Experimental report – SC-4260

Experiental dates:5-9.05.2017
Experiental team: Barbara Berke, Orsolya Czakkel, Krisztina László, Erik Geissler
Local Contact: Nathalie Boudet

Structure of thermoresponsible nanocomposites

We performed a detailed small and wide-angle X-Ray scattering study of carbon nanoparticle (CNP) containing thermoresponsive poly(*N*-isopropylacrylamide) (PNIPAM) nanocomposite systems. The aim of this study was to investigate the temperature dependent structure of carbon nanotube (CNT), graphene oxide (GO) and different reduced graphene oxide (rGO) containing PNIPAM based nanocomposite systems nearby the volume phase transition (VPT).

EXPERIMENT

We measured 5 different CNP concentrations at each case, plus the pure PNIPAM gels for comparison. The samples were swollen in H_2O. Measurements were done below (25°C) and above (40 and 50 °C) the VPT temperature. In total 35 samples at 3 temperatures were investigated. We also made measurements about the kinetics of the phase transition at 9 samples.

We used an incident wavelength of 16 keV and three samples-to-detector distances of 0.13, 0.36 and 2.93 m giving an observed Q-range of $2\text{x}10^{-3}$ Å^{-1} ≤ Q ≤ 50 Å^{-1}.

2D data were radially averaged and standard reduction procedures (subtraction of empty cell and solvent contribution) were applied. For equilibrium measurements, the samples were swollen in water and then kept at the desired temperature (25, 40 or 50 °C) for 30 days prior to the experiment.

RESULTS

Below the volume phase transition temperature (VPTT)

The data analysis was combined with the previously obtained SANS data on the same samples. In case of SANS the nanoparticles are practically invisible and the scattering of the polymer matrix dominates the signal, whereas with SAXS, the scattering signal of the polymer is relatively weak, therefore we can get structural information about the incorporated CNPs.

To get the contribution of the CNPs, the corresponding scattered SANS and SAXS signals were compared. Due to contrast differences in the techniques and the incoherent scattering of the SANS, the SANS signal was shifted to the SAXS curves. The contrast differences of the polymer matrix and the nanoparticles were calculated and in the overlapping Q-region, the proportional part of the SANS curves was subtracted from the SAXS signal. The difference of the signals corresponded to the nanoparticles.

The obtained difference curves, which therefore were the signal attributed to the CNPs in the composite matrix was fitted to the so-called Unified model in case of GO.

Fitting the SAXS response curves of CNT@PNIPAM gels using cylindrical structure factors did not give satisfactory results. On the other hand, using a size distribution function which assumes spherical nanoparticles with interfacial interactions satisfactory fits were obtained. This suggests that the CNT cylinders were forming spherical aggregates on the nanometric length scale.

The resulted characteristic length values from the Unified fit and the size distribution model can be seen in Figure 1.

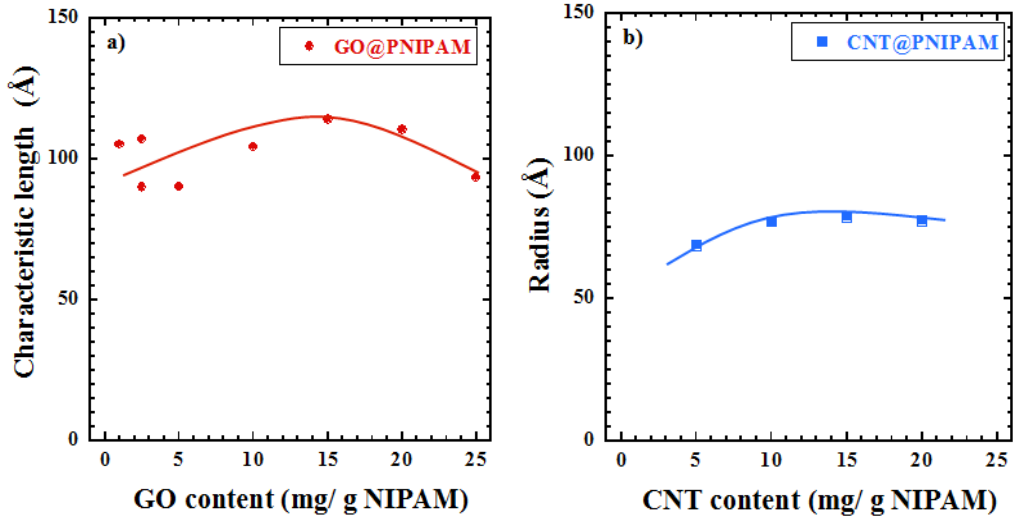

Figure 1. Characteristic values of the difference curves of a) GO@PNIPAM and b) CNT@PNIPAM at 25 °C. The solid lines are guides for the eye.

Above the VPTT

The SAXS response curves showed significantly increased intensity at higher temperatures (Figure 2), however, the difference between the curves measured at 40 and 50 °C was very small. A structure peak could be observed at Q=0.56075 $Å^{-1}$ in all cases. This value corresponds to an interchain distance of the PNIPAM in the collapsed state of D=2π/Q=11.2 Å.

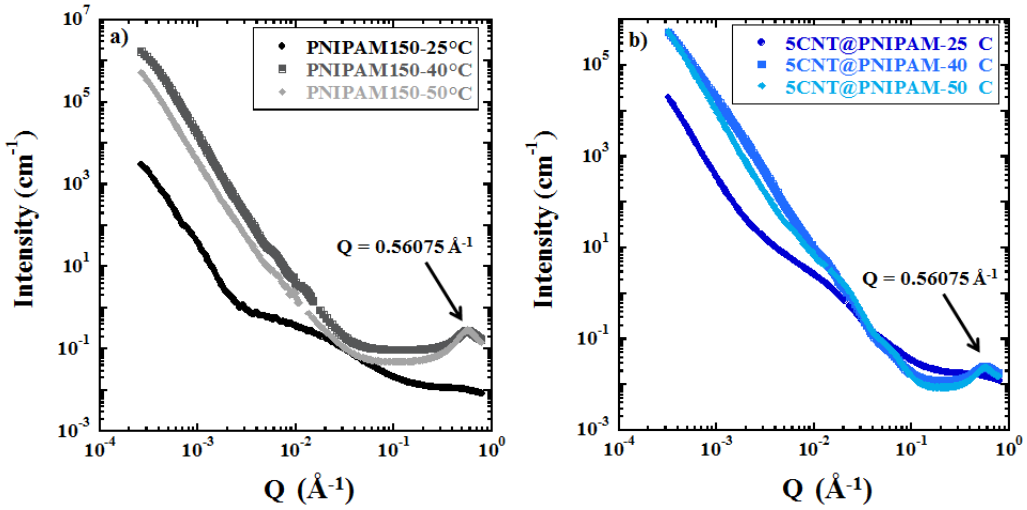

Figure 2. SAXS curves of a) PNIPAM150 and b) 5CNT@PNIPAM samples after water background subtraction at 25, 40 and 50 °C after 10 days. A structure peak could be observed at Q=0.56075 Å-1 in the 40 and 50 °C cases.

The calculation of the CNP signal was performed in the same way above the VPTT as it was shown in case of the low-temperature data to separate the signal of the nanoparticles from that of the polymer matrix.
At 50 °C, owing to the collapsed state the concentration of the polymer was higher, which resulted in that its scattering signal strength became comparable to that of GO particles. As a consequence in case of low GO concentration, no usable signal could be extracted with this method. On the other hand, in case of CNT@PNIPAM samples, the scattering of the CNT aggregates still dominated the overall signal of the nanocomposites. As a result, the obtained nanoparticle signals were satisfactory, even for low CNT concentration.
The obtained characteristic lengths are shown on Figure 3.

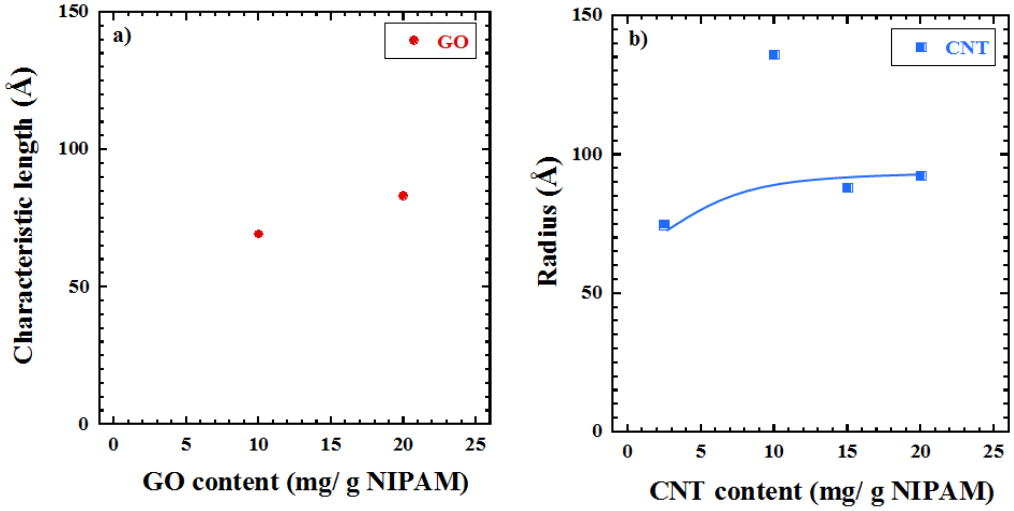

Figure 3. Fitted characteristic values of the difference curves of a) GO@PNIPAM and b) CNT@PNIPAM at 50 °C after 10 days. The solid lines are guide to the eye.

The interpretation of the results is ongoing.