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The features of the normal mode relaxation as studied by thermally stimulated currents

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ABSTRACT

The slow molecular mobility in high-*cis* poly (1,4-isoprene) has been studied by the dielectric technique of thermally stimulated currents. Three different kinds of motional processes have been identified: the Johari–Goldstein relaxation, the main or α -process and a mobility appearing above T_g that has been ascribed to the normal mode process. The temperature location of these relaxations was respectively at -85 to -80 °C, at -73 °C and at -65 °C. The fragility or steepness index was found to be $m_\alpha = 60$ and $m_n = 37$, respectively for the α and the normal mode processes, in excellent agreement with the results obtained by dielectric relaxation spectroscopy (DRS).

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1. Introduction

The normal mode process is an attribute of a relatively small number of polymers that exhibit a component of the dipolar electric moment parallel to the chain contour. These are type-A polymers according to the classification of Stockmayer [1], and the dipole moment of the whole chain is the summation over the monomer dipole moments parallel to the chain backbone. Among the polymers presenting the normal mode process are poly(propylene oxide), poly(1,4-*cis*-isoprene), poly(L-lactide) and poly(ϵ -caprolactone). The normal mode process is a higher temperature (or lower frequency) mobility compared with the glass transition mobility, and arises from the fluctuations of the end-to-end dipole vector (chain relaxation). It has been characterized in great detail using the technique of dielectric relaxation spectroscopy (DRS) [2].

Thermally stimulated depolarization currents (TSDC) is a dielectric technique in the time domain that was largely used to study the slow molecular mobility in amorphous and semi-crystalline polymers [3]. However, the published TSDC studies dealing with the normal mode process are very scarce, and most of them have very narrow or specific objectives, so that they cannot be considered as general and systematic studies of the kinetics of the normal mode mobility [4]. An exception is an interesting and well undertaken study by TSDC of the peak observed above T_g in poly(ϵ -caprolactone) [5]; however, and unfortunately, the obtained experimental results did not allow to clearly attribute this peak to the normal mode process, which was probably disguised by space charge events. Very recently, however, two papers have been published that use TSDC to study the chain mobility [6,7].

The scarcity of the published TSDC studies on the normal mode process probably arises from the observation that the relaxations above T_g are often found to be artifacts generated by space charge motions, and not true dipolar reorientations. Since the technique uses *dc* electric fields

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to polarize the samples, extrinsic charges (normally electrons) can be created in dielectrics submitted to high fields by injection mechanisms from the electrodes. The sample may also contain ionic impurities (intrinsic charges) that result from the chemical synthesis procedure. These different space charges can become mobile above T_g , giving rise to manifestations that sometimes interfere with the dipolar relaxations that eventually appear in this temperature region. That is why the attribution at the molecular level of the TSDC relaxation peaks observed above T_g is often a difficult problem that needs to be considered very carefully, and will be discussed later in detail.

In the present work we present a systematic analysis by thermally stimulated currents of the slow mobility in high-*cis* poly(1,4-isoprene), PI, including the amorphous state, the glass transformation region and the rubber state. PI appears as a good system to implement this study. First because, due to the absence of heteroatoms (oxygen, nitrogen etc.) in its chemical structure, this polymer is not expected to present particular hygroscopic and/or conductivity problems. Moreover, the very low frequency covered by TSC allows the investigation of the segmental and chain dynamics at low temperatures, near the glass transformation where the polymer melt vitrifies, and this temperature range is difficult to explore by other techniques. Finally because the segmental and chain mobilities of PI were studied in great detail by dielectric relaxation spectroscopy (DRS), so that our TSC study is a new opportunity to check the usefulness of the TSC technique and the complementarity between this two techniques [8].

2. Experimental

2.1. Materials

Linear 1,4-polyisoprene (high *cis*) with molecular weight, $M_w = 4650 \text{ g mol}^{-1}$, degree of polydispersity index $PDI = 1.04$, and average microstructures 70/24/6% of *cis*/trans/4,3-addition, was synthesized and characterized at the Jülich Centre for Neutron Science & Institute for Complex Systems (Germany).

2.2. Methods

2.2.1. Differential Scanning Calorimetry (DSC)

The calorimetric measurements were performed with a 2920 MDSC system from TA Instruments Inc. (USA). The samples of ~5–10 mg were introduced in aluminum pans. The measuring cell was continuously purged with dry high purity helium gas at a flow rate of 30 mL min^{-1} . An empty aluminum pan, identical to that used for the sample, was used as the reference. Cooling was achieved with a liquid nitrogen cooling accessory which permits automatic and continuous programmed sample cooling down to $-150 \text{ }^\circ\text{C}$ (123 K). The baseline was calibrated by scanning the temperature domain of the experiments with an empty pan. Additional details on the calibration procedures, including temperature and enthalpy, are given elsewhere [9].

2.2.2. Thermally stimulated depolarization and polarization currents (TSDC and TSPC)

Thermally stimulated current experiments were carried out with a TSC/RMA spectrometer (TherMold, USA) covering the range from $-170 \text{ }^\circ\text{C}$ to $+400 \text{ }^\circ\text{C}$. For these measurements the sample was placed between the disc-shaped electrodes (7 mm diameter) of a parallel plate capacitor.

TSC is a dielectric technique in the time domain, adequate to probe slow molecular motions (equivalent frequency range between $\sim 4 \times 10^{-4}$ and 10^{-1} Hz). The relaxation time of the motional processes is temperature dependent, such that it becomes longer as temperature decreases, allowing to make it exceedingly long (freezing process) compared with the timescale of the experiment. This is the basis of the thermally stimulated currents technique in the so-called *depolarization mode* (TSDC), where a dipolar electret is produced by cooling down the sample under study in the presence of an electric polarizing field, and the transient depolarization current is recorded in a linear heating process. The important parameters in a TSDC experiment are the polarization temperature, T_p , at which the polarizing electric field is turned *on*, and the temperature $T_{p'} < T_p$ at which the field is turned *off* (see Fig. 1).

The difference $T_p - T_{p'} = \Delta T$ is the width of the polarization window of the experiment. If it is wide, the retained polarization (and of course the current peak that is the result of a TSDC experiment) will correspond to a complex set of reorientational motions, and the experimental result will be a broad, widely distributed current *versus* temperature thermogram, $I(T)$. Oppositely, if the polarizing field is applied in a narrow temperature interval, the experiment allows probing narrowly distributed relaxation components, and the experimental result will be a single depolarization current peak. This is called the partial polarization (PP) procedure that is often used in order to analyse specific regions of the TSDC spectrum. For very narrow polarization window, the experimental PP peak is supposed to correspond to a very narrowly distributed relaxation [10]. In our TSDC experiments we most often use polarization windows two degrees wide, and we tacitly assume that this window isolates very narrowly

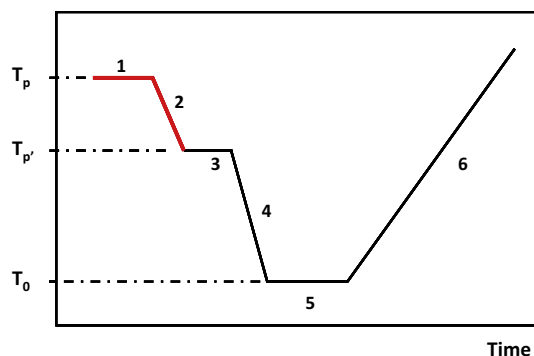


Fig. 1. Experimental protocol in the form of a temperature–time diagram of a thermally stimulated depolarization currents experiment (see text). The electric field is on in steps 1 and 2 (thicker lines). At T_0 the sample is a stable electret that is depolarized during the constant rate heating process (step 6) where the depolarization current, I , is recorded.

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