Nanostructured Polymer Networks Obtained by Photopolymerization in a Lyotropic Liquid Crystal Template

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Introduction

Micro- and nanostructured materials are of growing interest due to their potential applications in size-selective membranes, electronics or biomaterials, to name a few.[1] The internal organization at the nano-scale considerably enhances the performance of the generated polymer network. Recently, nanostructured hydrogels have demonstrated improved transport and mechanical properties.[2,3] A common way to control the morphology at the micro- and nanoscale is based on the self-assembly of block copolymers.[4,5] Because of thermodynamic incompatibility between the various blocks, block copolymers generate various mesophases in bulk (micellar, hexagonal, gyroid or lamellar in the case of a diblock copolymer) depending on the volume fraction of a given block.[4] The nanostructure is then locked in using a crosslinking reaction. However, this method requires the long and tedious synthesis of a specific block copolymer to target a particular morphology, which is neither straightforward nor versatile. A promising alternative route utilizes the order generated by surfactant molecules, namely lyotropic liquid crystal (LLC), as a template for photopolymerization of monomer and crosslinkers.[6]

The self-organized geometries of LLC mesophases provide a useful support to generate order at the nano-scale in organic polymers. LLCs are generally obtained at high concentration of amphiphiles to form morphologies including micelles, micellar cubic, sponge-like, hexagonally-packed cylinders and lamellar; the resulting self-assembly is dictated by the concentration, polarity, size and shape of a given surfactant. LLC mesophases exhibit periodic hydrophilic and hydrophobic domains with nanometer size dimensions, in which monomers are segregated according their affinity. Thus, these self-assemblies can be used as a template to produce either hydrogels with nanopores or interpenetrating hydrophilic and hydrophobic networks that are ordered at the nano-scale. Thermodynamically-driven phase separation, occurring during polymerization within the template, generally induces a decrease in order resulting in a loss of the properties related to the nano-periodicity. This phenomenon has been partially overcome by taking advantage of the rapid reaction rate of photopolymerization, kinetically hampering nanostructure changes, and thus preserving the performance of the nano-organized polymer network.[1]

Herein, we show how LLC-templating leads to enhanced water transport and mechanical properties of nanostructured hydrogels. Temperature-sensitive, nanostructured materials prepared using surfactant exhibit greater response in water than their isotropic analogues. Further, we demonstrate the benefit of utilizing LLCs in complement with high MW amphiphilic block copolymers to generate a periodically ordered hydrogel with improved performance.

Experimental

Materials

NiPAAm-based hydrogels were prepared using N-isopropylacrylamide (**1**) monomer [NiPAAm, Aldrich], sodium acrylate (**3**) monomer [SA, Aldrich], N,N'-methylene bisacrylamide (**2**) [bisAAm, Aldrich], deionized water, polyoxyethylene (2) cetyl ether surfactant (**4**) [Brij 52, Aldrich] and 2,2-Dimethoxy-1,2-diphenylethan-1-one photoinitiator [Irgacure 651, Ciba Specialties Chemicals].

PDMS-based systems contain poly(dimethylsiloxane) (PDMS)-poly(ethylene glycol) (PEG) pentablock copolymer PEG-b-PDMS-b-PEG-b-PDMS-b-PEG diacrylate (**5**) [MW(total) = 10,000 g/mol, MW(PEG) = 2100 g/mol, MW(PDMS) = 1800 g/mol] kindly given by Alcon Novartis-CibaVision, PDMS dimethacrylate (**6**) [MW = 4,500-5,500 g/mol, purchased at Gelest], polyoxyethylene (20) cetyl ether surfactant (**7**) [Brij 58, Aldrich], deionized water and 2-Hydroxy-2-methyl-1-phenyl-propan-1-one photoinitiator [Darocur 1173, Ciba Specialties Chemicals]. Figure 1 summarizes the chemical structures of monomers, crosslinkers and surfactants used. All chemicals were used as received.
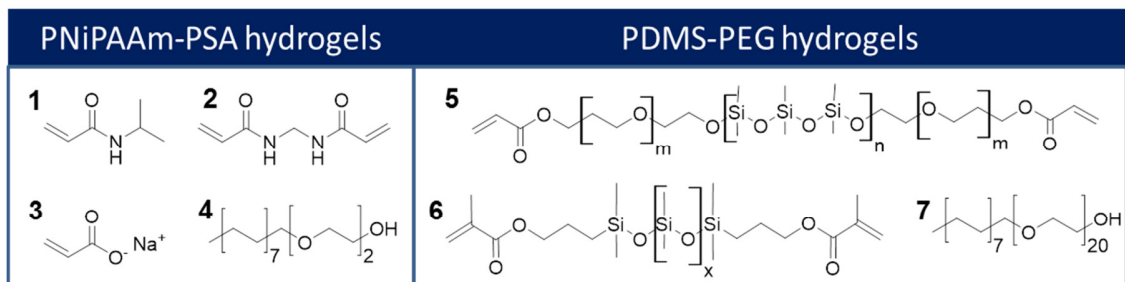
Figure 1. Chemical structures of the products used to prepare the presented hydrogels.

Methods

Sample preparation. Lyotropic liquid crystalline templated samples were prepared by mixing given amounts of monomer, crosslinker, surfactant, deionized water, and photoinitiator. NiPAAm-based mixtures were homogenized by heating and vortex mixing. Because of the use of high MW block copolymer, PDMS-based blends were mixed using manual stirring/centrifuging cycles. Isotropic samples were prepared by mixing similar concentrations of reactants in a common solvent (deionized water for NiPAAm-based mixtures, dioxane for PDMS-based blends); the amount of solvent used in isotropic samples was equivalent to the quantity of surfactant + water in LLC mixtures.

All LLC-templated NiPAAm samples contained 20 wt% monomer (2.6 wt% bisAAm, 3.5 wt% or 7.5 wt% SA and 13.9 wt% or 9.9 wt% NiPAAm), 0.2 wt% Irgacure 651 photoinitiator, 45 wt% Brij 52 surfactant and the corresponding amount of deionized water. Polymer disks were prepared by pipetting samples into acetal-teflon molds (12 mm diameter, 3 mm height) and irradiating samples with a medium pressure UV arc lamp (Ace Glass) with an intensity of 10 mW/cm^2 for 20 min. Surfactant was removed by soaking discs gently in 2 baths of agitated acetone for 48 hours. Samples were then air dried initially before vacuum drying 2-3 hrs.

LLC-templated PDMS samples consisted in 36.7 wt% pentablock copolymer PEG-b-PDMS-b-PEG-b-PDMS-b-PEG (**5**), 21.7 wt% PDMS dimethacrylate (**6**), 31.7 wt% Brij 58 surfactant (**7**), 9 wt% deionized water and 1 wt% Darocur 1173 photoinitiator.

Nanostructured PDMS-PEG hydrogel based on block copolymer only was prepared with the same amount of reactants but surfactant and water were replaced with dichloromethane (DCM) to homogenize the mixture. After pouring the mixture in molds, DCM was evaporated in a fumehood overnight to prevent formation of bubbles. Then, samples were placed in a vacuum oven at 50-65°C for 4 hours to evaporate the residual DCM and allow polymer chains to relax to ultimately self-assemble. Samples were cooled down overnight under atmospheric pressure, covered with aluminum foil, to assure self-assembly.

All PDMS-based mixtures were poured with a pipette or transferred with spatula (for the most viscous mixtures) into acetal-Teflon molds (12 mm diameter, 3 mm height) and cured under UV light using a medium pressure UV arc lamp (Ace Glass) with an intensity of 20 mW/cm^2 for 20 min on both sides. Surfactant was removed by soaking discs into 3 different baths of isopropyl alcohol for 2 days. Samples were then dried in a vacuum oven for 2-3h.

***Nanostructure characterization* .** Polymer morphology was characterized before and after polymerization with a Nonius FR590 small angle X-ray scattering (SAXS) apparatus using a standard copper target Röntgen tube with a Ni-filtered Cu Kα line of 1.54 Å as the radiation source, a Kratky collimation system, and a PSD 50M position sensitive linear detector (Hecus M. Braun, Graz). *d*-spacing ratios of scattering peaks were used to index the type of mesophase.

Water swelling. Vacuum-dried PNiPAAm-PSA and PDMS-PEG hydrogels were weighed and then soaked in deionized water for 24 hours at a given temperature (20°C for PDMS-PEG hydrogels and various temperatures comprised between 22°C and 55°C for PNiPAAm-PSA polymers). Excess water was removed by blotting with paper wipes before the swollen hydrogels were weighed. Hydrogel dry and swollen weights were used to calculate swelling ratio, as follow: $W = (W_{swollen} - W_{dry})/W_{dry} \cdot 100\%$. 6 to 8 replicates were analyzed to obtain the average value and standard deviation.

Mechanical properties. The PDMS-PEG dry disks were placed onto a compressive stress/strain clamp in a dynamic mechanical analyzer (DMA Q800 Series, TA Instruments) at 22°C. The gels were then compressed at a rate of 0.005 N/min up to 0.02 N. From the stress/strain profiles a compressive Young's modulus was determined as the slope of the linear range. 4 to 8 replicates were analyzed to obtain the average value and standard deviation.

Results and Discussion

PNiPAAm hydrogels are temperature responsive materials which become hydrophobic above a specific temperature, referred to as the lower critical solution temperature (LCST). From the LCST to higher temperatures, water-polymer affinity decreases and polymer-polymer interactions are favored, resulting in expelling of water. In our previous work, we showed that LLC-templated PNiPAAm hydrogels exhibit higher water uptake and faster response as compared to their isotropic analogues. Herein, sodium acrylate has been incorporated to improve the amount of water released after heating in isotropic hydrogels. We show that using LLCs as a template to synthesize nanostructured P(NiPAAm-co-SA) hydrogels can

provide even higher amount of water expelled at higher temperatures as compared to isotropic analogues.NiPAAm-based, nano-ordered hydrogels were prepared using the self-assembly of Brij 52 in water as a support for photopolymerization. The amount of total monomer and crosslinker was kept constant, only the amount of NiPAAm and SA was varied. Thus, crosslinking density was consistent for all the studied samples. SAXS profiles after polymerization indicate the presence of a hexagonal/lamellar mixed phase. To demonstrate the influence of nanostructure on temperature response of PNiPAAm networks, water uptake in templated and isotropic hydrogels was measured at different temperatures, below and above LCST, for various content of sodium acrylate (Figure 2). Figure 2 shows that the amount of expelled water in ordered materials increases as the quantity of sodium acrylate units is enhanced. For isotropic analogues, however, while the amount of water uptake is still higher with increasing content of sodium acrylate units, only a small quantity of water is expelled at high temperature, resulting in low water recovery. In the PNiPAAm hydrogel containing 7.5% of SA, around 1600 wt% water is expelled whereas the isotropic counterpart rejects approximately 200 wt% only. As described in our previous work, the periodic geometry of nanostructured hydrogels provides a more direct route to carry water out of the hydrogel when heated above LCST, inducing rapid deswelling process. This fast water expelling potentially prevents the formation of a thick and dense layer of collapsed polymer network, formed at the water-hydrogel interface, that often hinder the complete drying of the material.[2]
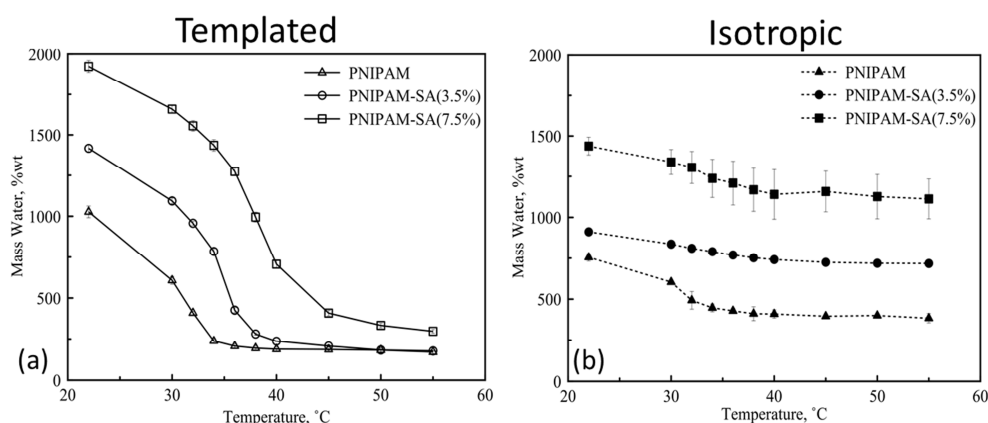

Figure 2. Water uptake with increasing temperature for (a) LLC-templated and (b) isotropic PNiPAAm-SA hydrogels containing various amounts of sodium acrylate units.

Such improvements of transport properties could be useful for biomedical uses. Because of their biocompatibility, poly(ethylene glycol) (PEG) and poly(dimethylsiloxane) (PDMS) are often present in biomaterials. While PEG isoften used for its hydrophilic character and biocompatibility, the superior oxygen transport characteristics of PDMS could be useful in applications as well. Ideally, both properties could be combined to obtain a material suitable for therapeutic uses including body reconstruction or medical devices. However, when mixed together in an isotropic interpenetrated network, one property is generally acquired at the expense of the other.[7] Hence, segregating PEG and PDMS into distinct domains through the self-assembly of PDMS-PEG block copolymers could be a solution. In addition, since PEG and PDMS are respectively hydrophilic and hydrophobic, acrylated oligomers of the similar chemical structure could be good candidates for LLC-templating. Herein, we investigate the fabrication of PDMS-

PEG hydrogels through photopolymerization of an acrylated, pentablock copolymer of PEG and PDMS within LLC mesophase. The resulting transport and mechanical properties are compared to what is observed for an isotropic counterpart and an analogue hydrogel obtained via self-assembly of the block copolymer only.

Pentablock PEG-b-PDMS-b-PEG-b-PDMS-PEG was mixed with PDMS crosslinker in presence of Brij 58 surfactant and water, then photopolymerized to produce an LLC-templated polymer network. Nanostructured analogues were obtained by mixing the same ratio of pentablock in dichloromethane to allow homogenization of the mixture. Then, DCM was evaporated and the mixture was heated above T_m of PEG to let block copolymer self-assemble. After cooling down to room temperature, the reactive mixture was photopolymerized to lock in the nanostructure. Non-nanostructured counterparts were based on a composition similar to the one used for LLC-templated polymers, except that water and Brij 58 were replaced with an identical amount of a solvent common for PDMS and PEG, dioxaneSAXS profiles indicate a bicontinuous cubic morphology for LLC-templated hydrogel and a double gyroid geometry for the nanostructured polymer based on self-assembly of block copolymer. These data suggest the presence of two co-continuous networks – hydrophilic and hydrophobic – in both ordered materials.

To show the impact of the synthesis route on the properties of the nanostructured polymers, the swelling behavior (Figure 3a) and mechanic characteristics (Figure 3b) of LLC-templated materials were compared to their nano-organized analogue obtained by self-assembly of block copolymers or their isotropic counterpart prepared with a common solvent.
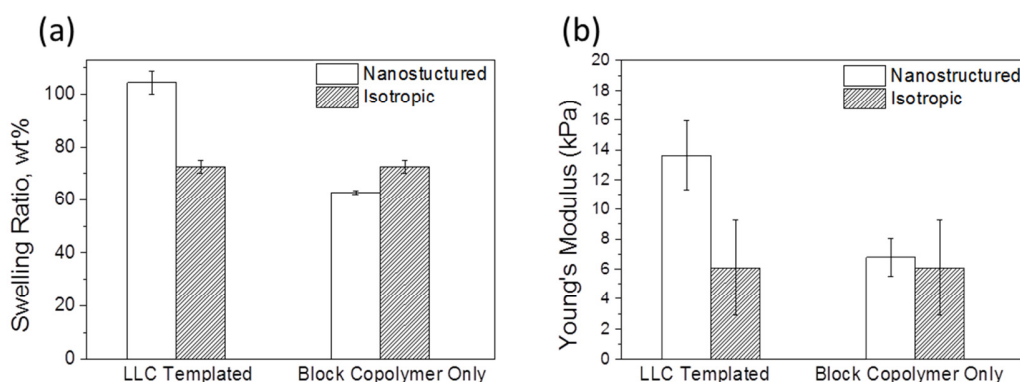
Figure 3. (a) Swelling ratio and **(b)** Young's modulus of nanostructured PDMS-PEG hydrogels (using LLC template or self-assembly of block copolymer only) compared to their isotropic counterparts.

Similarly to PNiPAAm hydrogels, LLC-templated polymers exhibit higher water uptake than their isotropic counterpart. Since PDMS is constrained into discrete domains, its hydrophobicity interferes less than in the case of isotropic, interpenetrated network, where PDMS is randomly located throughout the whole sample. Interestingly, the nanostructure resulting from the self-assembly of block copolymer does not lead to an improvement of - and may even decrease – the swelling ratio of PDMS-PEG hydrogels. Likewise, LLC-templated hydrogel exhibit a significantly higher compressive Young's modulus than its isotropic counterpart. However, the morphology induced by the nano-organization of block copolymer does not influence the mechanical properties either, as compared to the isotropic analogue. These results suggest that the geometry obtained from the thermodynamic rearrangement of block copolymer is not

sufficient to improve the inherent properties of the hydrogel; in contrast, LLC-templated morphology seems to provide an appropriate geometry of PEG and PDMS domains such that an overall enhancement of the properties is possible. Future investigation by TEM will help us to further elucidate the reasons behind these differences.

Conclusion

Photopolymerization in lyotropic liquid crystal template is a promising technique to generate nanostructure. LLC-templated PNiPAAm-PSA hydrogels that show improved temperature response and water recovery. In addition, this method seems to be a powerful technique to improve overall properties of hydrophilic-hydrophobic polymer network based on block copolymer, in which the self-assembly of the block copolymer itself appears to not be sufficient to allow synergistic combination of the two different moieties. These results may be useful to improve the performance of the current hydrogels.

Acknowledgements

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