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M. H. Godinho[ab]; J. P. Borges[ab]; J. C. Bordado[ab]; M. T. Cidade[ab]; A. F. Martins[ab]
[a] Universidade Nova de Lisboa, Faculdade de Ciências e Tecnologia, Monte da Caparica, Portugal [b] Centre de Física da Matéria Condensada, Lisboa Codex, Portugal

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Preparation and liquid-crystalline properties of toluene-4-sulphonyl urethane of hydroxypropylcellulose

by M. H. GODINHO*, J. P. BORGES, J. C. BORDADO,
M. T. CIDADE and A. F. MARTINS
Universidade Nova de Lisboa, Faculdade de Ciências e Tecnologia,
Monte da Caparica, 2825 Monte da Caparica, Portugal
and
Centro de Física da Matéria Condensada,
Av. Prof. Gama Pinto, 2, 1699 Lisboa Codex, Portugal

A novel liquid-crystalline polymer, the toluene-4-sulphonyl urethane of hydroxypropylcellulose (TSUHPC), was prepared through chemical modification of hydroxypropylcellulose (HPC) of $\overline{M}_w = 60000\,\mathrm{g\,mol^{-1}}$. The resulting polymer was characterized by infrared spectroscopy, differential scanning calorimetry (DSC) and polarizing microscopy. It was found that thermotropic liquid crystal phases are formed between about 60°C and 110°C. Concentrated solutions of TSUHPC in acetone and *N*,*N*-dimethylacetamide exhibit cholesteric behaviour, at room temperature. When approaching the lyotropic mesophase to solid transition, either by cooling or by solvent evaporation, very interesting arborescent structures of a seemingly fractal nature may be observed, depending on the kinetics of the transition. A banded texture can be observed when the polymer is sheared near the transition to the isotropic phase.

1. Introduction

2-Hydroxypropylcellulose (HPC) was the first cellulose derivative reported to form spontaneously anisotropic solutions when dissolved in aqueous and organic solvents (see, for example [1–3]). New cellulose derivatives have been prepared in order to study the effect of the substituents on the behaviour of the liquid-crystalline phase. It was found that HPC, its esters and ethers share the property of forming both thermotropic (see, for example, [3, 4]) and lyotropic phases [5]. In this paper we describe the preparation and characterization of a new cellulose derivative which exhibits both thermotropic and lyotropic behaviour, the toluene-4-sulphonyl urethane of hydroxypropylcellulose (TSUHPC).

2. Experimental section

2.1. *Synthesis of TSUHPC*

The toluene-4-sulphonyl urethane of hydroxypropylcellulose was prepared from toluene-4-sulphonyl isocyanate (TSI) and hydroxypropylcellulose (HPC) (Klucel $\overline{M}_w = 60000\,\mathrm{g\,mol^{-1}}$). To a three necked flask containing 50 ml of pyridine and 5 g of HPC was added dropwise 3 ml of TSI. The mixture was stirred for 2 h and 30 min at room temperature and then quenched in warm water. The precipitated product was

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* Author for correspondence.

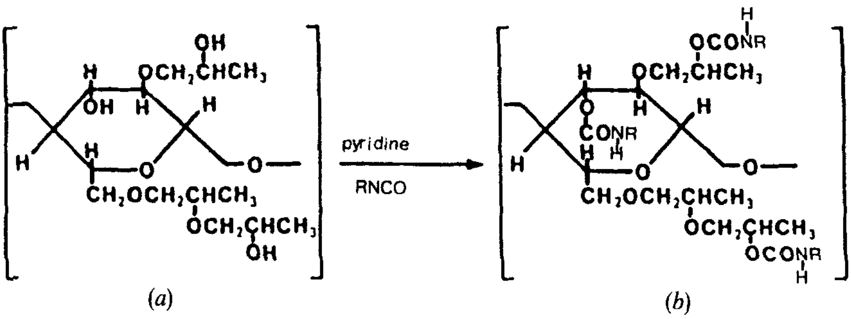
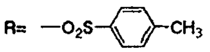


Figure 1. Schematic of the preparation of urethanes of hydroxypropylcellulose. (a) HPC with degree of etherification = 2 and molar etherification = 3; (b) Urethanes of HPC with number of molar urethane groups = 3. In this work



filtered. Purification was accomplished by reprecipitating the product several times from acetone in water. The final product (TSUHPC) was dried under vacuum (0·5 mm Hg) at room temperature. This product was a white powder and was soluble in chloroform, ethyl methyl ketone, tetrahydrofuran, *m*-cresol, and acetone, and insoluble in acetic acid, ethanol, benzene, diethyl ether and water. Figure 1 shows a general scheme for the preparation of urethanes of hydroxypropyl cellulose.

The lyotropic liquid crystal samples to be studied by optical microscopy were prepared by mixing appropriate weights of TSUHPC and *N*,*N*-dimethylacetamide (DMAC) and acetone. Once homogeneous, the liquid-crystalline solutions were sandwiched between a microscope slide and cover glass and sealed to prevent solvent loss.

2.2. *General analysis*

Infrared spectra of the polymers were recorded using a Perkin–Elmer model 700 FT Infrared Spectrometer at room temperature. Differential Scanning Calorimetry curves were recorded with a Setaram DSC model 111 from 298 K to 420 K under a nitrogen atmosphere. Liquid-crystalline textures were observed with an Olympus polarizing microscope.

3. Results and discussion

3.1. *Polymer characterization*

From the IR spectrum represented in figure 2 along with the spectrum of the initial HPC polymer, the absorption bands around 3650–3350 cm^{-1}, which are due to OH stretching vibrations, show that TSUHPC is not fully substituted. The strong band at 1746·4 cm^{-1} is due to the carbonyl group. There is no evidence of a band at 2222·2 cm^{-1}, observed for the TSI, which means that the new polymer does not have the group NCO. The band at 3234·0 cm^{-1}, due to the presence of NH, means that a urethane was formed. By polarizing microscopy we found that the TSUHPC has two transition temperatures around 60°C and 110°C which are identical to those found for the end temperatures of the endotherm peaks observed by DSC when the polymer is heated (see figure 3). The two peaks observed are very close; the first one, at the lower

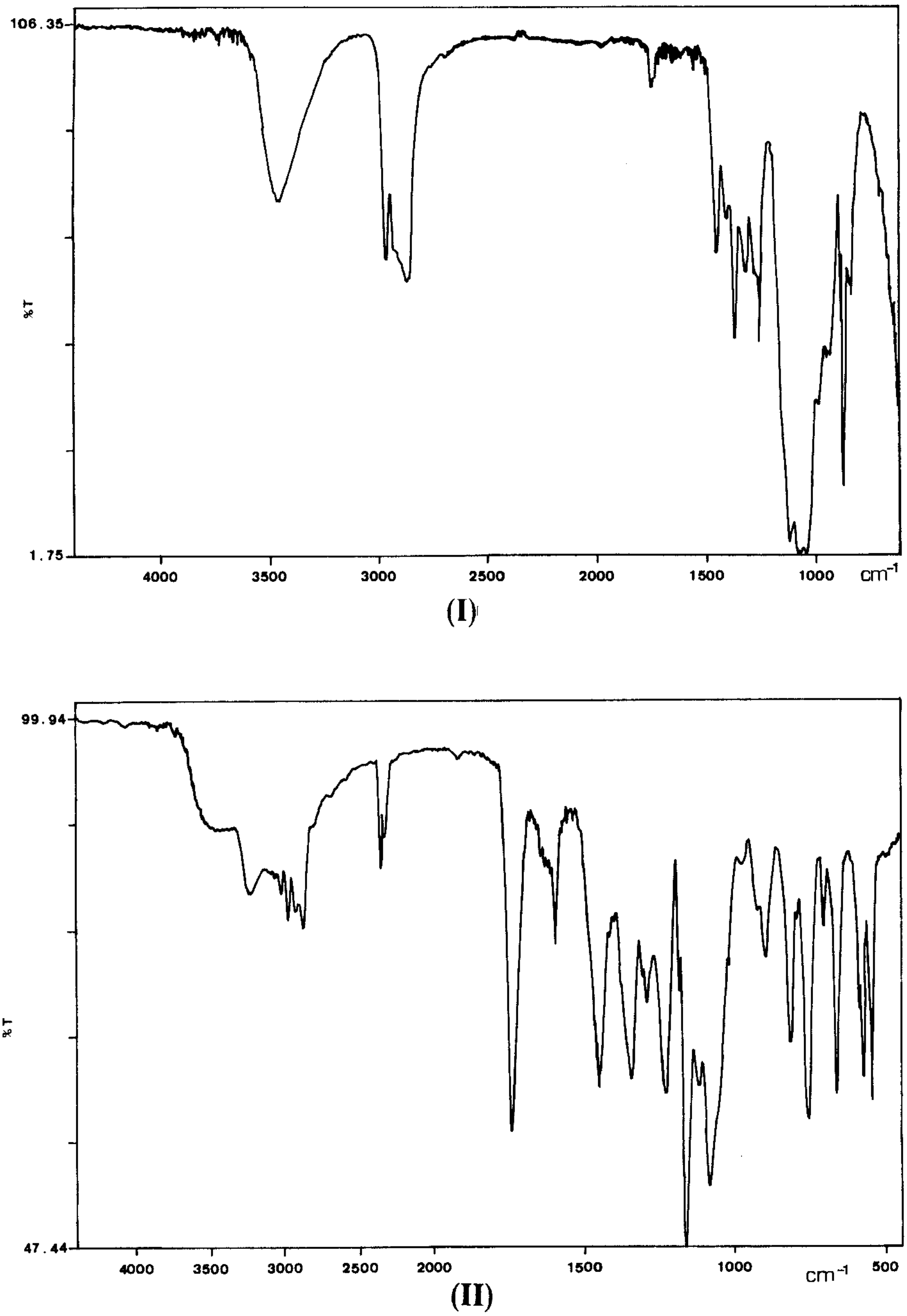


Figure 2. IR spectra of (**I**) hydroxypropylcellulose and (**II**) TSUHPC. Solid films were obtained from acetone solutions.

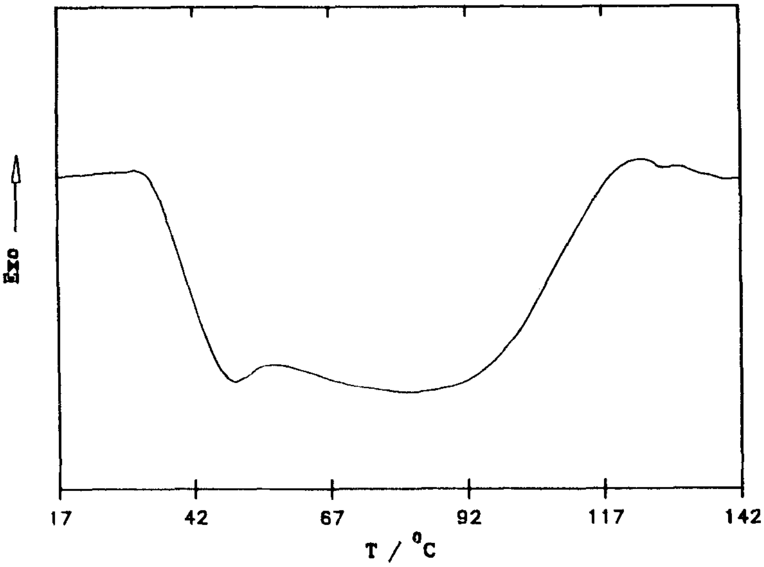


Figure 3. DSC thermogram (5°C min^{-1}) of TSUHPC, on heating.

temperature (T(initial) $= T_{\mathrm{i}} = 32{\cdot}8^{\circ}\mathrm{C}$; T(maximum of the peak) $= T_{\mathrm{m}} = 45{\cdot}4^{\circ}\mathrm{C}$) is due to the transition from the crystalline to the liquid crystal phase, and the other one, with $T_{\mathrm{i}} = 57{\cdot}8^{\circ}\mathrm{C}$ and $T_{\mathrm{m}} = 82{\cdot}3^{\circ}\mathrm{C}$, corresponds to the transition from the liquid crystal to the isotropic state. This is the usual behaviour of a thermotropic polymer.

Sheared liquid-crystalline polymers may exhibit a texture called the 'banded texture' after cessation of shear [6]. This texture was observed for the TSUHPC liquid crystal phase (see figure 4) when the polymer was sheared at temperatures close to the transition to the isotropic phase. A biphase of coexisting crystals and 'banded texture' can also be observed (see figure 4 (*b*)). The presence of this texture also indicates that we are dealing with a liquid crystal (thermotropic) polymer.

3.2. *TSUHPC lytropic liquid crystals*

The TSUHPC synthesized was found to form liquid crystal phases with acetone and DMAC. Observation of the texture of these lyotropic solutions was carried out at room temperature with a polarizing microscope. Typical fingerprint textures were observed for TSUHPC in acetone. An example is shown in figure 5. The distance between alternating dark and bright lines (half of the cholesteric pitch (P)) gives the value 3·7 μm for P. The textures of the lyotropic solutions in both solvents are difficult to characterize. There is evidence of the coexistence of liquid-crystalline and crystalline phases. Crystallization from polymer mesophases has been observed for polybenzamide (PBA) [7], for cellulose carbanilate [8] and for acetoxyethylcellulose (AEC) [9]. For TSUHPC arborescent structures may be observed (see figure 6). Further studies on this material are in progress.

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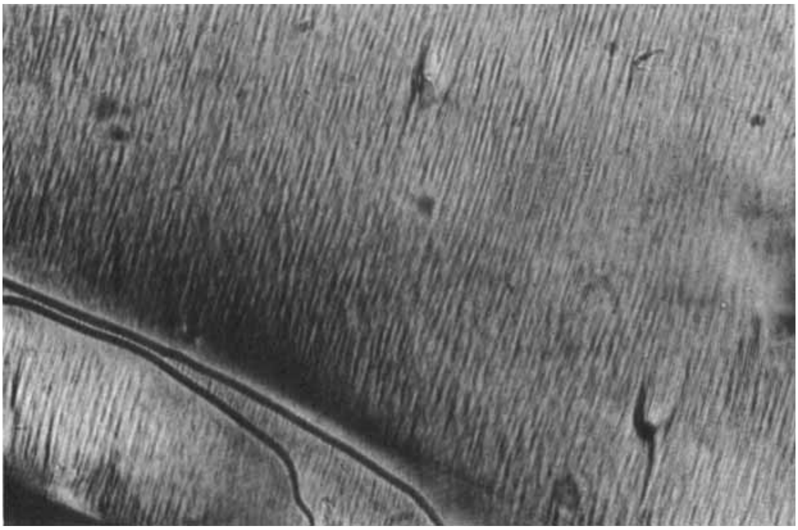
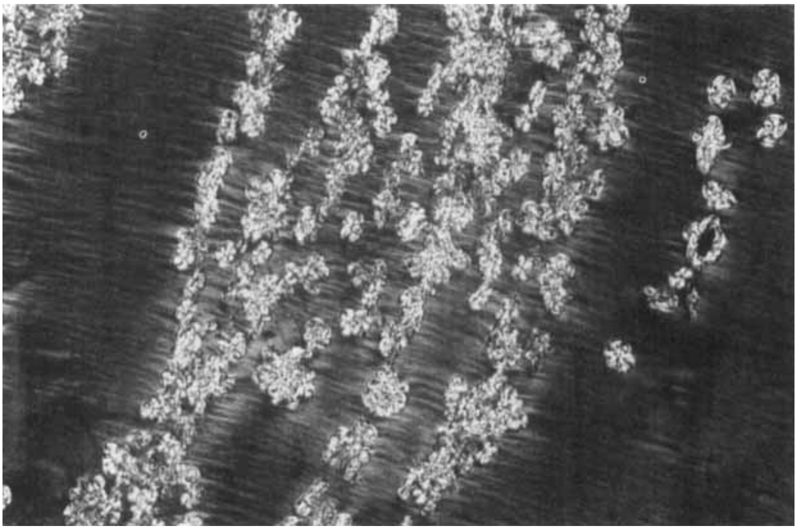


(*a*)



(*b*)

Figure 4. (*a*) Banded texture observed for the TSUHPC thermotropic liquid crystal phase (× 260). (*b*) band texture and crystal phase coexisting (× 260).

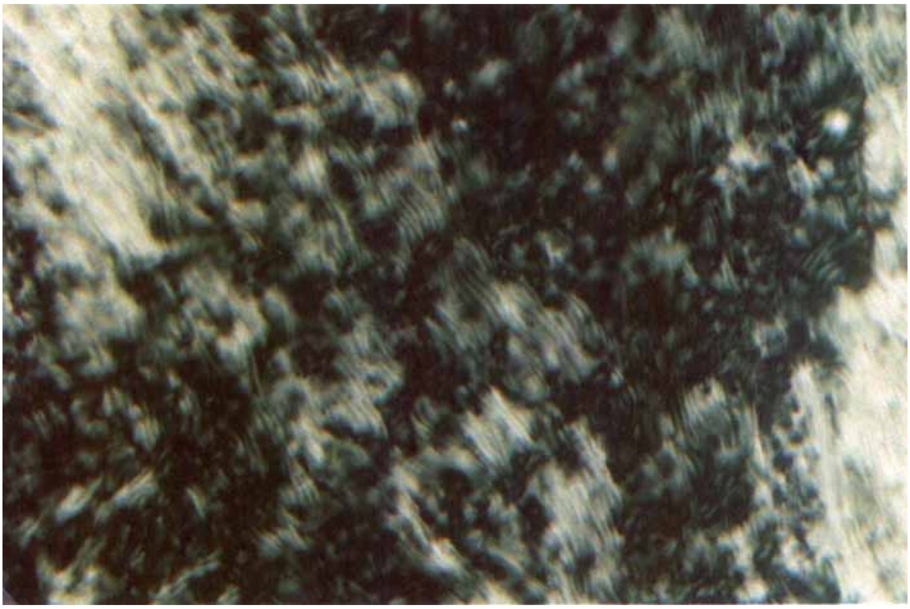


Figure 5. Photomicrograph of fingerprint pattern for the TSUHPC/acetone liquid crystal phase between crossed polars ($T = 25°C$) (× 680).

Figure 6. Arborescent structures observed for TSUHPC/DMAC solutions at about 25°C between crossed polars (× 680).

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