MODULATED DIFFERENTIAL SCANNING CALORIMETRY
Transitions between monotropic and enantiotropic phases of a cholesteric liquid crystal

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Abstract

The Modulated Differential Calorimetry (MDSC) is applied to the determination of the reversibility in the cholesteryl chloride, which presents a cholesteric monotropic phase between the isotropic and crystalline states. The experimental modulation parameters that govern this method i.e. frequency, amplitude and heating/cooling rate, are determined. MDSC curves and complementary thermomicroscopical observations assign melting, crystallization and liquid cholesteric transition as 'non reversing', and clarification as 'reversing'.

Keywords: cholesteric liquid crystal, Modulated Differential Scanning Calorimetry, monotropic phase

Introduction

The Modulated Differential Scanning Calorimetry (MDSC) [1–3] is stemmed from the combination of Differential Scanning Calorimetry and AC Calorimetry. The principle of this method is first to set the sample under a sine wave modulated heating rate, then to subject the calorimetric response to a mathematical treatment (Fourier transform). The three thermograms obtained represent the 'reversing', 'non reversing' parts of thermal events, and the convolution of both signals, called 'total', which is quite similar to a classical DSC thermogram. It can be proposed for french terminology: *inversible* for 'reversing', *non inversible* for 'non reversing', and *total* for 'total'. The 'reversing' part of the calorimetric response shows thermal events that can reverse over the time scale of the oscillation (e.g. heat capacity). The 'non reversing' part shows the component of the response that depends only on time and kinetic processes (e.g. crystallization, cure, ...). The comprehension of 'reversing' and 'non re-
versing" thermal events can then be carried out through the notions of reversible and irreversible processes developed in theoretical thermodynamics.

Previous works performed on polymers [4, 6] have shown that MDSC is a successful technique in deconvolution of superimposed processes e.g. two glass transitions or crystallization and glass transition...; all the studied transformations induce large thermal events. In order to extend the application domain of MDSC, we just have undertaken calorimetric studies of liquid crystal phase transitions. Such compounds exhibit original sequences between stable and/or metastable mesophases; in some cases, transformations occur on small temperature range and with low energy. In fact, most mesophases are enantiotropic, i.e. observable both on heating and cooling a stable or and a metastable phase. Some mesophases only appear on cooling a metastable phase, and are then called monotropic. The aim of this paper is to bring to the fore the influence of the thermal processing on the reversibility of transitions. Parameters, which govern the deconvolution of the calorimetric response: heating rate, frequency and modulation amplitude, were determined. MDSC curves are discussed and compared with complementary thermo-microscopical measurements.

**Experimental**

**Measurements**

The DSC and MDSC measurements were performed on a SEIKO DSC 220C. A liquid nitrogen cooling system allows both cooling and oscillating experiments. The DSC cell was purged with 30 ml min⁻¹ of helium [4]. The MDSC was calibrated for enthalpy and temperature determination with standard indium. All samples were weighted and sealed in hermetic aluminium containers. The reproducibility of temperature and enthalpy measurements were checked on different mass samples, from 3.080 to 9.857 mg.

The thermo-microscopical measurements were performed on an optical polarizing microscope LEICA DMRXP, equipped with a heater/cooler stage CHAIXMECA (93 to 873 K). Samples were prepared both free cell and between slides. Magnifications from 50 to 320 were used.

**Material**

The cholesteryl chloride (ChCl) was provided by Merck (purity 99.9). It presents a cholesteric (N') monotropic phase between the isotropic I and crystalline K states. The phase sequence is described as:

\[ K-(N')-I \]