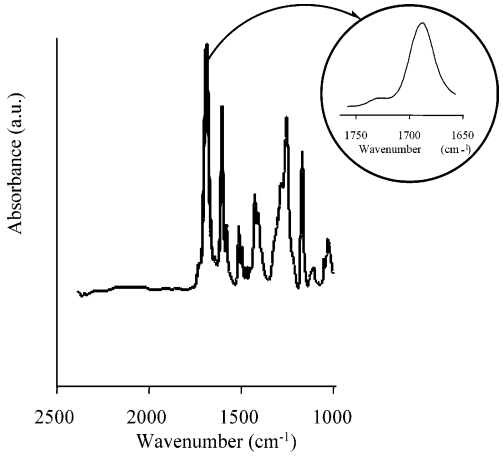

Figure 6. FT-IR spectrum of 4-(3-butenyloxy)benzoic acid.

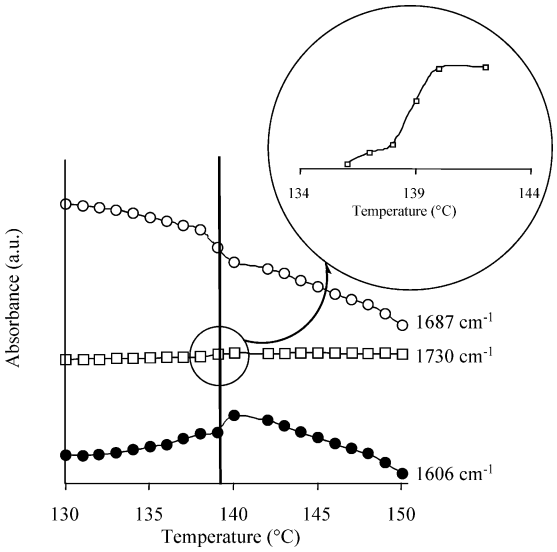

Figure 7. Thermal evolution of the signal relative to the C═O stretching in the free carboxylic group (1730 cm^{-1}) and the associated carboxylic group (1687 cm^{-1}) and of in-plane C═C vibrations of the phenyl rings (1606 cm^{-1}).

The (*R*)-α-methylbenzylamine/4-(3-butenyloxy)benzoic acid complex has no mesomorphic properties as checked by optical microscopy observations.

3.5. (*R*)-α-Methylbenzylamine/4-(3-butenyloxy)benzoic Acid Complex in the Presence of the Mesogenic Groups. The (*R*)-α-methylbenzylamine/4-(3-butenyloxy)benzoic acid complex previously studied was then mixed with the 4-methoxy-4′-(3-butenyloxy)phenylbenzoate mesogenic group (1/10 molar ratio). In this mixture, (*R*)-α-methylbenzylamine acted as a chiral inductor and induced an isotropic to monotropic cholesteric phase transition observed by optical microscopy at 42 °C.

The IR spectrum of the mixture presented a large number of signals, and unfortunately, some bands relative to the complex, in particular the 1550 cm^{-1} amine band, were not visible anymore. Therefore, to characterize the thermal evolution of this system, we selected several visible peaks that were specific to each component: those at 1169 and 1606 cm^{-1} for the different phenyl groups and those at 1368 cm^{-1} and 1378 cm^{-1}

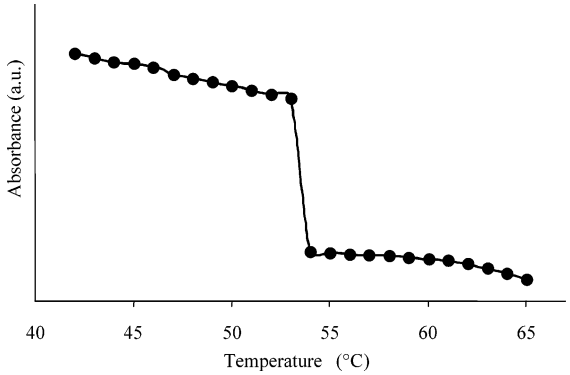

Figure 8. Thermal evolution of the signal relative to vibration of the aromatic ring (1606 cm^{-1}) in the mesogenic group.

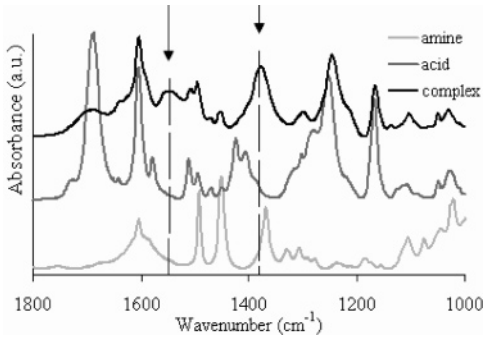

Figure 9. FT-IR spectra of the (*R*)-α- methylbenzylamine/4-(3-butenyloxy)benzoic acid complex, 4-(3-butenyloxy)benzoic acid, and (*R*)-α-methylbenzylamine.

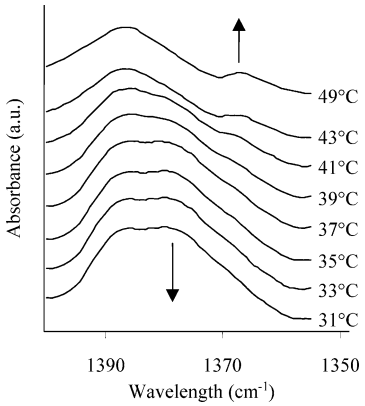

Figure 10. Thermal evolution of FT-IR spectra of the (*R*)-α-methylbenzylamine/4-(3-butenyloxy)benzoic acid complex in the mesomorphic solvent.

for (*R*)-α-methylbenzylamine, respectively, in the free form and in the associated form in the complex. The measurements were performed on a large range of temperature on both sides of the transition temperature (42 °C) of the mixture. Significant modifications of the relative intensities of the 1368 and 1378 cm^{-1} bands were observed (Figure 10) near the cholesteric−isotropic transition temperature: up to the transition, the free amine signal at 1368 cm^{-1} increased whereas the one corresponding to the associated amine at 1378 cm^{-1} decreased.

To evaluate the individual evolution of these peaks, the 1400−1350 cm^{-1} region was analyzed with ORIGIN 6.0

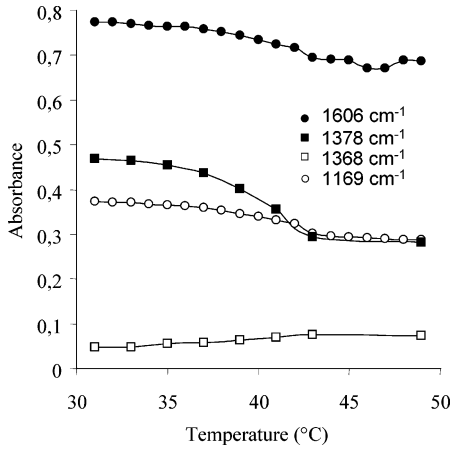

Figure 11. Thermal evolution of C═C vibrations in the phenyl groups (1169 and 1606 cm^{-1}) and of the C−N stretching in free (*R*)-α-methylbenzylamine (1368 cm^{-1}) or in (*R*)-α-methylbenzylamine associated with 4-(3-butenyloxy)benzoic acid (1378 cm^{-1}) in the mesomorphic solvent.

software as three Gaussian functions at 1368, 1378, and 1386 cm^{-1}. The frequency of peaks' top was defined without fixing their width. The background is automatically calculated as from chosen limits. The thermal evolution of the signals at 1368 and 1378 cm^{-1} are presented in Figure 11. The variations in the absorption band of the C═C vibrations of the phenyl rings are also reported to check any orientation phenomenon.

As previously observed, a small jump in the 1169 and 1606 cm^{-1} intensities occurred at the transition between the cholesteric phase and the isotropic state, proving that the sample was slightly oriented. At the same time, a clear decrease of the intensity of the associated amine functions was detected at 1378 cm^{-1} concomitant with a small increase of the free amine function intensity at 1368 cm^{-1}. This provided direct evidence for the jump in concentration of the (*R*)-methylbenzylamine/4-(3-butenyloxy)benzoic acid complex at the transition temperature between the cholesteric phase and the isotropic state. It gave an unambiguous indication that the mesomorphous field has a significant effect on the bonding between the functional acid groups and the amine template.

The liquid crystalline order increases the stabilization of the complex formed via hydrogen bonds; that is, there is an effective "extra bonding" energy due to the mesogenic interactions. At the isotropic transition, this "extra bonding" energy is broken. This fact might be used to facilitate the extraction of the template in the liquid crystalline imprinted materials simply by modifying the temperature of the material. Experiments are in progress to form, in this way, temperature-tunable imprinted networks.

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