SAXS/DSC/WAXD study of TiO_2 nanoparticles and the effect of γ-radiation on nano-polymer electrolyte

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Abstract. Polymer electrolytes as nanostructured materials are very attractive for components of batteries and opto-electronic devices. $(PEO)_8ZnCl_2$ polymer electrolytes and nano-composites were prepared using PEO γ-irradiated to a selected dose of 529 kGy and with addition of 10% of TiO_2 nanograins. The influence of the added nanosize TiO_2 grains to the polymer electrolytes and the effect of γ-radiation from a Co-60 source were studied by small-angle X-ray scattering (SAXS) simultaneously recorded with differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD) at the synchrotron ELETTRA. Infrared (IR) and impedance spectroscopy (IS) were also performed [1]. It was shown by previous impedance spectroscopy (IS) that the room temperature conductivity of nanocomposite polymer electrolyte increased more than two times above 65°C, relative to pure composites of PEO and salts. We observed changes between 293 K and 373 K for treated and as prepared polymer electrolyte in SAXS, DSC and WAXD spectra and during the phase transition to the superionic phase at 335 K [2, 3]. The SAXS/DSC measurements yielded insight into the temperature-dependent changes of the grains of the electrolyte as well as to differences due to different heating and cooling rates. The crystal structure and temperatures of melting and crystallization of the nanosize grains was revealed by the simultaneous WAXD measurements.

Keywords: Nanocomposite polymer electrolyte, SAXS/DSC/WAXD

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.

SAXS experiments are suitable to determine the structure of nanocomposite polymer electrolyte. 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, its ability to play host to a variety of metal salt systems in a range of concentrations and, recently, as material with the smallest ever prepared polymer crystals [4]. Polymeric complexes of $(PEO)_n$ containing $ZnCl_2$ have been used, due

to their stability and very high conductivity [5, 6]. 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 [1]. Since a polymer is a composite of an amorphous and a crystalline part, the conductivity is occurring in the amorphous part, the treatments by introducing TiO_2 nanograins and irradiation with γ-radiation from a Co-60 source, were directed towards the inhibition of the crystalline phase in the polymer matrix. The crystalline phase of polymer matrix consists of spherical shapes, spherulites, which are growing with time and temperature, thus impeding conductivity. The aim of the present investigation was to study the temperature behaviour of the $(PEO)_8ZnCl_2/TiO_2$ electrolyte by simultaneous SAXS/WAXD/DSC measurements measurements in order to observe the changes of the nanosized structure around the superionic phase transition.

2. Experimental

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, MW=$4x10^6$, Prod 29740) in 50 % ethanol-water solution in stoichiometric proportions with addition of TiO_2 (Degussa P25) nanograins of average size of 25 nm and spherical shape [1]. The polymer-salt complex solution was then poured onto a Teflon plate and resulting film dried, first in air, and then in vacuum of 10^{-6} mbar for 7 days and then stored in desiccators.

Simultaneous SAXS/WAXD/DSC measurements were performed at the Austrian SAXS beamline at the synchrotron ELETTRA, Trieste [7]. A. photon energy of 8 keV was used, and the size of the incident photon beam on the sample was 0.1 x 5 mm^2 (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 0.0007 - 0.032 nm^{-1}. The WAXD detector was mounted to cover a d-spacing range of 0.32-0.94 nm.

The scattering wave vector, q equals $q=4\pi \sin\theta/\lambda$, 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 q. For the central part of the scattering curve, the universal Guinier approximation for all types of scattering objects/grains is valid [8-12]:

$$I_1(q) = \frac{1}{2\pi}(\Delta\rho)^2 \exp^{\left(-2\pi \cdot q^2 R_g{}^2/3\right)} \qquad (1)$$

where R_g is the gyration radius which is the average square distance from the centre of masses within the grains which are clusters of 10 to 100 atoms.

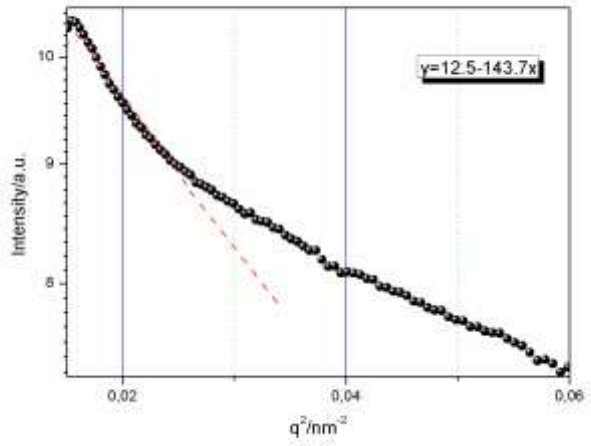

Figure 1. Linear fit y=a-bx to log(I)=f(s) for nanocomposite irradiated with dose of 529 kGy at 20°C.

Figure 1 represents the data for the sample at 20°C where we apply above mentioned Guinier law (1). The "average grain radii" R is estimated from the radius of gyration Rg in this formula. It is calculated from the slope in the linear fit of log(I) vs. f(q) (rad). From this fit line we have obtained Rg and the average grain radius R using $R=(5/3)^{1/2}R_g$ for spherical shapes as R=10.7±0.3 nmFor WAXD the diameter of the nanocrystalline grains is obtained by the Debye-Scherrer equation:

$$D = \frac{0.9 \cdot \lambda}{\beta \cdot \cos\theta} \qquad (2)$$

where λ is wavelength of the incident X-ray beam, and β is full width at half maximum (FWHM) of the WAXD line.

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The in-line micro-calorimeter built by the group of Michel Ollivon (CNRS, Paris, France) [13] was used to measure simultaneously to SAXS/WAXD also high sensitivity DSC from the same sample. The DSC phase transition temperature was determined at the intersection of the tangent to the peak and the baseline.

The grain size and the morphology were observed using scanning field emission electron microscopy (SEM Zeiss Supra 35 VP).

3. Results

Figure 1 shows the results from the SAXS, DSC and WAXD measurements on γ-irradiated nanocomposite polymer electrolyte $(PEO)_8ZnCl_2/TiO_2$.The evolution of the average radii of the grains obtained by applying equation (1) is compared to the corresponding DSC and WAXD spectra behaviour.

The average radius of grains varies from 10.9 nm to 11.0 nm in the region below the phase transition temperature and then 10.6 nm in the highly conductive phase. The cooling cycle in the SAXS data shows the change of grain sizes in the range from 10.6 nm to 10.5 nm.

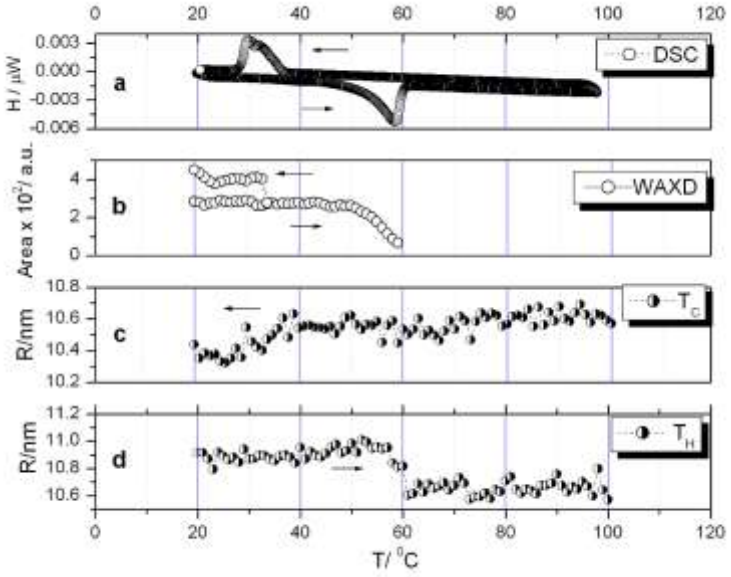

Figure 1. SAXS/DSC/WAXD results for γ-irradiated nanocomposite polyelectrolyte $(PEO)_8ZnCl_2/TiO_2$ in the temperature range from 20°C to 100°C obtained at a rate of 1C°/min: a) DSC heating and cooling cycle, b) the evolution of the intensity of the strong WAXD line at 2θ

=19.21, c) the radius of gyration (R) in the cooling cycle of SAXS and d) R in the heating cycle of SAXS.

From the SAXS measurements of the second run (also performed at a rate of 1°C/min, see Fig. 2), it results that the grain sizes change from 10.7 nm to 11.3 nm, the third run (with 3°C/min, Fig. 3), registers changes from 10.5 nm to 11.0 nm and during the fourth run (with 5°C/min, Fig.4), the grain sizes change from 10.4 nm to 11.1 nm. From these values we can generally conclude that the average grain sizes in all four runs remained in the same range from 10.4 nm to 11.3 nm. In a lamellar picture of PEO [14, 15] these grain sizes would correspond to the lamellae LP2 with no integrally folded (NIF) chains [16, 17] combined with salt and TiO_2.

The SAXS and DSC data show a hysteresis, i.e. much lower phase transition temperatures than 65°C in the cooling cycle. This temperature is the melting temperature of the PEO crystallites i.e. of the spherulites [18-20]. In the case of the nanocomposite polymer electrolyte, combined forms of PEO and $ZnCl_2$, $ZnCl_2$ or both in combination with TiO_2 crystallites, influence the melting temperature. The combined WAXD, SAXS and DCS results are presented in the Table 1.

The WAXD recordings were done simultaneously with the SAXS and DSC measurements. The WAXD obtained radius values for the grain sizes are higher than the SAXS values. For the rate of 1°C/min the WAXD values of the crystallites radii are equal to 73 nm at 20°C, increasing up to 100 nm at 59°C. In the cooling cycle the grain size is 73 nm at 33°C, and again 74 nm at 20°C. The WAXD data are giving the information of the side chain order. During the heating and cooling cycles the side chain ordering is giving us information of the lateral domain sizes or spherulites. The WAXD results for all heating and cooling rates are, together with the SAXS and DSC data, presented in the Table 1.

The differences in the phase transition temperatures for different heating and cooling rates for all SAXS, WAXD and DSC results are evident. The best agreement between the phase transition temperatures among the four runs is achieved for the first run with a heating-cooling rate of 1°C/min. It leads to the conclusion a that it is necessary to achieve good equilibrium conditions and thus slower rates of 1°C/min, such as ½°C/min [21], should be tested in order to achieve better agreement between the results of WAXD, DSC and SAXS measurements for this system.

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. In contrast to WAXD, which exhibits lines and crystalline grains only in the low temperatures crystalline phases, SAXS is showing the existence of nanograins in both the low and high temperature phase. The nature of the nanograins as seen by SAXS is not just the pure crystalline, but also the partly amorphous form, while WAXD records only 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/$ZnCl_2$ and TiO_2 structures, which could also contribute to Zn^{2+}-ion conduction by a hopping mechanism. Under proper circumstances, the presence of ion-transport pathways can be as important as polymer segmental motion [22-24].

The effect of γ-irradiation is seen in lower phase transition temperatures 61°C, 59°C and 50°C versus 71°C, 71°C and 66°C in pure nanocomposite for SAXS, WAXD and DSC, respectively. Also the conductivity in irradiated nanocomposite is higher [1] as compared to pure nanocomposite PEO/$ZnCl_2$ /TiO_2 [3, 25].

SEM photograph of PEO/$ZnCl_2$/TiO_2 irradiated with 529 kGy is shown on Figure 5 with magnification of 10.00 K. This picture is taken at room temperature and is here presented to support visually the SAXS/DSC/WAXD results. On the surface of the sample, beside polymer chains crosslinked by irradiation, some nanoaglomerated grains are visible. Addition of TiO_2 nanograins combined with crosslinking of polymer chains, reduced crystallinity. The space for spherulite growth is reduced, so in nanocomposite prepared from irradiated PEO, spherulites are not visible.

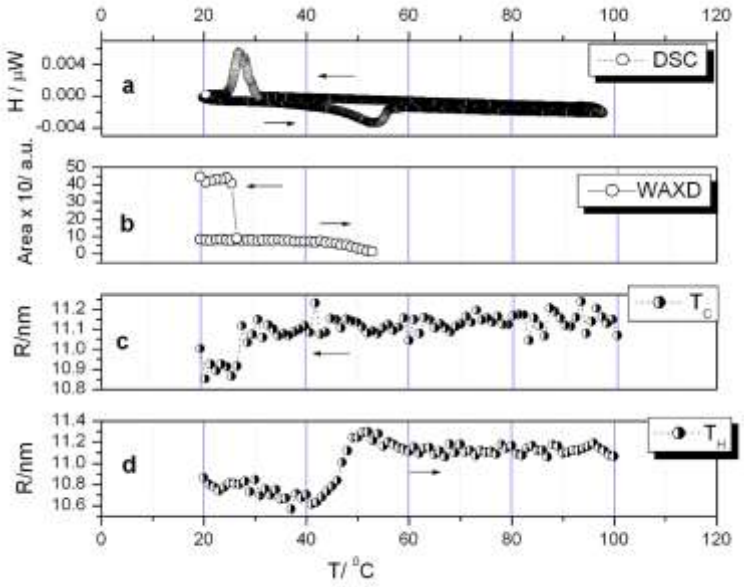

Figure 2. SAXS/DSC/WAXD results for γ-irradiated nanocomposite polyelectrolyte $(PEO)_8ZnCl_2/TiO_2$, obtained during the second cycle with again a rate of 1C°/min.

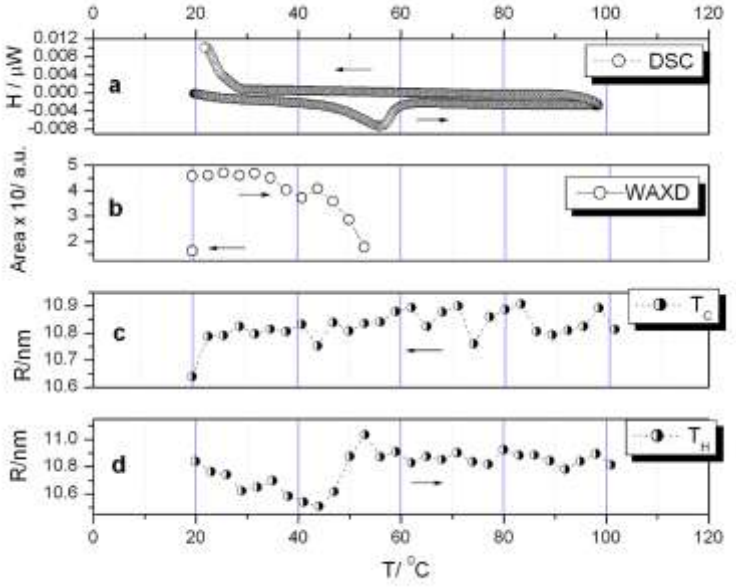

Figure 3. SAXS/DSC/WAXD results for γ-irradiated nanocomposite polyelectrolyte $(PEO)_8ZnCl_2/TiO_2$, obtained at a rate of 3C°/min.

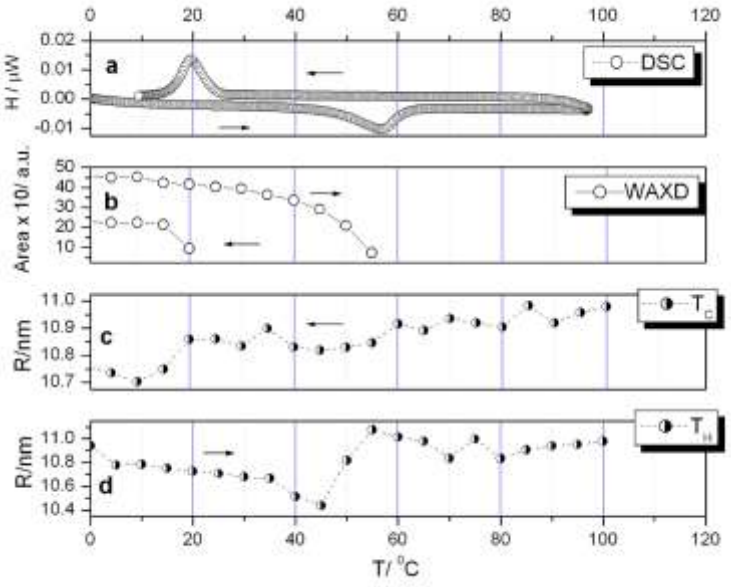

Figure 4. SAXS/DSC/WAXD results for γ-irradiated nanocomposite polyelectrolyte $(PEO)_8ZnCl_2/TiO_2$ obtained at a rate of 5C°/min.

The same combined SAXS/WAXD/DSC experiments were also performed on polymer electrolytes treated by irradiation with γ-rays of different doses of 200 kGy and 309 kGy and by simultaneously adding of TiO_2 nanograins of 25 nm size. Our goal was to find the optimum dose for the best electrical, morphological and elastical properties of nanocomposites. They should be implemented as electrolytes in the second generation of galvanic cells. These results will be presented in the next paper.

4. Conclusion

The combined SAXS/WAXD/DSC measurements have shown that the nanostructure of the polymer electrolyte $(PEO)_8ZnCl_2/TiO_2$ is changing during the crystalline-amorphous phase transition to a highly conductive superionic 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 components of batteries or other types of electronic devices.

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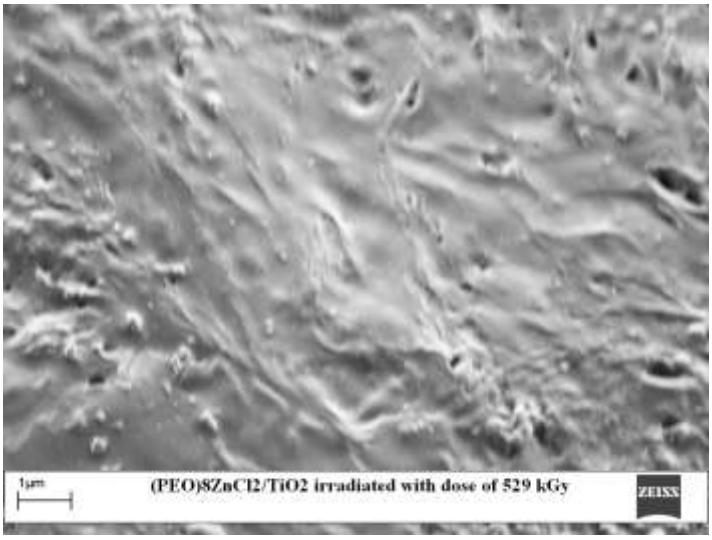

Figure 5 SEM photograph of nanocomposite irradiated with 529 kGy.

Table 1. Changes of average grain radius <R>/ nm calculated by (1), error ~ 3%; r=D/2 as determined from (2), error ~ 10%; and phase transition temperatures t (in °C) in γ-irradiated $(PEO)_8ZnCl_2/TiO_2$ polyelectrolyte during heating and cooling as determined by SAXS/WAXD/DSC measurements.

$(PEO)_8ZnCl_2/ TiO_2$	**heating**				
	SAXS		**WAXD**		**DSC**
heating *(°C/min)*	*t (°C)*	*R (nm)*	*t (°C)*	*r (nm)*	*t (°C)*
1	61	10.9-11.0 10.6-10.7	59	73-100	50
1	51	10.7-10.9 11.1-11.3	53	72-90	47
3	53	10.5-10.8 10.8-11.0	53	61-81	45
5	45	10.4-10.9 11.0-11.1	55	58-81	44
$(PEO)_8ZnCl_2/ TiO_2$	**cooling**				
	SAXS		**WAXD**		**DSC**
cooling *(°C/min)*	*t (°C)*	*R (nm)*	*t (°C)*	*r (nm)*	*t (°C)*
1	37	10.5-10.6	33	73-74	37
1	31	11.0-11.1	27	61-66	30
3	23	10.6-10.8	20	61	29
5	20	10.8-11.0	20	68-74	26

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