Scientific paper

SAXS/WAXD/DSC Study of Zn^{2+}-ion Conducting Polymer Electrolyte

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Dedicated to the memory of Professor Ljubo Golič

Abstract

Electrolytes are nanostructured materials that are very attractive for batteries or other types of electronic devices. $(PEO)_8ZnCl_2$ polymer electrolytes were studied by small-angle X-ray scattering (SAXS) simultaneously recorded with wide-angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC) at the synchrotron ELETTRA. It was shown by previous impedance spectroscopy (IS) that the room temperature conductivity of polymer electrolyte increased two times above 65 °C. The SAXS/DSC measurements yielded insight into the temperature-dependent changes of the grains of the electrolyte. The crystal structure of the nanosize grains was revealed by the simultaneous WAXD measurements.

Keywords: SAXS, WAXD, DSC, polymer electrolyte, nanocomposite

1. Introduction

Understanding the structure of new materials on the mesoscopic scale (2–50 nm), such as clusters, aggregates and nanosized materials, requires suitable experimental techniques. Electromagnetic radiation can be used to obtain information about materials whose dimensions are on the same order as the radiation wavelength. Scattering of X-rays is caused by differences in electron density. Since the larger the diffraction angle the smaller the length scale probed, wide angle X-ray diffraction (WAXD) is used to determine the crystal structure on the atomic length scale while small-angle X-ray scattering (SAXS) is used to explore the microstructure on the nanometer scale.

SAXS experiments are suitable to determine the structure of nanocomposite polymer electrolyte. The solid electrolyte poly(ethylene oxide) (PEO) is one of the most extensively studied systems due to its relatively low melting point and glass transition temperature T_g, and its ability to play host to a variety of metal salt systems in a range of concentrations. Polymeric complexes of $(PEO)_n$ with $ZnCl_2$ have been used, due to their stability and very high conductivity[1,2]. We have observed that the ionic conductivity at room temperature is up to two times larger compared to that above the phase transition temperature of 65 °C[3]. Our research was aimed at optimizations of electrolyte properties[3] as these materials are attractive as electrolytes for second generation of polymer-based rechargeable batteries[4] or other types of electronic devices.

The aim of the present investigation was to study by simultaneous SAXS/WAXD/DSC measurements the thermal behavior of the $(PEO)_8ZnCl_2$ electrolyte. The polymer-salt complex was prepared by dissolving $ZnCl_2$ (p.a. Merck) and poly(ethylene oxide) (laboratory reagent, BDH Chemicals, Ltd., Poole, England, Polyox WSR-301, $M_W = 4 \cdot 10^6$, Prod 29740) in 50% ethanol-water solution in stoichiometric proportions[3].

Simultaneous SAXS, WAXD and DSC measurements were performed at the Austrian SAXS beamline at the synchrotron ELETTRA, Trieste[5]. Photon energy of 8

keV was used, and the size of the incident photon beam on the sample was 0.1 · 5 mm (h x w). For each sample, SAXS and WAXD patterns were measured simultaneously in transmission setup using two 1D single photon counting gas detectors. The SAXS detector was mounted at a sample-to-detector distance of 1.75 m, corresponding to a q-range of 0.007–0.32 $Å^{-1}$. The WAXD detector was mounted to cover a d-spacing range of 0.32–0.94 nm.

The scattering wave vector, s equals $s = 2 \sin \theta/\lambda = q/2\pi$, where 2θ is the scattering angle and $\lambda = 0.154$ nm the used wavelength. The method of interpreting the SAXS scattering data is based on the analysis of the scattering curve, which shows the dependence of the scattering intensity, I, on the scattering wave vector s.

The in-line micro-calorimeter built by the group of Michel Ollivon (CNRS, Paris, France)[6] as used to measure simultaneously SAXS/WAXD and high sensitivity DSC from the same sample. DSC phase transition temperature was determined at the intersection of tangent to the peak and the baseline. The heating and cooling cycles were performed at controlled rates of 1 °C/min, 3 °C/min and 5 °C/min. Thus, recording of one heating-cooling cycle took 160 min, 54 min and 32 min respectively. Here we present the run of 1 °C/min which lasted 2 hours and 40 min.

SAXS is observed when electron density inhomogenities of nanosized objects exist in the sample. If identical grains of constant electron density ρ are imbedded in a medium of constant ρ_0, only the difference $\Delta\rho = (\rho - \rho_0)$ will be relevant for scattering. If the grains are separated from each other widely enough, it is possible to assume that they will independently contribute to the scattered intensity. The central peak arises from all added secondary waves in phase at $s = 0$. The amplitude is equal to the number of excess electrons as only the contrast to the surrounding medium is effective. For the central part of the scattering curve, the universal Guinier approximation for all types of scattering objects/grains is valid[7]

$$I_1(s) = \frac{1}{2\pi}(\Delta n_e)^2 \exp^{(-4\pi^2 s^2 R^2/3)} \qquad (1)$$

where R is the gyration radius and Δn_e is the number of the excess electrons, as for SAXS only the contrast towards the surroundings is effective. The radius of gyration is the average square distance from the centre of masses that are electrons.

Figure 1 shows the results from the SAXS and DSC measurements on polymer electrolyte $(PEO)_8ZnCl_2$ which were performed simultaneously at the SAXS-beamline of ELETTRA. The average radii of grain sizes obtained by applying equation (1) are compared to the corresponding DSC spectra. In the heating cycle of the SAXS data there are two trends, first an increasing of the grain size up to 65 °C and then a sudden drop at this phase transition temperature. In the cooling cycle of SAXS a hysteresis can be seen as the recrystallization occurs at lower temperature. The exothermic and endothermic peaks found in DSC du-

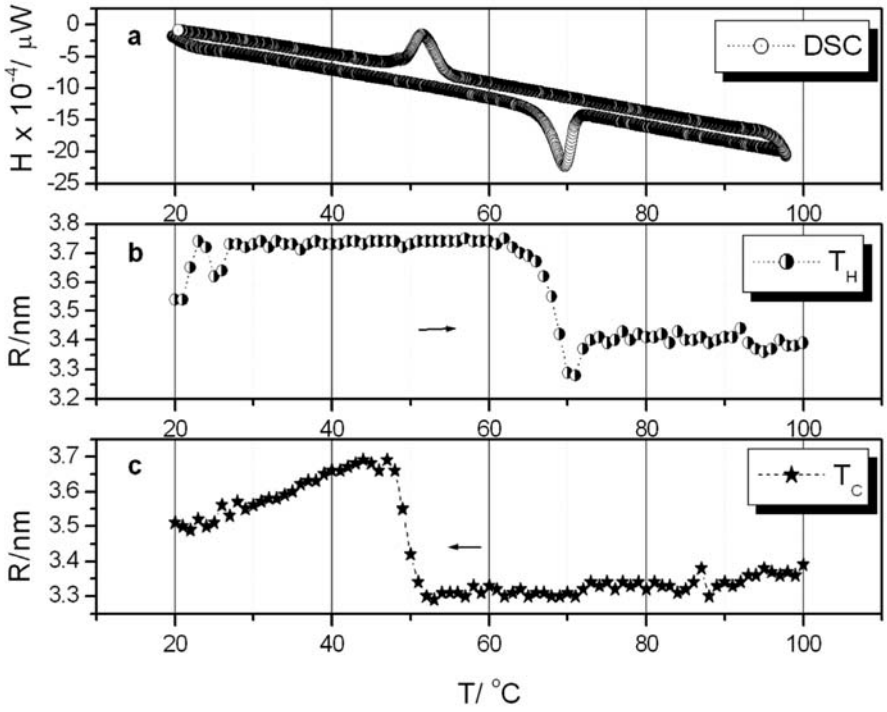

Fig.1: DSC and SAXS-results for polyelectrolyte $(PEO)_8ZnCl_2$ in the temperature range from 20 °C till 100 °C, a) showing the DSC cycle (denoted with DSC), b) presenting the heating cycle of SAXS (denoted with T_H) and c) is the cooling cycle of SAXS (denoted with T_C).

Table 1. Changes of average grain radius <R>/ nm calculated by (1), R=D/2 as determined from (2) and phase transition temperatures T (in °C) in $(PEO)_8ZnCl_2$ polyelectrolyte during heating and cooling as determined by SAXS/WAXD/DSC measurements. DSC recorded in previous measurements[8] are shown in the second column of DSC data presented in the Table.

heating							
	SAXS		WAXD		DSC		
T °C	<R>/nm 20–65 T °C	<R>/nm 65–100 T °C	T °C	R/nm	T °C	T °C[(8)]	ΔH J/g[(6)]
65	3.5–3.8	3.3–3.4	65	33.7–29.7	65	62.6	151.3
cooling							
	SAXS		WAXD		DSC		
T°C	<R> /nm 100–65 T °C	<R>/nm 65–20 T °C	T °C	R/nm	T °C	T °C[(8)]	ΔH J/g[(8)]
53	3.4–3.2	3.7–3.5	58	35.3–27.4	55	37.0	–112.0

ring the same temperature cycle are in agreement with the sudden changes in the average nanograin sizes as obtained from the SAXS measurements.

The average radius of grains varies from 3.5 to 3.8 nm in the region below the phase transition temperature and then from 3.3 to 3.4 nm in the highly conductive phase of the polymer electrolyte[3]. The DSC spectrum shows the start of the endothermic peak at 65 °C in the heating cycle. The cooling cycle in the SAXS data shows the start of the recrystallization at 53 °C, and final grain sizes in the range from 3.7 nm to 3.5 nm. The DSC spectrum shows a phase transition temperature at 55 °C, which is determined at the beginning of the peak in the cooling cycle. Both, the SAXS and DSC data in the cooling cycles show a hysteresis, that is much lower temperatures for the re-crystallization than 65 °C. This temperature is the melting temperature of the PEO crystallites i.e. "spherulites"[8], but in the case of the polymer electrolyte we have combined forms of PEO and $ZnCl_2$ or just $ZnCl_2$ crystallites. The combined SAXS and DSC results are presented in the Table 1. WAXD recordings were performed simultaneously to SAXS/DSC measurements. In the Figure 2 a) and b) the WAXD results are shown as 3-D plots for a heating and a cooling cycle. In the heating cycle the phase transition occurs at 65 °C and in the cooling cycle there is again a hysteresis and the recrystallization occurs at 58 °C. Above the phase transition temperature the WAXD spectra are registering the amorphous phase of the polymer electrolyte. Figure 3 is showing WAXD spectra at 20 °C with h k l indices obtained from Powder Diffraction File PDF-2 (2003) card number: 16-0869[9]. An assignation of the WAXD lines in the heating and the cooling cycle is given in Table 2.

The most intensive lines in WAXD attributed to combined $PEO/ZnCl_2$ crystallites disappear at 65 °C, but lines of lower intensity representing the PEO "spherulites" are disappearing at a somewhat lower temperature of 61 °C. In the cooling cycle the strongest WAXD lines re-appear at 58 °C, and those lines of lower intensity at 56 °C.

a)

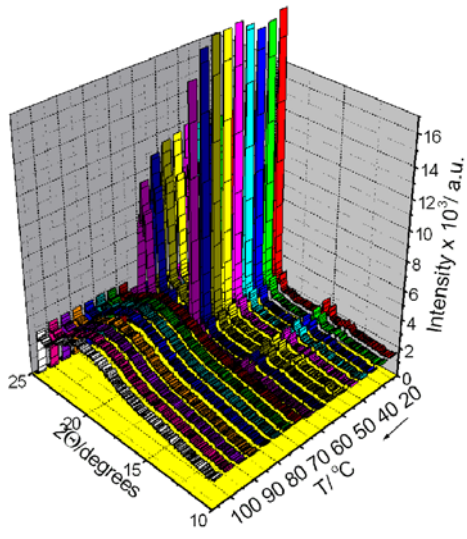

Fig. 2: a) 3D WAXD of $(PEO)_8ZnCl_2$ during a heating cycle.

b)

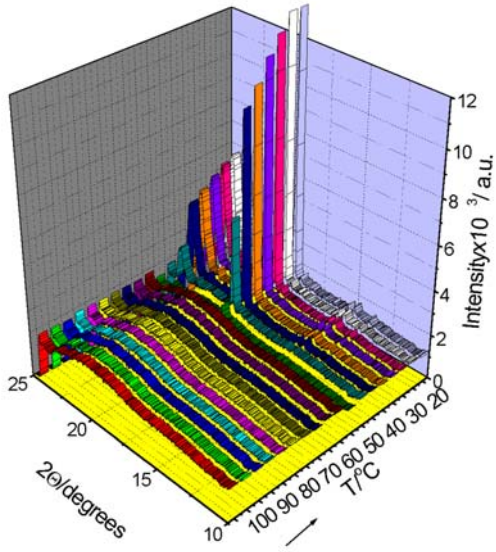

Fig. 2: b) 3D WAXD of $(PEO)_8ZnCl_2$. during a cooling cycle.

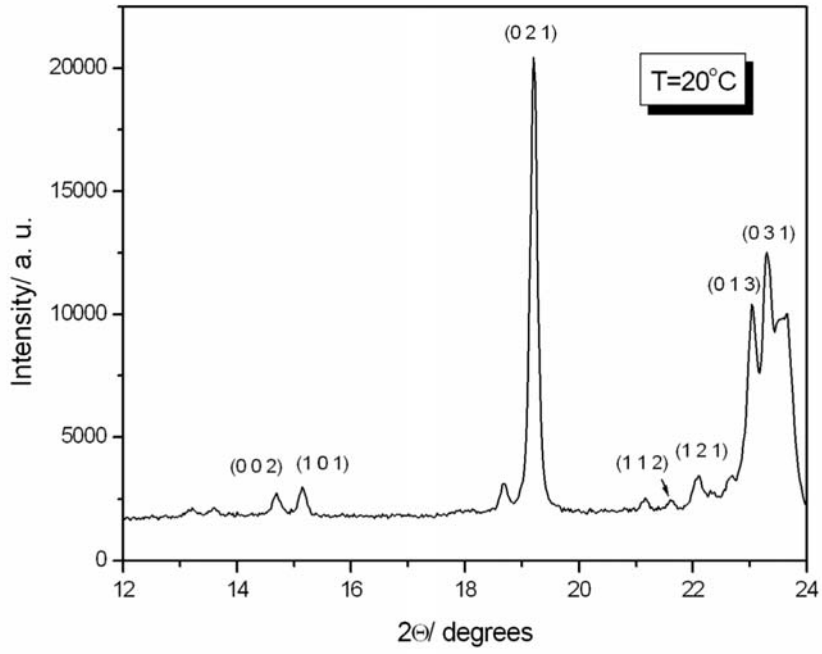

Fig. 3: WAXD of $(PEO)_8ZnCl_2$ at 20 °C with h k l indices determined for β-$ZnCl_2$.

With SAXS nanograins were recorded as melting and/or changing sizes within a 10 °C range around the phase transition temperatures. In the heating cycle for DSC the range of temperatures from 65 °C to 70 °C goes from the beginning of the phase transition till the exothermic peak. The range of temperatures in the cooling cycle for DSC goes from 55 °C to 53 °C. For WAXD the diameter of the nanocrystalline grains is obtained by the Debye-Scherrer equation:

$$D = \frac{K \cdot \lambda}{\beta \cdot \cos\theta} \qquad (2)$$

where K is a dimensionless constant, λ is wavelength of the incident X-ray beam, and β is full width at half maximum (FWHM) of the WAXD line. K may range from 0.89 1.39 depending on the specific geometry of the scattering objects. In our calculation we have used K = 0.9. It is value between 0.89 for perfect two dimensional lattices[10] and 0.94 for a cubic three-dimensional crystal[11]. We have analyzed the strongest line at 2θ = 19.23, which we assigned to PEO/$ZnCl_2$ contribution with calculation error of 15%. This error could count for decreasing trend in WAXD nanocrystallites in the heating cycle. Peaks for PEO and $ZnCl_2$ are of lower intensities and they disappear at slightly lower temperatures than the strongest PEO/$ZnCl_2$ peak. This material is nanocomposite and all these components are mixed together. The results are summarized in Table 2.

WAXD obtained radius values for the grain sizes are higher than the SAXS values and at 20 °C are equal to 33.7 nm, decreasing to 29.7 nm at 64 °C. In the cooling cycle the grain size at 58 °C is 35.3 nm, and again at 20 °C is 27.4 nm. The trend of gyration radius in the cooling cycle after phase transition is the same as for the radius of WAXD crystallites and it is decreasing. Possible explanation for radius of gyration is that at the phase transition it has sudden jump to higher value and than gradually it decreases to the initial value of the thermal cycle. As SAXS obtained nanograins can be partly amorphous it could be explained by total crystallization and thus shrinkage at lower temperatures. Then picture of smaller nanograins incorporated in bigger ones recorded by WAXD could explain decrease of WAXD obtained radius. In the heating cycle increasing of radius of gyration can suppress growth of WAXD crystallites and their radius is decreasing. The WAXD results are, together with SAXS and DSC data, presented in the Table 1.

The combination of the three methods reveals the nature of the physical transformation of the polymer electrolyte into a super ionic conductor. The nanocomposite crystalline and amorphous polymer matrix is turning into an amorphous highly conductive phase. Parallel to WAXD, SAXS is showing the existence of nanograins in both the low and high temperature phase. At the phase transition temperature the grain size changes, is becoming smaller at higher temperatures. The nature of the nanograins as seen by SAXS is not just the pure crystalline, but also the partly amorphous form, while WAXD records on-

Table 2. Assignments of the $(PEO)_8ZnCl_2$ WAXD lines according to values reported in the Powder Diffraction File PDF-2 (2003) cards numbers: 49–2201 and 16-0869[9].

Assignation	Intensity	h k l β–$ZnCl_2$	2θ/degrees heating 20 °C	heating 64 °C	cooling 58 °C	cooling 20 °C
1= PEO	6		13.22			13.14
2 = PEO	5		13.60			13.57
3 = PEO/ZnCl2	14	002	14.68			14.68
4 = PEO/ZnCl2	14	101	15.14			15.11
5 = PEO	16		18.66			18.68
6 = PEO/ZnCl2	100	021	19.23	19.09	19.17	19.19
7 = $ZnCl_2$	12	112	21.16			21.15
8 = PEO	13		21.65			21.60
9 = $ZnCl_2$	17	121	22.10			22.09
10 = PEO	18		22.70			22.66
11 = PEO/ZnCl2	51	013	23.05	23.02	23.00	23.08
12 = PEO/ZnCl2	61	013	23.33	23.24	23.27	23.32
13 = PEO/ZnCl2	49	031	23.61			23.56

ly pure crystalline nanograins. Thus the picture of the highly conductive phase consists of a completely amorphous polymer matrix, which is known to be suitable for ion-conduction by elastic movement of PEO chains, and of nanograins of combined PEO/$ZnCl_2$ structure, which could contribute to Zn^{2+}-ion conduction by a hopping mechanism. The presence of ion-transport pathways can be as important under right circumstances as polymer segmental motion[12–14].

The same experiments were also performed on polymer electrolytes treated by irradiation with γ-rays and by adding of TiO_2 nanograins of 25 nm size. These results will be presented in the next paper.

The combined SAXS/WAXD/DSC measurements have shown that the nanostructure of the polymer electrolyte $(PEO)_8ZnCl_2$ is changing during the crystalline-amorphous phase transition to a highly conductive super ionic phase. The significant role that the nanodimensions of the electrolyte material play in the Zn^{2+}-ion mobility was discussed. The combined SAXS/WAXD information about the evolution of the average grain sizes during the phase transition gave insight into the nanomorphology, which influences the ionic transport in a nanocomposite polymer electrolyte. Further optimizations of the electrolyte properties are in progress since these nanostructured materials are very attractive for batteries or other types of electronic devices.

2. Acknowledgment

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Povzetek

Elektroliti kot nanomateriali se izkazujejo kot zelo primerni pri baterijah in pri različnih elektronskih napravah. Z metodo ozko- (SAXS) in široko- (WAXD) kotnega sipanja rentgenske svetlobe in z uporabo diferenčne skaning kalorimetrije (DSC) na sinhrotronu ELETTRA, Trst, Italija, je bil v detajle preiskan vzorec $(PEO)_8ZnCl_2$ polimernega elektrolita. Kombinacija SAXS/DSC meritev je omogočila spremljanje spreminjanja zrn v elektrolitu. Meritev WAXD je tudi pokazala zrna nano velikosti.