The research activities in this subdivision cover structural studies and molecular motion analyses of highly organized polymer materials in the different states by high-resolution solid-state NMR, electron microscopy, X-ray diffractometry, and so on, in order to develop high-performance and high-functionality polymer materials such as organic electron luminescence devices and different molecular hybrid materials. The structure formation process of bacterial cellulose is also characterized in detail and environmentally friendly cellulosic nanohybrid materials are examined to develop in different stages of the biosynthesis.

Scope of Research

Research Activities (Year 2007)

Presentations

Investigation of Dynamics of Poly(dimethylsilane) in the Mesophase by Solid-State $^{29}$Si NMR: Evidence for Rotator Phase¹

The characterization of the dynamics of materials is an important fundamental to understand their properties. For polymers, intermediate states, called “mesophases” often appear between the crystalline and liquid (or amorphous) states. The dynamics in the mesophases is closely related to important problems in polymer science, such as chain folding and (ultra)drawability. However, the dynamics of polymers with Si-Si backbones are not well characterized. In this study, the dynamics of poly(dimethylsilane) (PDMS) in the mesophase was studied.

Figure 1 shows the $^{29}$Si cross polarization/chemical shift anisotropy (CP/CSA) spectra of PDMS. Below the transition temperature of 166°C, which was observed by DSC measurements, we can observe typical CSA line shapes. The simulated CSA spectrum, shown on the experimental CSA spectrum at 23°C by a green curve, agrees well with the experimental spectrum. Above the transition temperature of 166°C, the observed CSA line shapes are found to be different from the typical CSA line shapes. The intensity near the isotropic chemical shift becomes small compared to the typical CSA line shapes. This intensity “hole” is experimental evidence of uniaxial rotational motion of the PDMS chains. Under the uniaxial rotation, the $^1$H-$^{29}$Si dipolar interaction averages to be parallel to the direction of the rotation axis (see Figure 2). The $^1$H-$^{29}$Si dipolar vector is then always directed to the polymer chain axis. The angular-dependence of the dipolar interaction is described by the second-order Legendre polynomial, $P_2$. Therefore, the signal intensity attenuation occurs during the CP process for polymers whose rotation axis is oriented near along the magic angle relative to the applied magnetic field, $B_0$. The theoretical simulation considering the orientation-dependence of the CP efficiency, as shown on the experimental CSA spectrum at 240°C by a pink curve in Figure 1, successfully explains the experimental spectrum with the “magic angle hole.” This concept is confirmed by the $^{29}$Si direct polarization (DP)/CSA and ultra-slow magic angle spinning (MAS) CP/CSA experiments. The change in the interchain packing from a monoclinic to a hexagonal lattice at 166°C, which is analyzed by electron diffraction experiments, is therefore found to originate from the chain rotation dynamics around the molecular chain axis. From an analytical point of view, we provide an easy way to detect the rotational motion in solid materials.


Grants


Figure 1. Temperature dependence of $^{29}$Si CP/CSA spectra of PDMS from 23 to 240°C. The arrow indicates the isotropic chemical shift, that is, the theoretical position of the magic angle hole. The simulated spectra for the experimental spectra of 23°C and 240°C are shown by the green curves.

Figure 2. Rotational motion of PDMS in the mesophase.