# Experimental report

03/08/2016

**Proposal:** 9-12-446 **Council:** 4/2016

**Title:** Structure of thermoresponsible nanocomposites below and above the volume phase transition temperature

**Research area:** Soft condensed matter

**This proposal is a continuation of 9-12-374**


**Main proposer:** **Barbara BERKE**

**Experimental team:** Barbara BERKE
Orsolya CZAKKEL

**Local contacts:** Lionel PORCAR


**Samples:** heavy water D2O
poly(N-isopropyl acrylamide) (C6H11NO)n
graphene oxide (C2O)n
carbon nanotube C92O8

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| D22 | 2 | 2 | 22/06/2016 | 24/06/2016 |


**Abstract:**

This proposal is a complementary SANS study to the "Dynamics of thermoresponsive nanocomposites below and above the volume phase transition temperature" proposal also submitted in this round. This study aims to investigate the temperature dependent structure of CNT, GO and rGO containing PNIPA based nanocomposite systems nearby the volume phase transition (VPT). This phenomenon is the key for any future application of these responsive "smart" systems. Despite the increasing number of publications on such nanocomposite systems their temperature response behaviour is still poorly understood. With our experiment we expect to gain deeper knowledge on the VPT of the nanocomposites, which would lead us to a better perception of their responsive behaviour. The experiment is related to the ILL PhD project "Carbon nanoparticle - responsive gel composites for controlled delivery".

# Experimental report – 9-12-446

*Experiental dates:22-23.06.2016*
*Experiental team: Barbara Berke, Orsolya Czakkel*
*Local Contact: Lionel Porcar*

Structure of thermoresponsible nanocomposites below and above the volume phase transition temperature

## INTRODUCTION

'Smart' polymer gels exhibit a thermoresponsive behavior in which the matrix swells or deswells according to external stimuli. This phenomenon is the key for any future application of these responsive "smart" 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 poly-N-isopropyl-acrylamide (PNIPA) based nanocomposite systems nearby the volume phase transition (VPT).

## EXPERIMENT

We measured 5 different CNP concentrations at each case, plus the pure PNIPA gels for comparison. The samples were swollen in $D_2O$. 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 D22 with a setup that covers the 0.002-1 $Å^{-1}$ q-range. Sample changer with precise temperature control was used.

## RESULTS

The change of the scattering signal upon the volume phase transition in pure PNIPA gel is shown on Figure 1.

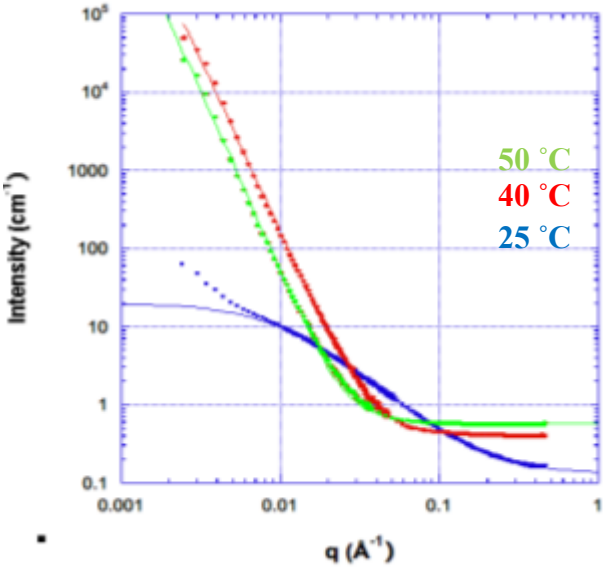


Figure 1 – Scattering signals after background corrections of pure PNIPAgel at 25 (blue), 40 (red) and 50 °C (green) Dots: experimental data points, solid lines: best fits of the data (fitting functions are described in the text).

The measured curves were corrected with background, empty cell, empty beam and were normalized in order to get the scattered signal in absolute units. Before analysis the scattering signal of the corresponding nanoparticle suspensions (in case of the composites) or pure $D_2O$ (in case of the pure PNIPA gel) were subtracted to obtain the pure polymer signal. The curves obtained below the VPTT of the systems could have been fitted by the Ornstein-Zernike (OZ) model (in the q range of 0.01-0.4 $Å^{-1}$), which is a widely used empirical model for polymer gels. Above VPTT, however, this model did not give satisfactory fits. A combined OZ+Porod model fitted the obtained SANS curves well in this case.
We found that the resulted static correlation length depends on the quality and quantity of the used nanoparticle, as well as the temperature (Figure 2).

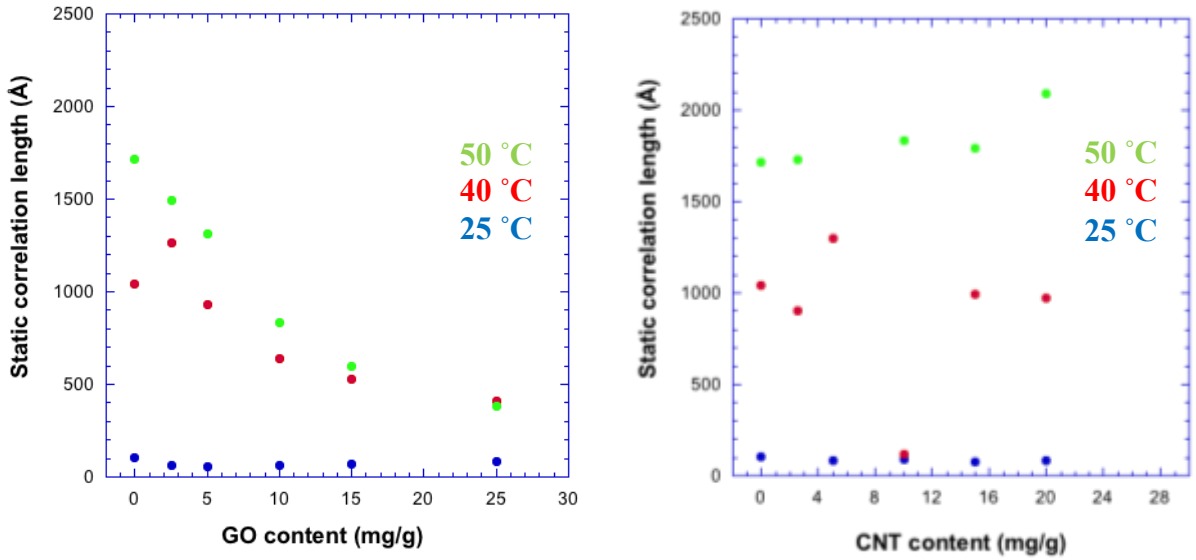


Figure 2 – Static correlation length values of GO (left) and CNT (right) containing gels at different temperatures -25 (blue), 40 (red) and 50 °C (green)

The data evaluation of the rGO containing samples and the kinetical measurement is still in progress.