

# **In Situ SAXS and GISAXS Studies of Polymeric Membranes for Energy Applications**

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Introduction: In recent years, a new class of materials has been developed by dispersing layered silicates with polymers at the nanoscale level. These new materials have attracted wide interest because they often exhibit chemical and physical characteristics that are very different from the starting material [1, 2]. In some cases, the silicates and polymers exist as alternating layers of inorganic and organic [3]. Nanocomposite materials of PEO and phyllosilicates were first suggested by Ruiz-Hitzky and Aranda [4] as candidates for polymer electrolytes. Within these materials, the polymer chains are intercalated between the silicate layers. The polymer chains then provide a mobile matrix in which cations are able to move. A considerable amount of interest has been shown in nanocomposites of PEO and montmorillonite, a layered aluminosilicate clay. When this composite contains  $\text{LiBF}_4$ , it displays conductivities up to 2 orders of magnitude larger than that of PEO itself at ambient temperatures. However, the addition of lithium salts, which is needed to obtain such conductivity values, is not desirable for two reasons; the first one relates to a more complicated synthetic route and the second relates to the fact that transference numbers are not unity since in this case both cations and anions move.

We have prepared a series of nanocomposites containing PEO intercalated in the layers of hectorite clays. These clays belong are composed of two tetrahedral silicate layers sandwiching a central octahedral layer in a so-called 2:1 arrangement. In hectorite, isomorphous substitutions in the lattice of Li(I) for Mg (II) in the octahedral layers cause an overall negative charge that is compensated by the presence of interlayer, or gallery, cations. A significant amount of interlayer water is also present and the cations are easily exchangeable. Catalytic nanocomposite membranes have also been prepared by ion exchanging  $\text{Pt}^{2+}$  for  $\text{Li}^+$  in synthetic hectorite clay and dispersing this inorganic component within a polymeric matrix. Transparent, self-supporting membranes from the polymer-clay nanocomposite are then made.

Experimental: Preparation of the SLH clay via hydrothermal crystallization at 100°C of silica sol, magnesium hydroxide, and lithium fluoride can be found in detail in reference 1. Colloidal suspensions of 1 g SLH/100 ml de-ionized water were stirred for one-half hour. The desired amount of PEO (100 000 average molecular weight, from Aldrich) was then added, and the mixture stirred for 24 hours. Mixtures contained 0.6, 0.8, 1.0, and 1.2 g of PEO/g of clay. Films were prepared by puddle-casting the slurries onto Teflon-coated glass plates and air-drying. Further drying was carried out at 120 °C under an inert atmosphere for at least 48 hours. The typical thickness of the films is about 40 μm.

The reduction of  $\text{Pt}^{2+}$  to Pt(0) nanoclusters in the catalytic membranes is accomplished by thermal reduction under  $\text{H}_2$  at temperatures higher than 120°C. Loadings are in the 1-2 wt% Pt range. The size of the Pt(0) nanoparticles is determined by in situ small angle x-ray scattering (SAXS) techniques.

*In situ* SAXS and GISAXS were carried out at the Sector 12 of the Advanced Photon Source at Argonne National Laboratory. For the SAXS measurements, monochromatic x-rays (18 keV) were scattered and collected on a 15 x 15 cm<sup>2</sup> CCD camera. The scattering intensity is corrected for adsorption and instrument background. The differential scattering cross section is expressed as a function of scattering vector  $q$ . The value of  $q$  is proportional to the inverse of the length scale ( $\text{\AA}^{-1}$ ). The instrument was operated with a sample to operator detector distances of 228 cm and 390 mm to obtain data at  $0.01 < q < 0.3 \text{ \AA}^{-1}$  and at  $0.08 < q < 2.3 \text{ \AA}^{-1}$ , respectively. For these studies, a specially designed sample holder was used to heat the sample and collect SAXS data at the same time. Films of about 1.25 cm in diameter and 40  $\mu\text{m}$  in thickness were placed in the sample holder and held using Kapton tape. The furnace temperature program was set to ramp from room temperature to 200°C at 5°C/min, and the gas flow of H<sub>2</sub> and He was started at room temperature. For the GISAXS experiments, the membranes were deposited on a silica substrate and an incident angle of 0.15°.

**Results:** Figure 1 shows SAXS data obtained from a film made of PEO/SLH 1.2:1 mass ratio. The data was collected at different room temperatures, as shown in the inset. It is clear that the structure of the polymer has changed as indicated by the near complete disappearance of the PEO crystalline peaks. It is therefore assumed that the polymer chains have relaxed inside the clay layers. Other evidence of such relaxation is the decrease in  $d_{001}$  spacing, which indicates a denser polymer phase. Under these circumstances, the polymer matrix is more mobile and the lithium ions associated with the polymer can have higher transference number, leading to a higher conductivity.

Figure 2 shows the  $R_g$  of the Pt particles formed upon the *in situ* reduction of the polymeric catalytic membranes. The Pt particles start to form above 100°C and the radius reaches a plateau at about 175°C ( $R_g$  is about 12  $\text{\AA}$ ).

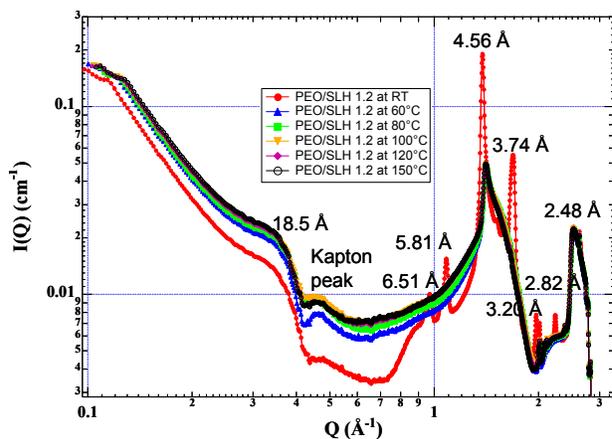


Figure 1: *In situ* SAXS data of a SLH:PEO 1.2:1 ratio film.

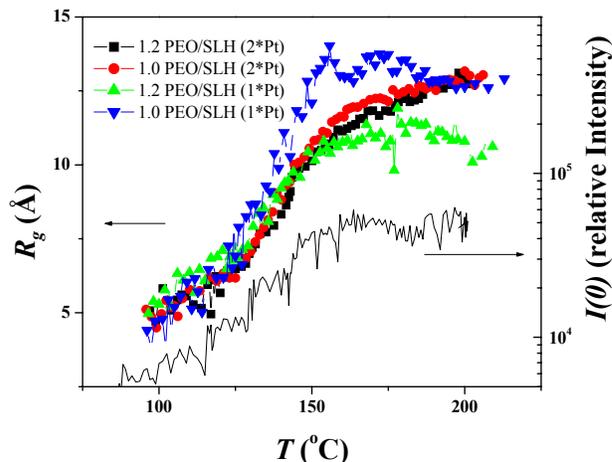


Figure 2: *In situ* GISAXS data of the Pt particle formation in catalytic membranes

## References

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