Enhanced Surface Chemistry of Carbon for Soft Matter Composites

Final report
(1 January 2012 – 31 December 2015)

1. Introduction

Polymer hydrogels, a type of responsive soft materials, consist of a solid three-dimensional network that spans the volume of the liquid medium, water, and establishes a network through surface tension effects. By weight (or volume), gels are mostly liquid, yet they behave like solids due to the three-dimensional cross-linked network within the liquid. The cross-linked polymer network is formed via chemical or physical interactions. Chemical cross-linking is permanent due to covalent bonds. Physical interactions are non-covalent in nature and often result from hydrogen bonding, hydrophobic, or ionic interactions. These gels can be produced from various types of chemical molecules (monomers) or polymer precursors, which can be both synthetic and natural, thus providing unique chemistry to tailor for specific applications. Another important aspect has been that these polymers can be synthesized in different monolith formats, such as disc shaped, thin sheets, beads, etc.

Despite their numerous advantages, their weak mechanical strength, for example, restricts applications involving repetitive loading. Composite hydrogels that incorporate nanoparticles into the matrix, could overcome this drawback. Nanoparticles physically trapped within the hydrogel matrix or crosslinked into the network structure by surface functionalities add unique properties to polymer hydrogels such as mechanical stability or responsiveness to mechanical, optical, thermal, acoustic, magnetic, electric stimulation, etc. The new features may open the way for various applications in separation devices, drug delivery, catalysis, in several biotechnological areas as well as in the electronics, optics, sensors, actuators and microfluidic sectors. Applications of nanoparticles are still under debate because of their potential toxicity. Fixing the nanoparticles into a polymer matrix however eliminates their free release into the environment during operation.

The majority of thermosensitive hydrogels investigated in the past decades are synthetic polymers based on poly(*N*-isopropylacrylamide) (PNIPA). PNIPA hydrogels exhibit a non-linear volume phase transition around 34 °C, i.e. close to the temperature of the (human) body. This can be of use in different biomedical applications.

Carbon nanoparticles (CNPs), owing to their outstanding mechanical and conductive properties, unique structure, and low density, are among the most common polymer fillers. In the past 20 years the exceptional physicochemical properties of carbon nanotubes (CNTs) have stimulated their emergence as an essential platform in nanoscience. Graphene and its derivatives, a new class of two-dimensional carbon nanostructures, also have attracted tremendous attention from both the experimental and theoretical scientific communities in recent years. These nanocarbons possess high electrical and thermal conductivity, high chemical stability and high specific surface area, which may offer advantages for their use as

scaffolds for chemical and biochemical catalysis, decontaminating adsorbents, electronic networks. Nanocarbons in all their forms are difficult to disperse and dissolve in water (and also in organic media), as they are extremely resistant to wetting. The poor dissolution CNPs often limit the development of new designs of electrochemical sensors and biosensors was prevented in this work by using surface modified CNPs.

2. Interactions in nanoparticle free PNIPA gels

2.1. Acid/base properties [1]

PNIPA hydrogels change their hydrophilic/hydrophobic character at the phase transition temperature around 34 °C in pure water, close to the temperature of the human body. As PNIPA is generally reputed to be neutral and non-ionic, previous observations in our laboratory, however, suggest that PNIPA hydrogels are indeed sensitive to both these parameters. In a wide range of pH and ionic strength we considered the possibility that the effects of these two parameters may not be independent.

The pH and ionic strength sensitivity of PNIPA hydrogel was investigated in different acid (0≤pH≤3), base (11≤pH≤14), salt and buffer (3≤pH≤9) solutions (**Figure 1**).

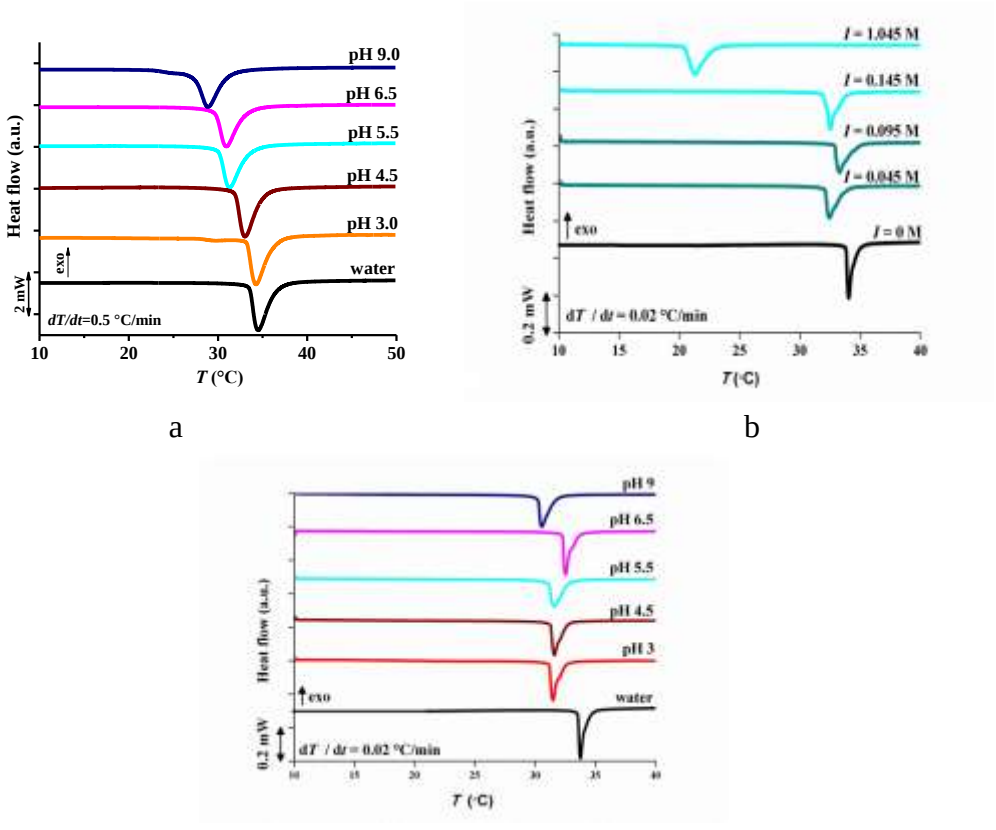

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Figure 1 Differential scanning microcalorimetry (DSC) response of PNIPA swollen (a) in phosphate buffer solutions of different pH, (b) in Britton-Robinson buffers pH 4.5 of various ionic strengths and (c) in buffers with constant ionic strength 0.15 M

Potentiometric titration, swelling and differential scanning calorimetric measurements confirmed that PNIPA hydrogels are sensitive to pH and to ionic strength, both separately and in combination. The equilibrium swelling degree of PNIPA is a function of pH in HCl acid, in KOH base, in phosphate and in Britton-Robinson buffer solutions. At high pH, however, the network chains tend to disintegrate and the physical integrity of the gel is compromised. The effect of the hydroxyl anion OH^- of KOH on the depression of the onset temperature of PNIPA is an order of magnitude greater than that of the Cl^- anion in HCl. In buffers with constant ionic strength I = 0.15 M the swelling degree is practically independent of the pH, i.e., the added salt masks the pH effect. In buffers at constant pH, as well as in acid and salt solutions, the phase transition temperature is a decreasing function of the ionic strength.

Measurements performed in different acid, base, and salt environments and in various buffer solutions confirmed the strong influence of pH and ionic strength conditions on the osmotic pressure and the phase transition properties of the hydrogel. The swelling properties are therefore affected not only by the pH set by a buffer but also by the composition of the buffer, as setting the pH modifies the ionic strength. These findings highlight the importance of the background electrolyte. Although guest molecules such as ionic salts and phenols affect the osmotic pressure, the phase transition temperature has no direct relationship to the value of the osmotic pressure at the transition threshold. The measurements indicate, on the contrary, that the guest molecules disturb the hydrophilic/hydrophobic balance of PNIPA through local interactions on the molecular scale. In particular, phenols are more than an order of magnitude more efficient in modifying the balance than ionic salts.

2. 2. Host-guest interactions in responsive PNIPA hydrogels [2-5]

Responsive hydrogels are one of the most frequently proposed vehicles for targeted and controlled drug delivery. Interaction between the transported drug and the three-dimensional polymer network could compromise the kinetics and the efficiency of delivery in thermoresponsive polymers. These smart stimuli-sensitive hydrogels change their physical properties in response to external physical (temperature, mechanical effect, electromagnetic radiation, electric or magnetic field) or chemical stimuli (solvent conditions: composition, dissolved species, pH, ionic strength). Their ability to store and release drugs puts them at the focus of interest as possible drug eluting systems. In terms of kinetics and efficiency of controlled delivery, the nature and strength of the interaction between the drug molecule and the polymer chains are of vital importance. Chemical properties of the guest molecule and potential drug - polymer interactions are crucial in the swelling and release process.

All phenols reduce the degree of swelling and induce rapid collapse at a “critical” concentration (c_{crit}) that is characteristic of the guest molecule (**Figure 2**).

These critical concentrations are related neither to the pK_a nor to the solubility of these compounds. Comparing the phenols having OH groups in meta positions (phenol, 1,2-dihydroxybenzene and 1,3,5-trihydroxybenzene) a systematic shift can be observed in c_{crit} with the increasing number of hydroxyl groups: more OH groups results in lower critical concentration (Figure 2a). Ortho positions increase, and meta positions decrease the critical concentration relative to phenol at 20 °C (Figure 2b). On comparing phenols with two OH groups, the sequence is meta < para < ortho. The shift in the critical concentration is the

greatest for trihydroxy-benzenes. The shape of the swelling curves is also affected by the dissolved small molecule. Multiple OH substituted phenols show a stronger influence already below the critical concentration and at the same time their transition range is wider. Generally speaking, if the effect of the concentration below VPT is more pronounced then the phase transition appears to be wider and less steep.

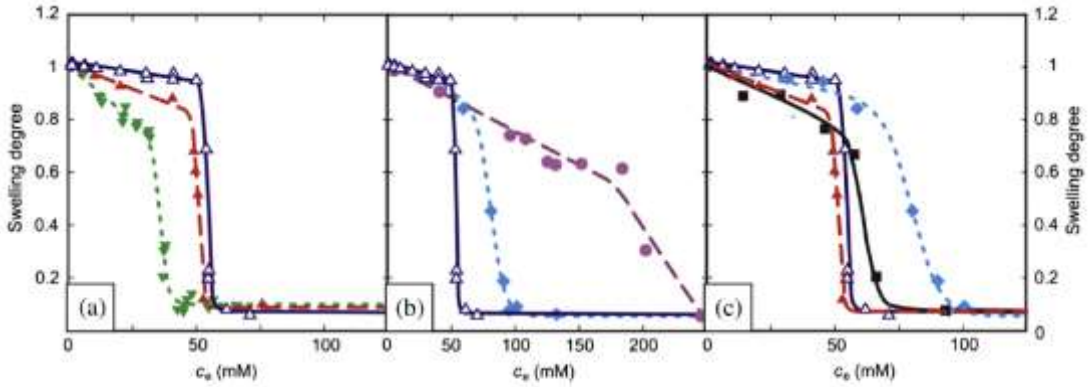

Figure 2 Swelling degree of PNIPA hydrogel in different phenolic molecule solutions at 20 °C as the function of equilibrium concentration in the free liquid phase. (a) Meta substituted phenol solutions: Δ phenol, ▲1,3-dihydroxybenzene (resorcinol), ▼ 1,3,5-trihydroxybenzene (phloroglucinol) (b) Ortho substituted phenol solutions: Δ phenol, ◆ 1,2-dihydroxybenzene (catechol), ● 1,2,3-trihydroxybenzene (pyrogallol) (c) Δ phenol, ◆ 1,2-dihydroxybenzene (catechol), ▲1,3-dihydroxybenzene (resorcinol), ■1,4-dihydroxybenzene (hydroquinone).

Although phenol is frequently used as a model for various drug molecules with substituted aromatic rings, such as tyrosine, it was used as reference and two further drug molecules, ibuprofen[1] and dopamine[2] were selected (**Figure 3**).

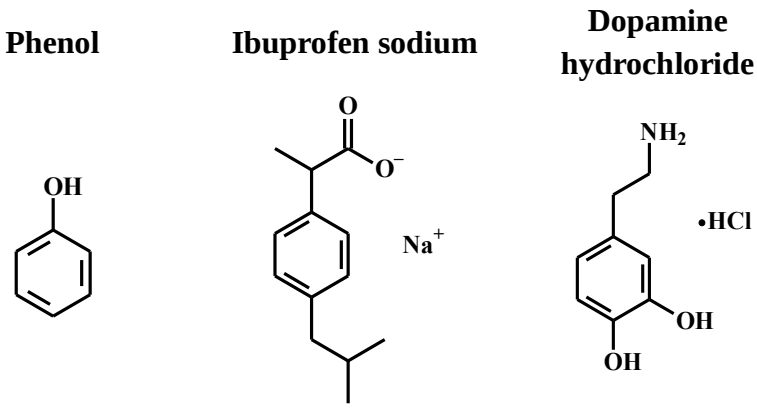

Figure 3 The drug molecules investigated

The influence of the three probe molecules selected for these studies is different not only on the swelling properties of the PNIPA hydrogel but also on its thermal responses on

[1] Ibuprofen (2-(4-isobutylphenyl)-propionic acid) is a hydrophobic non-steroidal anti-inflammatory drug. It is usually commercialized as (*R*,*S*)-(±)-ibuprofen sodium salt. The *S* enantiomer of ibuprofen is the active agent.

[2] Dopamine (4-(2-aminoethyl)benzene-1,2-diol) is a neurotransmitter present in the brain and the nervous system. Abnormal levels of dopamine may result in Parkinson's disease and mental disorders

the dry loaded gel. PNIPA gel discs were equilibrated with excess 500 mM aqueous solutions of the three model drug molecules. After determining the drug uptake and drying to constant mass the loaded samples were studied with simultaneous thermal analysis (STA). The difference in thermal response can be interpreted in terms of the different typical molecular interactions in these systems under confined conditions (**Figure 4**). Dopamine has practically no influence either in the swollen or the dry state. Most probably the strong guest - guest interaction prevents the interaction with the polymer even in confined conditions. Although phenol has a strong effect on the swelling properties of PNIPA in aqueous medium, in dry state its effect on the thermal properties is moderate. The remaining water and phenol are released simultaneously at relatively low temperature, which is high enough (> 200 °C) to indicate a strong phenol - water interaction. The limited degradation in the decomposition temperature of the gel may be explained by its porosity. The ibuprofen - gel interactions may explain the striking difference between the behaviour of ibuprofen in aqueous and dry conditions. For phenol and dopamine the water – phenol and dopamine – dopamine interactions, respectively, are stronger than that between the guest and polymer. For ibuprofen – PNIPA the synergy in the thermal decomposition may stem from a strong polymer – ibuprofen relation.

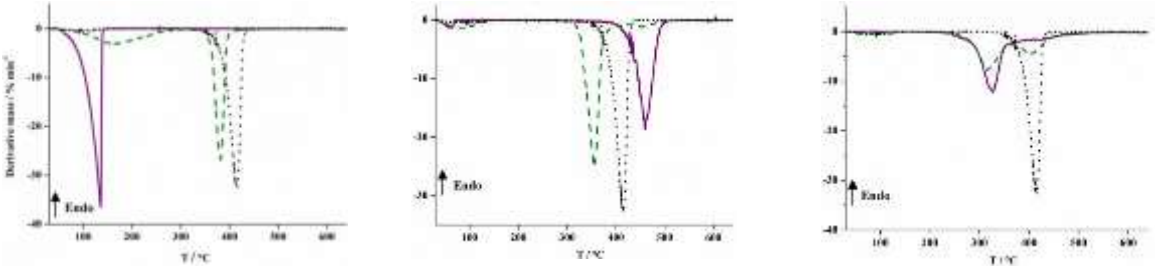

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Figure 4. Comparison of the DTG response of PNIPA equilibrated in 500 mM drug solution to the pure systems in N_2 flow. (a) phenol; (b) ibuprofen sodium; (c) dopamine hydrochloride. Pure PNIPA: dotted line, drug molecule: solid line, drug loaded PNIPA: dashed line

The effect of phenol and dopamine was further studied using DSC, solid state ^{1}H NMR (**Figure 5**) and X-ray powder diffraction (XRD, **Figure 6**) methods. As it was shown earlier, phenols exert a major influence on PNIPA by reducing its phase transition temperature. The strong interaction between phenol and the polymer that is detected by NMR hinders the crystallisation of phenol when the water is gradually evaporated. The amino ethyl phenol derivative dopamine has a much more limited effect, but in the opposite direction – the transition temperature increases slightly. The strong interaction observed among the dopamine molecules disables the polymer – dopamine interaction and favours crystallization of the dopamine when water is removed. These results reveal that embedding the drugs into polymer matrices for controlled delivery can alter the crystallinity of the stored molecules. As morphology is one of the crucial factors in delivery, this may compromise the rate and the efficiency of release. Secondly, by corollary, strong drug–polymer interactions also reduce the amount of drug released.

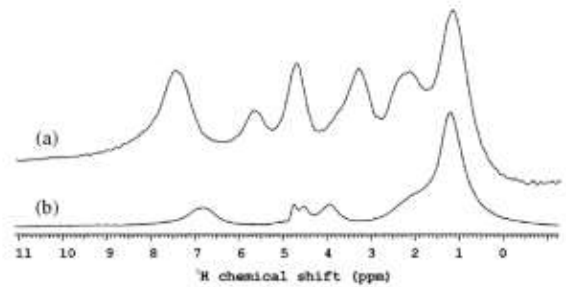


Figure 5 Combined rotation and multiple-pulse spectroscopy (CRAMPS) solid state ^{1}H NMR spectra of PNIPA above the LCST with spinning speed of 10 kHz: (a) dopamine containing gel (b) phenol containing gel.

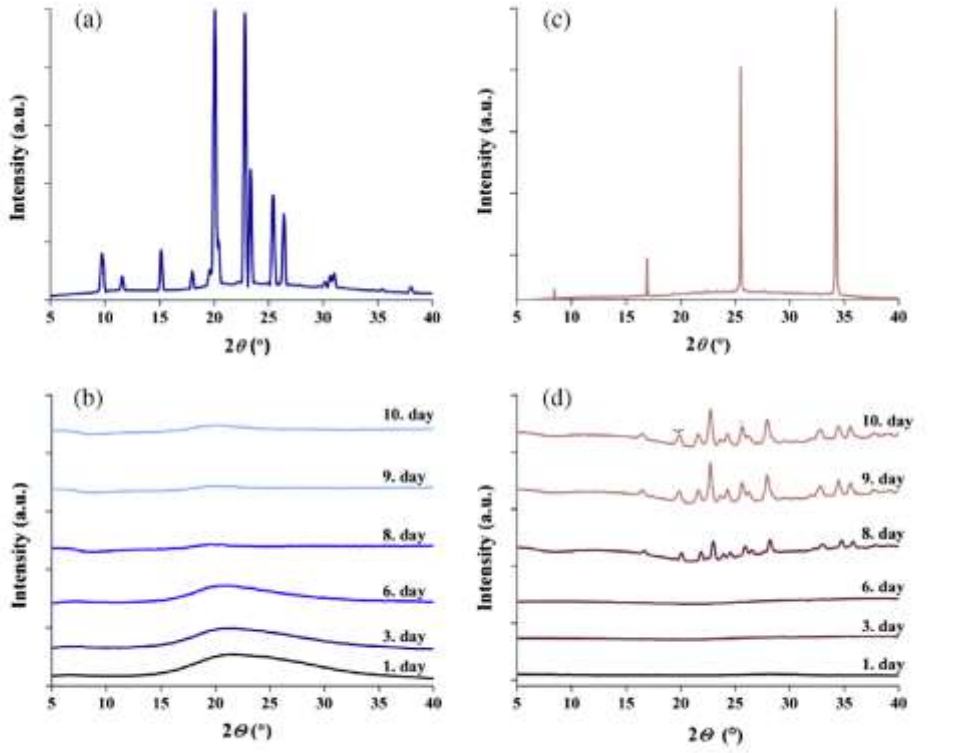


Figure 6. XRD responses of the guest molecules and the guest – PNIPA systems during the drying process: (a) phenol, (b) phenol loaded PNIPA gel, (c) dopamine hydrochloride oriented by the glass sample holder during drying, (d) dopamine loaded PNIPA gel: all the peaks can be identifyed in the reference patterns of polycrystalline dopamine hydrochloride. Successive curves are shifted vertically for clarity.

3. CNP doped responsive gels

3.1. Carbon nanoparticles[3]

In order to enhance the dispersibility of the CNPs multiwalled CNT and graphene were used in oxidised form. The C/O ratio of the CNT (from X-ray photoelectron spectroscopy (XPS)) and the BET surface area (determined from low temperature nitrogen adsorption) were respectively 11.2 and 221 m^2/g. Graphene oxide (GO) was obtained from

[3] CNPs were thoroughly characterized in students' theses [6, 7]. Some of these data, also completed with further novel findings were published in peer reviewed journals [8-12]

natural graphite (from Madagascar) by the improved Hummer's method. The C/O ratio and BET surface area measured on lyophilized monoliths of GO were 1.7 and 22 m^2/g, respectively. Typical images of the CNPs investigated are shown in **Figure 7**.

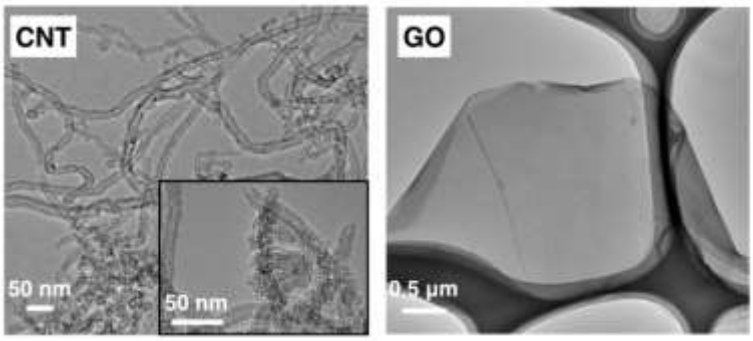


Figure 7 HRTEM images of the oxidized CNT and GO used in hybrid synthesis

3.2. Characterisation of hybrid gels [13-16]

PNIPA gels of various CNT and GO content were synthesized in identical conditions, allowing a direct comparison of the macroscopic (swelling behaviour and stress-strain measurements) and microscopic (scanning electron microscopy) behaviour. At low CNT contents hybrid gels appear to be homogenous, however, exceeding 12 mg CNT/g_{NIPA} concentration evenly distributed nanotube aggregates can be observed, which is associated with the sedimentation of nanotubes in cylinders (**Figure 8a**).

a b

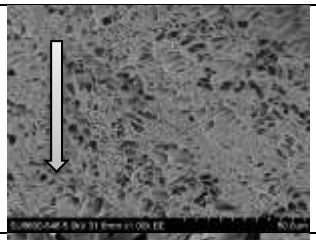
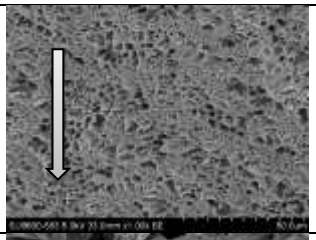
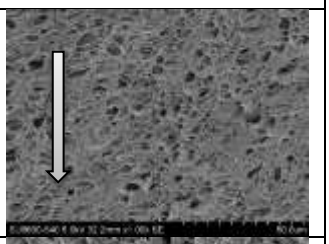
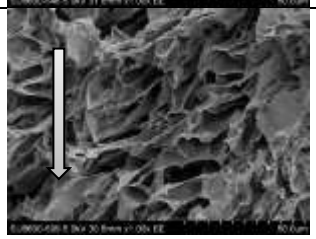
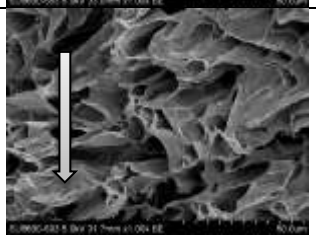
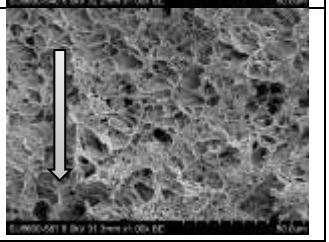
Figure 8 PNIPA hybrid gel cylinders with increasing CNT content (a) and the internal surface as used for SEM sample preparation (b)

While large, flat pores are characteristic to the upper and middle sections of the cylinder, much finer structure is observed at the bottom, probably due to excessive sedimentation (**Table 1**). By contrast, the pore structure of pure PNIPA gel is uniform in the whole sample.

No obvious effect of the different shapes of the CNPs was found. The influence of the CNPs is related to their different surface reactivity during free radical polymerization. CNT@PNIPA composites exhibited swelling and mechanical properties similar to those of pure PNIPA. In contrast, the mechanical properties of PNIPA gel were improved by incorporating GO, while the swelling degree of the GO@PNIPA systems significantly decreased. The relationship between the two properties can be described by a power law with exponent ~3.2. This unusually high value is attributed to an increasingly star-like architecture of the network resulting from chain nucleation at the surface of the GO. This picture is consistent with MicroDSC measurements, which show that the volume phase transition

temperature of PNIPA is not affected by the presence of GO. Conversely, the enthalpy of the volume phase transition decreases substantially with increasing GO content. The enthalpy loss is attributed to immobilisation of a substantial fraction of the network chains on the GO sheets, which prevents them from participating in the VPT. In the composite gels, the GO mediates evacuation of water in the high temperature collapsed state, which, in pure PNIPA, remains trapped in the network in the form of microscopic droplets.

Table 1 SEM images of lyophilized unloaded and CNT loaded gel cylinders
(axes of cylinders are marked with arrows)

CNT content	Section of cylinder (according to **Figure 8b**)		
	Top	Middle	Bottom
0			
12 mg CNT/g_{NIPA}			

As shown in **Figure 9** the CNPs in the concentration range revealed do not influence the drug uptake efficiency of the hydrogel [16].

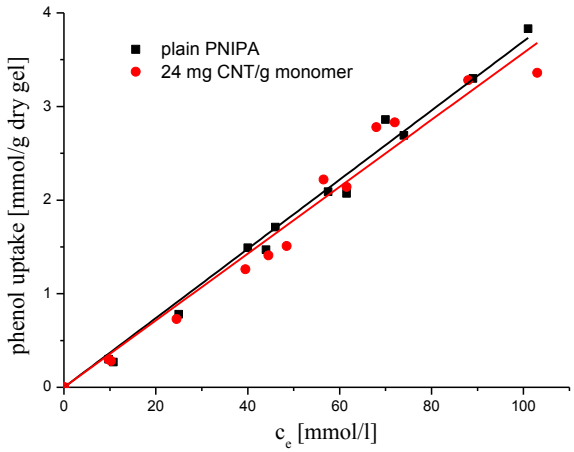


Figure 9 Phenol uptake isotherms of PNIPA and CNT@PNIPA at 20 °C

3.3.Dynamic behaviour of responsive composite gels [13, 14]

Neutron spin-echo (NSE) spectroscopy is well suited for measuring fast motion even in non-transparent soft matter systems, with the highest energy resolution among all types of

neutron spectrometer. To our knowledge, no investigation of composite systems using NSE has yet been reported in the literature. The neutron scattering observations in the swollen state confirm that the thermodynamic and hydrodynamic properties of the network chains are little affected by the incorporated GO (**Figure 10, Table 2**).

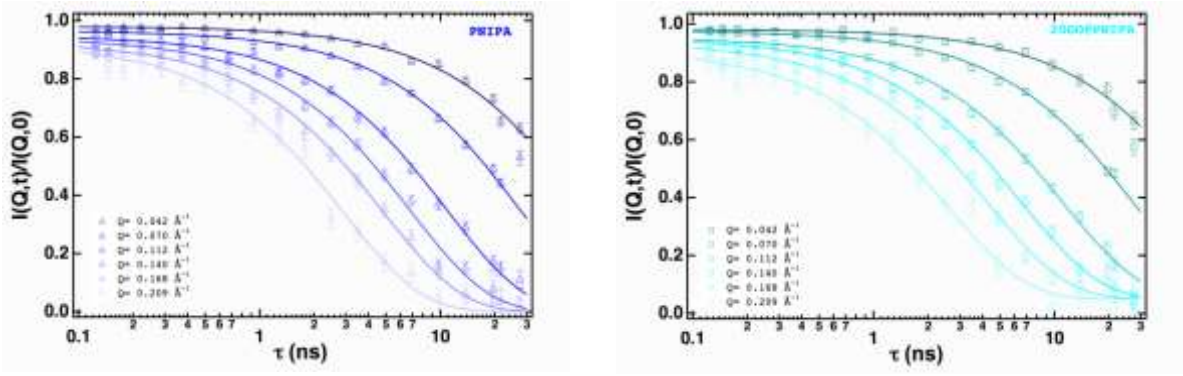


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Figure 10 Experimental intermediate scattering functions from NSE with the corresponding single exponential fits for pure PNIPA hydrogel (a) and 20GO@PNIPA composite (b), measured at 25 °C.

Table 2 Characteristics of the samples from neutron scattering experiments measured at 25 °C.*

Sample	$D_{diff}\times10^{11}$ (m^2/s)	ξ_H (Å)	ξ (Å)	Power law exponent
PNIPA	7.03±0.14	28.4±0.01	92.0±1.09	1.6
5GO@PNIPA	7.41±0.24	26.9±0.08	90.0±1.11	1.7
20GO@PNIPA	8.1±0.30	24.6±0.9	66.7±0.67	1.6

*D_{diff}: diffusion constant from NSE; ξ_H: hydrodynamic length from NSE; ξ: static correlation length from small angle neutron scattering (SANS)

Thermal response tested through deswelling at temperatures above the volume phase transition of PNIPA in macroscopic scale. An illustration is given in **Figure 11**. Besides the structural characteristics and direct information about drug release efficiency knowledge of the dynamics of nanocomposite systems is of crucial importance for sensing and controlled release applications. Such investigations could, however, prove to be a challenge at the nanoscale level (in progress), owing to the limited number of appropriate methods.

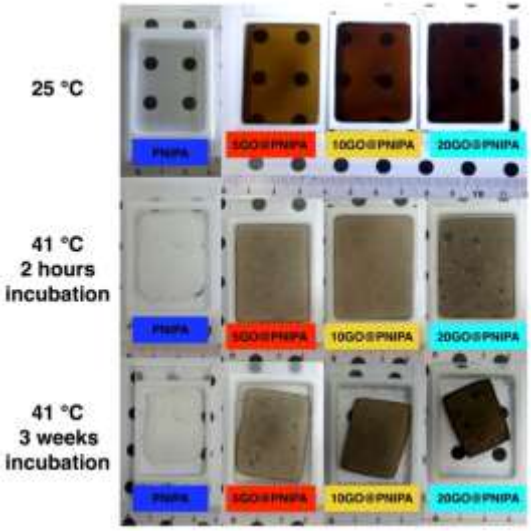

Figure 11 Images of PNIPA and GO@PNIPA samples below (25 °C) and above (41 °C) the volume phase transition temperature after different times of incubation.

Significant differences were observed in the macroscopic thermal response of the different systems (**Figure 12**).

Whereas 2000 s was largely sufficient for the relaxation of CNT@PNIPA composites, a timeframe of even an order of magnitude longer was insufficient for the GO@PNIPA gels. At this stage the GO@PNIPA samples the values of the parameters can be used only for qualitative comparisons, as the absence of measured baseline for the curves makes the resulting parameter values uncertain. Nevertheless, it can be concluded that, contrary to CNT, the lowest GO content has the strongest effect on the deswelling kinetics. A significant deceleration of the thermal response was observed at all the three concentrations, which resembles the effect of the increased cross-linking density. All curve fits yielded a stretching parameter $p<1$, indicating multiple processes.

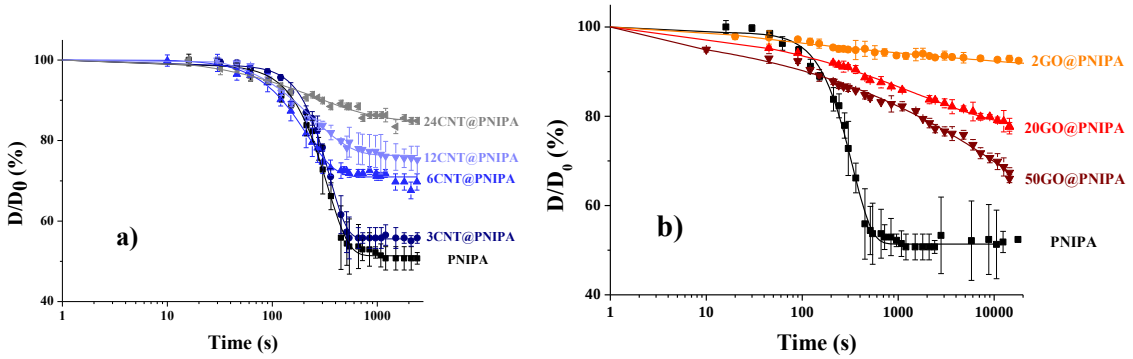

Figure 12 Deswelling kinetics of CNT@PNIPA (a) and GO@PNIPA (b) at 50 °C. Note the order of magnitude difference in range of the time axis scales. Symbols are experimental values, continuous lines are fits to

$$\frac{D}{D_0} = \left(\frac{D}{D_0}\right)_\infty + Ae^{-\left(\frac{t}{\tau}\right)^p}$$ [4]

[4] D/D_0 and $(D/D_0)_\infty$ are the swelling ratio at time t and $t\to\infty$, respectively, τ is the time constant of the thermal response, A and p are fitting parameters

Although no obvious effect of the different shapes of the CNPs was found, the time constant and the swelling ratio of the temperature-induced shrinkage can be adjusted by selecting the type and amount of nanoparticle loading (Figure 11). This could provide a means for accurately controlling deswelling kinetics, e.g., in the drug release profile of PNIPA systems. This facility may also be employed in sensor applications, where fast and excessive shrinkage can be a significant drawback.

The performance of the composites was characterized also by the thermal response to a 2 min infrared exposure (**Figure 13**).

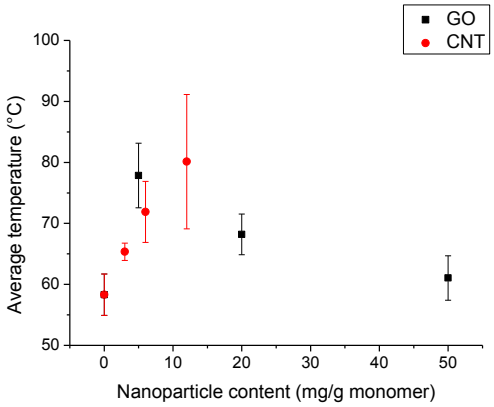

Figure 13 Average temperature in CNT and GO loaded of PNIPA composites during IR laser irradiaton. External temperature: 20 °C

Fast shrinkage on exposure to IR laser irradiation, and quick recovery of the gels after the exposure was observed in all cases. The measured temperature fluctuations may be attributed to the low thermal conductivity of the gels, even in the presence of CNPs. In both systems a monotonic correlation is found between nanoparticle content and temperature rise in the sample. In the CNT@PNIPA systems the gel exhibited a stronger response with increasing concentration, whereas an opposite trend was detected with the GO doped samples. Understanding such opposing trends is the subject of further investigations. It may be associated with the loss of electron delocalization in the graphene oxide. In the multiwall nanotubes the internal tubes are still complete, thus ensuring thermal conduction via the CNT.

4. Supermacroporous hydrogels [17, 18]

Investigation of supermacroporous responsive gel - CNP hybrid materials might be further step in exploring the potential of these novel systems. As a first step, pH responsive CNP free supermacroporous, chemically cross-linked poly(aspartic acid) (PASP) hydrogels were studied. The gels were obtained by cryogelation in DMSO. The pore sizes of the resultant PASP hydrogels were in the supermacroporous range and could be controlled by the gelation temperature and the cross-linking ratio (**Figure 14**).

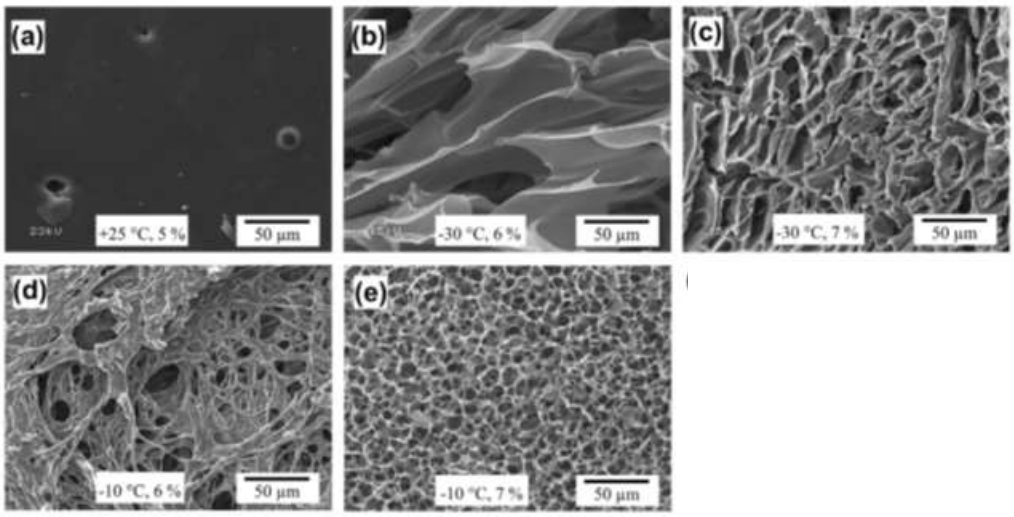

Figure 14 SEM micrographs of supermacroporous PASP cryogels (gelation temperature T_{gel} and cross-linking ratio X_{DAB} are indicated in each micrograph)

Interconnectivity of the pores was confirmed by small flow resistance. Compression tests indicated that, upon compression, the hydrogels released part of their swelling solution, which was taken up again upon release of the load. The supermacroporous PASP hydrogels displayed pH-responsive swelling similarly to the conventional PASP hydrogels. Results indicate that the hydrogels developed can be suitable for in vitro cell seeding with pH-induced detachment of the grown cells (**Figure 15**). The easy modification of the precursor polymer and the cytocompatibility of the PASP hydrogels argue in favor of the feasibility of future biological applications.

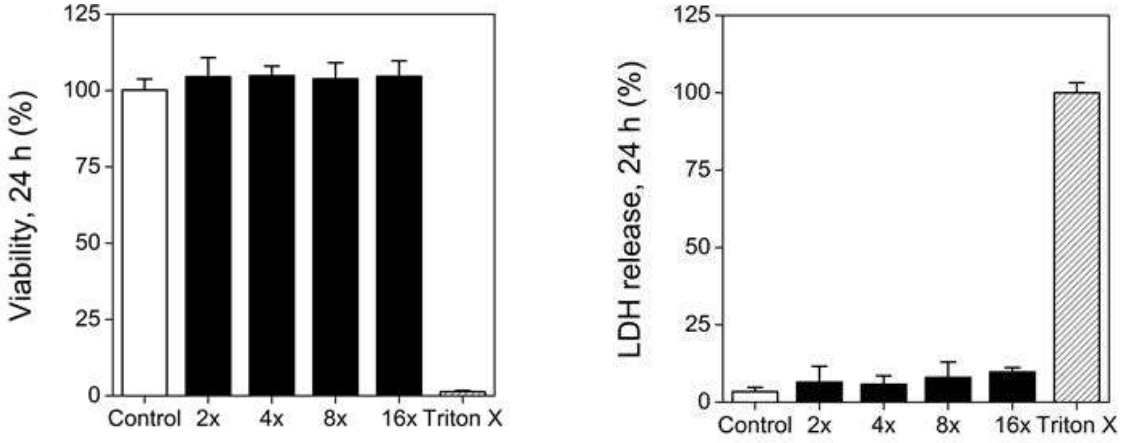

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Figure 15 Cellular viability (a) and cytotoxicity (b) after 24 h treatment of human epithelial cells with PBS solution in which the PASP hydrogels were sterilized. LDH: lactate dehydrogenase [16]

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