MOLECULAR DYNAMICS OF POLY(L-LACTIDE) BIOPOLYMER STUDIED BY WIDE-LINE SOLID-STATE ^{1}H AND ^{2}H NMR SPECTROSCOPY

F. Nozirov (NHMFL); A. Nazirov (UAM, Physics, Poland); S. Jurga (UAM, Physics, Poland); R. Fu (NHMFL)

Introduction

High molecular mass PLA shows mechanical and barrier behavior comparable to synthetic polymers such as polystyrene (PS) and polyethylene terephthalate (PET) [1]. X-ray analysis [2] indicated that PLA crystallizes in the orthorhombic lattice unit cell with a=1.07, b=0.645, and c=2.78~1.05 nm. It was shown that PLA forms the 10_3 α-helical conformation [3]. However, the molecular dynamics of such materials has not been well understood, even though some materials such as PHB and poly(glicolide/caprolactone) [5] have been studied. Here, comprehensive solid state nuclear magnetic resonance (NMR) studies are performed in order to understand the molecular dynamics of poly(L-lactide) (PLLA).

Experimental

A sample of poly(L-lactide) (PLLA) (20,000 g/mol) was purchased from Aldrich. A PLLA sample (8,600 g/mol) selectively deuterated at the -CH_3 and -OH sites. The proton spin-lattice relaxation times, T_1 were measured and the ^{2}H NMR spectra were recorded as a function of temperature on a Bruker NMR spectrometer.

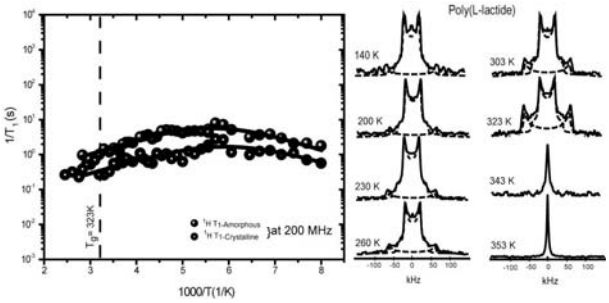

Figure 1. A) Arrhenius plot of the relaxation rate ($1/T_1$) for the PLLA samples. B) ^{2}H NMR line-shape versus temperature.

Results and Discussion

Fig.1A shows the ^{1}H relaxation rates in the Arrhenius representation for the PLLA sample. Two ^{1}H spin-lattice relaxation times were obtained from the bi-exponential fittings from the proton relaxation measurements, which correspond to two different (i.e. the amorphous and crystalline) phases in the biopolymer. As shown in Fig.1B, when increasing temperatures, more and more termini hydroxyl groups in the segments of the biopolymer chains are involved in the hydroxyl reorientation, resulting in the increase of the intensity stemming from the motional hydroxyl groups. When the temperature goes above the glass transition temperature T_g (i.e. 323 K), the segments of the biopolymer chains start to break down or the so-called onset of the entangled process starts, and eventually reaches a liquid state upon the melting at 330 K of the biopolymer resulting in a narrow ^{2}H NMR peak.

Conclusions

The molecular dynamics of the PLLA biopolymer has been well characterized by various wide-line ^{1}H and ^{2}H solid-state NMR techniques. Our results indicate that the methyl groups' three-fold (C_3) reorientation and the hydroxyl groups' two-fold (C_2) reorientation are the two major motions existing in the biopolymer. The methyl group rotation is dominant at low temperature (e.g. 90 K), while the hydroxyl reorientation plays an important role in the dynamics when the temperature is above the glass transition temperature Tg of 323 K. In the temperature range of 130 – 325 K, both the methyl and hydroxyl reorientation coexist in PLLA, although the former plays a much greater role in the dynamics than the latter one.

Acknowledgements

This work was supported by the NHMFL In-House Research Program, and in part by the Department of Macromolecular Physics, University of Adam Mickiewicz, Poland.

References

[1] Auras, R.A., *et al*., J Plast Film & Sheeting, **19**(2): p. 123-135 (2003)
[2] Miyata, T. *et al.* Polymer, **38**(16): p. 4003-4009 (1997).
[3] De Sentis, *et al*, Biopolymers, **6**: p. 299 (1968)
[4] Nozirov, F., *et al.*, Solid State Nucl. Magn. Reson., **22**(1): p. 19-28 (2002).