Order-disorder states in Li^+-doped poly(ethylene glycol) distearates: a SAXS/WAXS/DSC study

T.S. Plivelic,[1] G.L. Mantovani,[2] E.R. deAzevedo,[2] P. Judenstein,[3] T.J. Bonagamba,[2] I.L.Torriani[1,4]

[1]Laboratório Nacional de Luz Síncrotron, Campinas, SP Brazil; [2]Instituto de Física de São Carlos, USP, São Carlos, SP Brazil; [3]RMN en Milieu Orienté, ICMMO, Université Paris-Sud, Orsay France; [4]Instituto de Física, IFGW, Cps, SP Brazil

Introduction

Li-doped ABA triblock copolymer poly(ethylene glycol) distearates (PEGD) is a potential candidate to be used as solid-state polymer electrolytes substituting liquid electrolytes in rechargeable lithium batteries. Li^+ mobility takes place in the amorphous phase and its diffusion occurs through a complex mechanism involving PEG segmental mobility. Crystallization has to be avoided by modifying the polymer structure or by adding fillers to inhibit regular packing [1]. However, the phase behavior and conductivity of this material depends on the PEG/PE molecular weight ratio ($R = Mw_B/Mw_A$) and on the oxygen-to-lithium ratio (y), where the oxygen considered are only those of the ethylene glycol segments. The effects of these two parameters on the phase behavior of Li-doped PEGD were studied by simultaneous and time resolved SAXS/WAXD/DSC experiments.

Methods and Materials

The PEGD samples with two molecular weights (Mw~ 930 (R=0.83) and 6500 (R~12.5)) were obtained from PolySciences and lithium perchlorate ($LiClO_4$) from Aldrich. The complexes with several y values were mixed at 80 °C under vigorous stirring appropriate amounts of $LiClO_4$ and PEGD. After preparation, the samples were dried at 60 °C under vacuum during 16 hours and encapsulated in modified aluminum DSC pans with mica windows for the experiments. Measurements were performed at the Small Angle Scattering workstation of the LNLS (LNLS-D11A). A *Linkam DSC (THM 600)* of single-pan design was used for the calorimetric measurements. The X-ray experiments were recorded simultaneously in two linear position sensitive detectors[3]. All the samples were first melted to 100 °C. Subsequently they were cooled to -70 °C and heated again to 100 °C at two different rates: 10 or 2 °C/min.

Results and Discussion

For block copolymers with R=0.83, SAXS experiments indicate the presence of long range order above the stearate melting point and show an order-disorder transition when at least one Li^+ per PEG chain is present ($y \leq 9$), in agreement with previous NMR and cross polarized light microscopy (PLM) observations [2]. The temperature at which the transition takes place increases as a function of the Li-doping level. The order-disorder kinetics was studied following the SAXS intensity maxima, $I(q_m)$, as a function of the sample temperature. Significant hystereses, of about 20 °C, between heating and cooling scans are observed at the higher temperature rate (10 °C/min) whereas at 2 °C/min a near reversible process is noticed.

For PEGD with R ~ *12.5*, simultaneous WAXS and DSC data seem to indicate that for lower doping levels ($y \geq 9$), both branches of the copolymer crystallize, whereas higher lithium concentrations prevent PEG crystallization. SAXS curves during heating scans reveal a very complex morphology depending on temperature range and doping level. For example, for y = 12 and $-70 \leq T < 5$ °C, the coexistence of a lamellar morphology (with a characteristic average long period equal to 210 Å) and two other correlation peaks (at $q = 0.105$ and 0.165 Å^{-1}) are observed. Above the stearate melting point ($T > 60$ °C), a correlation peak is observed (Fig. 1). WAXS data are also shown in Fig. 1. For higher doping levels (y=5), more than one correlation peak is detected with a relation between the q-value of the maxima that seems to indicate an hexagonal packing of PE cylinders. Moreover, the principal peak indicates bigger correlation distances and has reduced FWHM due to the steric hindrance caused by Li intercalation in the PEG chains.

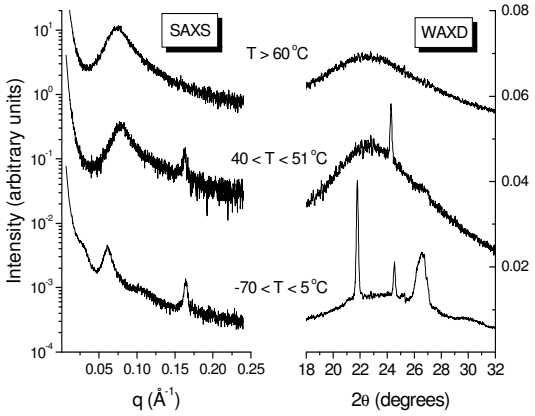

Fig. 1. Typical SAXS and WAXD intensity curves for PEGD 6500 with y=12, in the three temperature ranges indicated in the figure.

The above results represent a contribution to the understanding of the structural phase behavior and the existence of order-disorder states in Li+ doped PEGD. Further experiments are underway with copolymers of different molecular weights and doping levels.

Acknowledgements

Combined X-ray and DSC experiments were performed at LNLS under proposal D11A-SAXS 2915. Research partially supported by FAPESP, CNPq and CAPES.

References

[1] F.M. Gray: Polymer Electrolytes, RSC Materials Monograph, Cambridge UK, 1997.

[2] MV Giotto, CL Sangiorge, DJ Harris, AL Oliveira, K. Schmidt-Rohr, T.J. Bonagamba. Macromolecules **35** (2002) 3576.