

Soft Matter

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

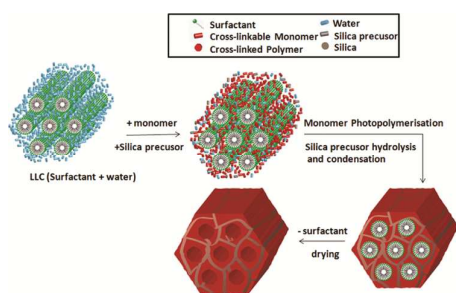
You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Retention of Original LLC Structure in Cross-linked Poly(ethylene glycol) Diacrylate Hydrogel with the Reinforcement from Silica Network

Juan Zhang,^{1,2} Zongli Xie,² Manh Hoang,² Anita J. Hill,² Weiwei Cong,¹ Feng

Hua She,¹ Weimin Gao¹ and Ling Xue Kong^{1*}



A sufficient and well dispersed silica network stabilizes the nanostructure in cross-linked poly(ethylene glycol) diacrylate templated from hexagonal lyotropic liquid crystals (LLC).

Retention of Original Lyotropic Liquid Crystal Structure in
Cross-linked Poly(ethylene glycol) Diacrylate Hydrogels Reinforced
via Silica Networks

**Juan Zhang,^{1,2} Zongli Xie,² Manh Hoang,² Anita J. Hill,² Weiwei Cong,¹ Feng Hua
She,¹ Weimin Gao¹ and Ling Xue Kong^{1*}**

¹ Institute for Frontier Materials, Deakin University, Waurn Ponds, VIC 3216, Australia

² CSIRO Material Science and Engineering, Private Bag 33, Clayton, VIC 3169, Australia

* Corresponding Author.

Lingxue Kong, email: lingxue.kong@deakin.edu.au

Tel: +61 3 5227 2087

Fax: +61 3 5227 1103

Abstract

Cross-linked poly(ethylene glycol) diacrylate (PEGDA) hydrogels with uniformly controlled nanoporous structures templated from hexagonal lyotropic liquid crystals (LLC) represents a separation membrane material with potentially high permeability and selectivity due to its high pore density and narrow pore size distribution. However, retaining LLC templated nanostructures is a challenge as the polymer gels are not strong enough to sustain the surface tension during the drying process. In the current study, cross-linked PEGDA gels were reinforced with a silica network synthesized via an in-situ sol-gel method, which assists in the retention of the hexagonal LLC structure. The silica precursor does not obstruct the formation of hexagonal phases. After surfactant removal and drying, these hexagonal structures in samples with a certain amount of tetraethoxysilane (TEOS) loading are well retained while the nanostructures are collapsed in samples without silica reinforcement, leading to the hypothesis that the reinforcement provided by the silica network stabilizes the LLC structure. The study examines the conditions necessary for a sufficient and well dispersed silica network in PEGDA gels that contributes to the retention of original LLC structures, which potentially enables broad applications of these gels as biomedical and membrane materials.

1 Introduction

Cross-linked poly(ethylene glycol) diacrylate (PEGDA) hydrogels templated with lyotropic liquid crystal (LLC) mesophases have a 100% increase in water uptake, a 3-fold increase in mechanical strength, and a 3-fold increase in diffusive transport compared to the nontemplated gels¹ and have therefore received attention in the applications of tissue engineering, drug delivery, and separation membranes.²⁻⁶ These cross-linked gels also exhibit excellent antifouling and solvent-resistant properties when used as ultrafiltration membranes for water treatment.⁷

The high performance of these membranes is largely because of the nanopores with smooth surfaces similar to those of carbon nanotubes^{8,9} that can have a gas and water permeability several orders of magnitude higher than that of commercial track-etched polycarbonate membranes. It is postulated that cross-linked PEGDA nanofiltration (NF) membranes with aligned nanopores templated by hexagonal LLC perpendicular to the membrane surface have the potential to match the performance of carbon nanotube membranes and significantly improve the efficiency of current wastewater treatment and desalination processes.

However, it is entropically challenging to maintain the ordered structure of the original LLC phase in polymeric materials and often the morphologies generated are not the same as the original LLC structure.¹⁰⁻¹² Studies of the influence of polymerization conditions on the templated nanostructure^{11,13} suggest that photo-polymerization with an extremely rapid

initiation rates enable better template structure retention than thermal polymerization. Our previous study¹⁴ also suggests that after photo-polymerization the samples retain the original LLC structures intact, leaving the drying process as a critical step to retain the original structure. To retain the nanostructure, the material's intermolecular bond strength must be larger than the surface tension,¹⁴⁻¹⁷ or the rate of drying must be faster than the material response as in the case of critical point drying.¹⁴⁻¹⁷

Inorganic ceramic materials can have excellent mechanical strength and thermal stability, and it has been shown that the addition of inorganic nanoparticles or networks into polymer materials can greatly improve the polymer composite mechanical strength and thermal stability.¹⁸⁻²⁶ For example, Liu and Kontopoulou²⁷ demonstrated that well-dispersed nanosilica in the polyolefin polymer matrices improves Young's modulus, tensile stress and impact properties. The silica network is a continuous skeleton and can be prepared under certain chemical conditions (typically via an acid-catalyzed in-situ sol-gel process); the interparticle forces can have sufficient strength to cause considerable aggregation and/or flocculation prior to their growth.²⁸⁻³⁰ The formation of an open continuous network of low density silica provides certain advantages with regard to physical properties in the formation of high performance silica based composites. Another advantage of this in-situ sol-gel process is the possibility of preparing polymer/inorganic composites without phase separation between polymer and silica. The starting metal alkoxides materials for making inorganic networks are usually liquids which can be mixed with polymer solutions or with monomers to

be polymerized later in order to make well-dispersed silica networks in the polymer matrix.^{31,32}

Furthermore, highly ordered cage and cylindrical mesoporous silica monoliths (HOM) with 2- and 3-dimensional structures have been successfully synthesized by using LLC phases as templates.³³⁻³⁷ Thus, it is hypothesized that a silica network reinforced polymer might have enough intermolecular bond strength to resist the surface tension during the drying process, thereby able to retain the original hexagonal LLC structures.

In this work, a uniformly distributed silica network will be introduced to reinforce the cross-linked PEGDA gels in order to retain the original hexagonal LLC nanoporous structure. The PEGDA will be photopolymerized in its hexagonal LLC mesophase formed from the dodecyltrimethylammonium bromide (DTAB) / water system. DTAB is a quaternary ammonium, which is stable to pH changes, both acid and alkaline, especially acid (even HF).³⁸ The silica network will be obtained via an in-situ sol-gel method catalysed by hydrochloric acid (HCl).

2 Materials and Experimental

2.1 Materials

Polyethylene glycol diacrylate (PEGDA) (n=11, MW=575 g/mol), dodecyltrimethylammonium bromide (DTAB) (99%), and 2-hydroxy-2-methylpropiophenone (HMPP) (97%) were purchased from Sigma-Aldrich (USA). Methanol (99.8%) was

purchased from VWR International Ltd (USA), and tetraethoxysilane (TEOS) (99%) was sourced from Merck Chemicals (Germany). All chemicals were used as received.

2.2 Material synthesis

LLC system was prepared by mixing cationic surfactant (DTAB), monomer (PEGDA) + TEOS, deionised water, photoinitiator (HMPP) and methanol (100 / 97 / 45.5 / 0.97 / 28.8 by weight). The percentages of TEOS given in the text are based on the weight of monomer and weight of TEOS. HCl as a catalyst was added to adjust the system pH to 2.0. The order of chemical addition was PEGDA, water, HMPP, DTAB and methanol. The solution was mixed in a 50 °C water bath for about 5 minutes to form a homogeneous solution, and then TEOS was added drop wise with vigorous stirring followed by HCl addition. The mixture was continuously stirred in the 50 °C water bath for 2 hours and then left for 2 days for the hydrolysis and condensation reaction to take place. The resulting mixture was then cast on a quartz glass sheet and sealed. A flow of nitrogen was introduced for 30 minutes to replace air and evaporate methanol before being placed under a 300-400nm UV light source (intensity 2.0 mW/cm²) for 20 minutes for photopolymerization. After polymerization, some samples were put in a fan forced oven for heat treatment at 140 °C for 2 hours. The samples with or without heat treatment were immersed in a large quantity of deionised water to remove DTAB followed by vacuum drying. In our previous work¹⁴, the SEM-EDX results (Fig.7) show that the Br peak disappeared after removing the surfactant DTAB by immersing the sample in deionised water, demonstrating that DTAB was completely removed.

2.3 Characterisation

Polarized light microscopy (PLM) (Olympus BH2-UMA) was utilized to characterise textures of the mesophase of samples before and after photopolymerization. Images from PLM were analyzed for birefringent light patterns that are characteristic of specific LLC nanostructure. Liquid samples were placed between a glass slide plate and cover slip on the microscope stage.

XRD was used to examine the phase behavior of the samples before and after photopolymerization. XRD was conducted using a Bruker AXS diffractometer with a Cu K α radiation (wavelength $\lambda=1.542\text{\AA}$) operating at a voltage of 40 kV and a current of 30 mA in transmission mode. The measurements were performed in the range of $0.5^\circ - 18^\circ$ (2θ) using a step size of 0.02° . The d-spacing of the primary (100) reflection of the sample, d_{100} , is calculated according to the equation $2d\sin\theta=n\lambda$ ($n=1$).

Small angle X-ray scattering experiments (SAXS) were performed to characterize the crystalline structure using the SAXS/WAXS beam line at the Australian Synchrotron with a beam of wavelength $\lambda=1.0322\text{\AA}$ (12KeV). 2-D diffraction images were recorded on a Pilatus 1M detector and analyzed using IDL Demo software.

Scanning electronic microscopy (SEM) with energy-dispersive system (EDX) (Leica 440) was employed to analyze the homogeneity of the samples with different TEOS loading. The

distribution of Si atoms in the PEGDA gel matrix was obtained by SEM EDX mapping (Leica 440). Prior to measurements, the samples were coated with carbon using a Polaron E6700 Evaporative Carbon Coater in a high vacuum evaporator. All measurements were detected at a voltage of 10 kV and with Iprobe of 500. Mapping of Si for each sample took about 15 minutes with 50 frames.

The FTIR spectra were recorded using the Bruker Vetex-70 FTIR spectrometer. Prepared samples were added to KBr powder and ground evenly to make a KBr disk. An average of 32 scans per spectrum was recorded in the standard wavenumber range of 400-4,000 cm^{-1} at a resolution of 4 cm^{-1} .

Differential scanning calorimetry (Pyris Series- DSC 8500) was used to determine the glass transition temperature (T_g) of templated samples, and the analysis was conducted under nitrogen and at a scan rate of 10 $^{\circ}\text{C min}^{-1}$.

Thermogravimetric analysis (PerkinElmer Pyris 1 TGA) was employed to study the thermal degradation properties of the templated samples. The analysis was conducted on 10 mg samples under a nitrogen flow (20 ml/min) and at a heating rate of 10 $^{\circ}\text{C/min}$.

Contact angle measurements were performed to examine the surface wettability of templated samples with different TEOS loading. Measurements were done using a KSV CAM200

instrument equipped with a video capturing system. The interval of the frames captured by camera was set at a fast mode with 10ms.

3 Results and Discussion

Figure 1 shows the LLC templating process with the reinforcement of a silica network in cross-linked PEGDA gel to help maintain the LLC structure by resisting the collapse in structure due to the surface tension during drying. The whole process involves the dispersion of surfactants and TEOS in monomers to form the hexagonal phase, the photopolymerization of the monomers, and the hydrolysis and condensation of TEOS. This process was followed by the removal of surfactants and drying to obtain the nanoporous structure with cylindrical pores.

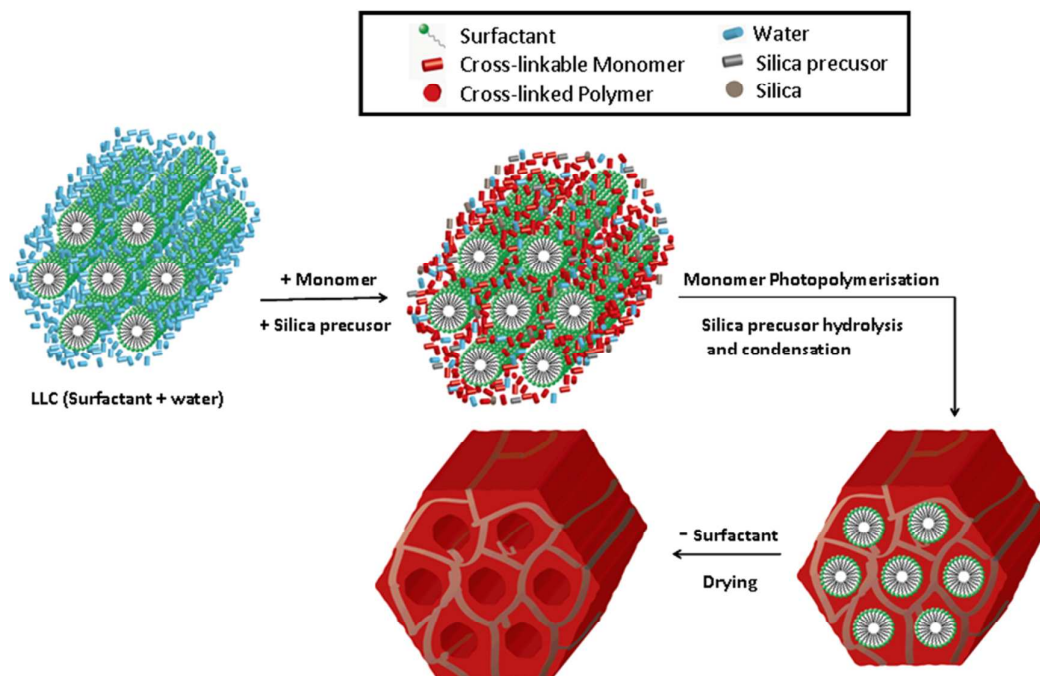


Figure 1 LLC templating process with silica network reinforcement for nanostructure retention in PEGDA.

3.1 LLC Structure formation and retention upon polymerization

Different characterization techniques were used to confirm the formation and retention of the hexagonal phase before and after polymerization. Figure 2 shows the PLM images before and after polymerization for different hexagonal phases. Before polymerization, all samples show focal conic textures indicating the hexagonal mesophase was successfully formed^{37,39,40} in all samples.

The addition of TEOS did not disturb the formation of template structure as the TEOS had already been hydrolyzed before casting for polymerization and its hydrophilic hydrolyzate was mixed in water and PEGDA phase.

After polymerization, all the samples preserved the focal conic textures, suggesting the retention of the hexagonal LLC phase. However textures of the sample with 10% and 30% TEOS appear slightly different, perhaps due to the structure being slightly changed upon polymerization.

Figure 3a shows the XRD profiles of samples with different TEOS loading before polymerization. Table 1 lists the d-spacing of the primary (100) reflection, d_{100} , and the corresponding center to center distance, α , which is given by $d_{100}/\cos(30)$ ^{37,41} of samples with different TEOS loading. As the TEOS loading increases, the lattice parameter d_{100} increases, and the center to center distance increases. The total weight ratio of TEOS and PEGDA in each sample is a constant. The PEGDA, TEOS and its hydrolysate stay in the hydrophilic hexagonal exterior phase. The density of TEOS at 25°C is 0.93g/ml which is lower than that of PEGDA (MW = 575), 1.12g/ml. With an increasing weight ratio of TEOS, the weight ratio of PEGDA decreases, while the total volume of the hexagonal exterior phase increases. This results in an increase in the lattice parameter and center to center distance of the hexagonal arrays before polymerization.

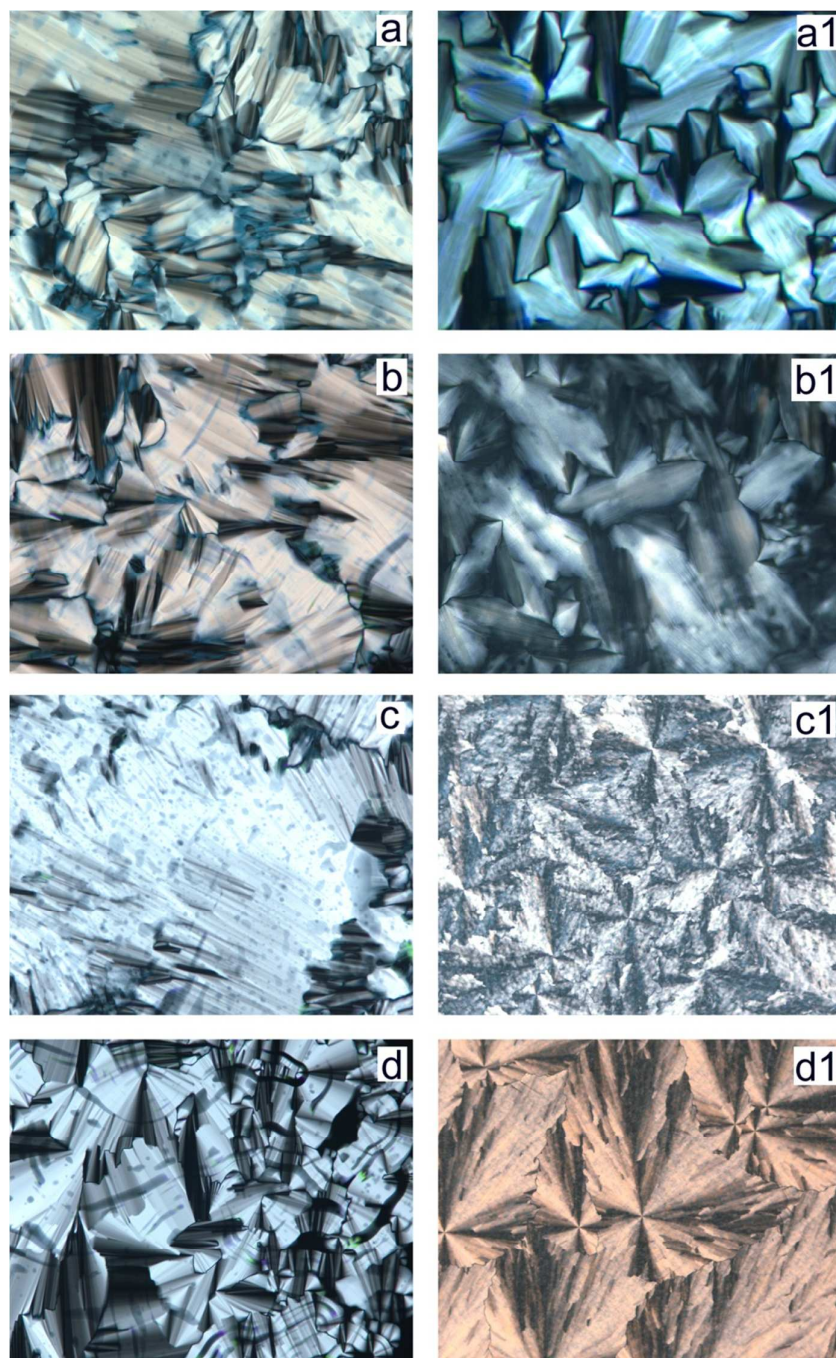


Figure 2 Polarized light microscopy (PLM) images for the hexagonal phases with different TEOS loading: (a) before and (a1) after polymerization without TEOS; (b) before and (b1) after polymerization with 10% TEOS; (c) before and (c1) after polymerization with 30% TEOS; (d) before and (d1) after polymerization with 50% TEOS.

The polymerization significantly improves the compactness of materials as demonstrated from the XRD results of samples with different content of TEOS after polymerization (Figure 3b and Table 1). The d_{100} and center to center distance of the samples without TEOS and with 10% TEOS loading change only slightly compared with that of the corresponding samples before polymerization, while these d_{100} and center to center distance values for the samples with 30% and 50% TEOS loading are smaller than their corresponding samples before polymerization. During the polymerization of monomer, the hydrolysis and condensation of TEOS still goes on. The hydrolysis and condensation of TEOS and the cross linking of PEGDA make the hexagonal arrays more compact. So, the d_{100} and center to center distance of the samples decrease after polymerization and the values for samples with 30% and 50% TEOS loading become much smaller (Table 1).

Table 1 XRD results of samples with different content of TEOS loading before surfactant removal.

Dried samples with different TEOS loading	Before		After		After heat	
	polymerization		polymerization		treatment	
	d_{100} (Å)	α (Å)	d_{100} (Å)	α (Å)	d_{100} (Å)	α (Å)
0%	31.1	36.0	33.7	39.0	-	-
10%	31.8	36.8	31.1	36.0	35.9	41.5
30%	34.4	39.8	29.9	34.6	35.3	40.8
50%	39.9	46.1	28.6	33.1	34.2	39.5

d_{100} : d-spacing of the primary (100) reflection

α : center to center distance

The heat treatment has stabilized the silica reinforced nanostructure as the d_{100} and the center to center distance (α) (Table 1) are almost the same for all samples with different TEOS loading. This result is further supported by the XRD and SAXS results (Figures 4 and 5). The observed d -spacing ratios of 1, $1/3^{1/2}$ for d_{100} , d_{110} in all the samples are characteristic of a hexagonal LLC phase. Unlike samples before and after polymerization without heat treatment, which are dominated by the intensity of peaks corresponding to the (100) orientation, the samples with heat treatment have intense peaks corresponding to the (110) orientation, and Figures 4 and 5 also display the d -spacing ratio of $1/7^{1/2}$ for d_{210} characteristics of a hexagonal LLC phase. The XRD of the sample with 10% TEOS is dominated by a very high intensity of the (110) peak.⁴² With an increasing TEOS content, the intensity of the (100) peak gets stronger while the peaks associated with other orientations still hold significant proportions.

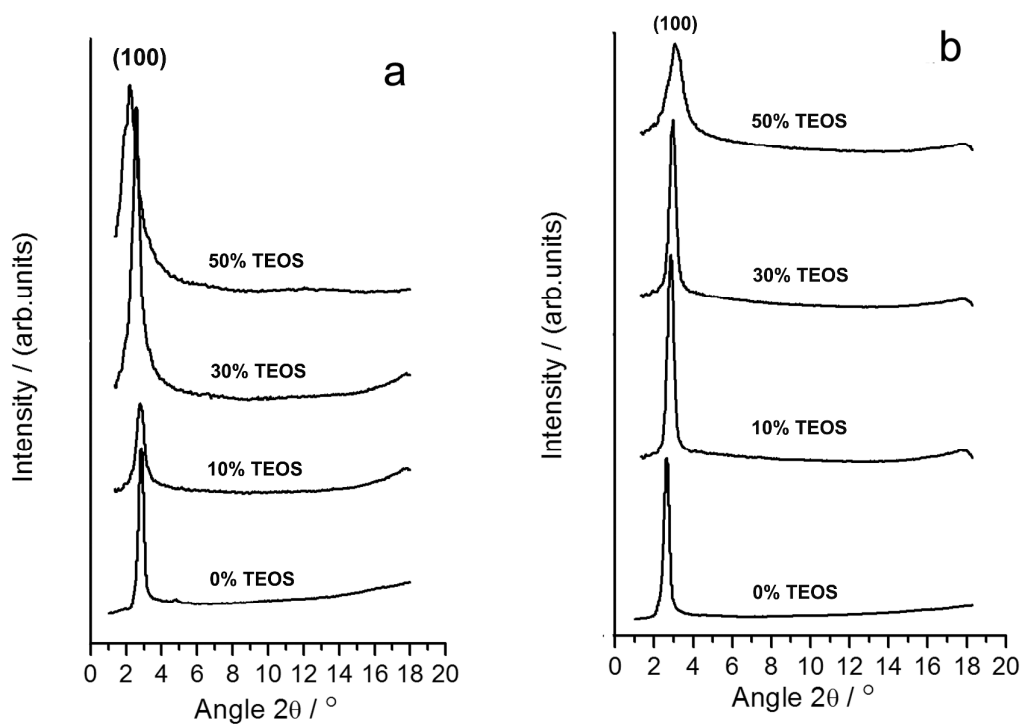


Figure 3 XRD spectra for samples with different content of TEOS. a): before and b): after polymerization.

After heat treatment, the center to center distance (α) of these three samples is about 6 Å bigger than without heat treatment (Table 1). This increase might be due to the water and ethanol, obtained from the TEOS hydrolysis, evaporating during the heat treatment. As the surfactants still left inside the pores, when the water and ethanol evaporates, it has to pass through the material which might make the material expanding a bit, resulting in a slight increase in the center to center distance of the samples after heat treatment.

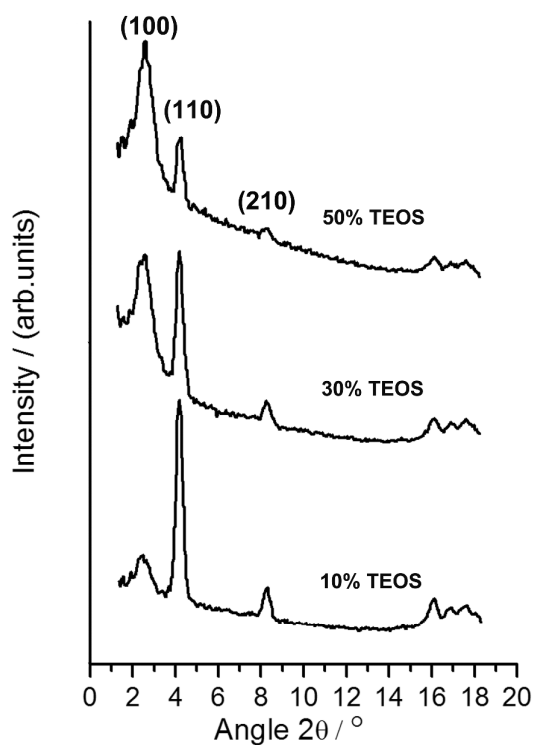


Figure 4 XRD spectra for samples after heat treated at 140 °C for 2 hours and before surfactant removal.

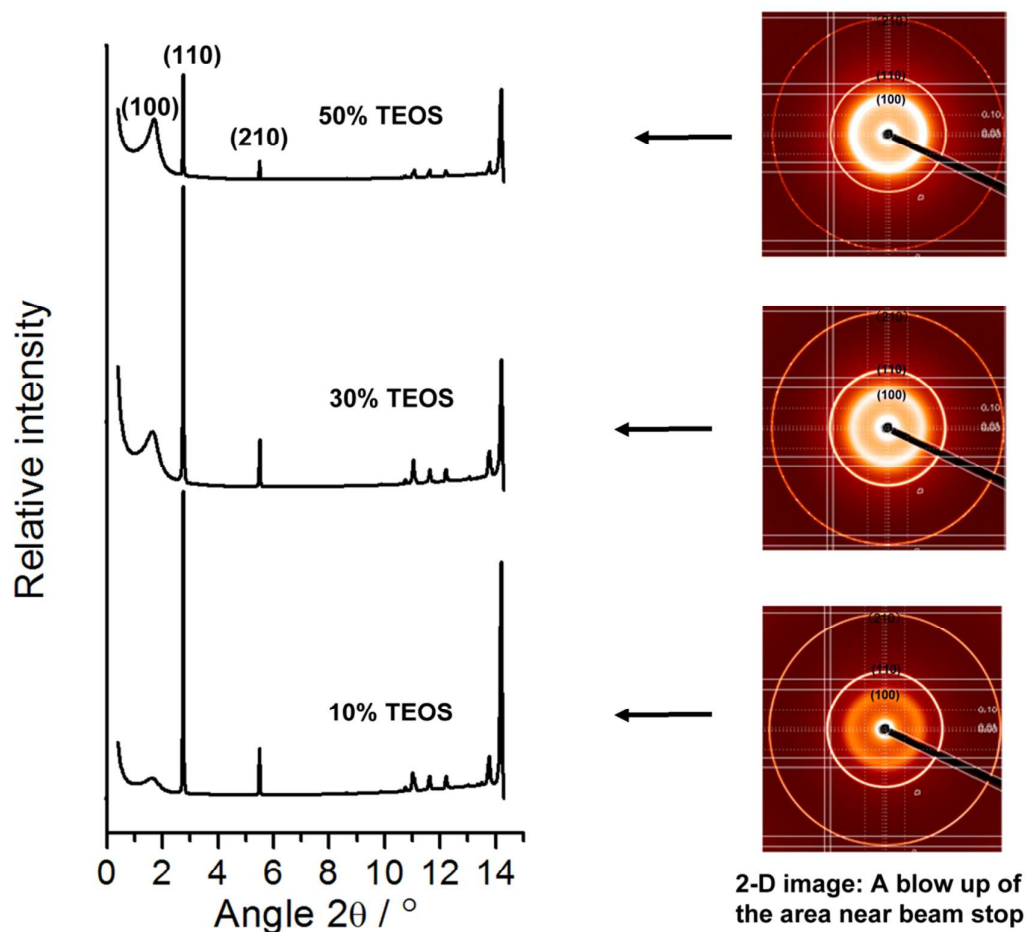


Figure 5 Synchrotron SAXS spectra for samples after heat treated at 140 °C for 2 hours and before surfactant removal.

3.2 Structure retention with the reinforcement of silica network

To preserve the hexagonal LLC structure the polymer material has to overcome a surface tension of 71.7 mN/m during drying.¹⁴ When drying the templated sample using a vacuum oven at room temperature, the cross-linked PEGDA gels could not overcome this surface tension, which results in structure collapse.¹⁴ Reinforcing the cross-linked PEGDA gels with a silica network is examined as an option to retain the LLC structure during drying.

XRD results indicate that the silica network in PEGDA gels contributes to the retention of original LLC structures in the final dried samples. The XRD spectrum of silica (Figure 6a samples without heat treatment) prepared using the same sol-gel method is featureless indicating an amorphous silica structure. The samples without and with 10% TEOS do not have an apparent peak, suggesting amorphous structures. The samples with 30% and 50% TEOS preserve the ordered nanostructure as indicated by a strong primary peak in the XRD spectra. The d -spacings from the primary (100) reflection for samples with 30% and 50% TEOS are 82.5Å and 83.6Å corresponding to center to center distances of 94.3Å and 95.5Å, respectively.

Figure 6b demonstrates the XRD profiles of dried samples with different TEOS loading and heat treated at 140°C for 2 hours. All the samples possess the primary reflection peaks, suggesting ordered structure. The sample with 10% TEOS loading has a less intense primary reflection peak than the samples with 30% and 50% TEOS loading, suggesting that the sample with 10% TEOS has a less ordered structure. The d -spacing from the primary reflection for all samples is about 87.3Å and the corresponding centre to centre distance is about 99.8Å. The lattice parameters of dried samples are higher than the ones of the samples before surfactant removal. Similar results have been observed previously in cross-linked PEGDA hydrogels with LLC structure maintained through critical point drying (CPD).¹⁴ The retention of the hexagonal structure for hydrogels dried by CPD also displayed a shift of the primary reflection towards a lower angle after surfactant removal indicating an increase in the lattice

parameter with the center-to-center distance for the hexagonal array after CPD of approximately 94Å.

When soaking the samples with or without heat treatment in deionised water to remove the surfactants, the cross-linked PEGDA will swell, increasing the volume of the polymer between the pores and in turn increasing the center-to-center distance of the hexagonal arrays. The cross-linked PEGDA reinforced with sufficient silica network is able to withstand the surface tension during drying thereby preventing collapse of the hexagonal LLC structure.

From the XRD results, the samples with 30% and 50% TEOS loading either with or without heat treatment preserve the hexagonal LLC structure, and samples with 10% TEOS that are heat treated also preserve a less ordered hexagonal LLC structure. The silica content of the samples is provided in Table 2 and indicates that heat treatment increases the degree of silica condensation in the samples. When the silica content in cross-linked PEGDA is equal to or greater than 2.2% (Table 2), the silica network provides enough mechanical strength to overcome the surface tension forces, 71.7 mN/m,¹⁴ generated from water evaporation, resulting in maintained LLC structure. As many literatures have shown that the addition of inorganic nanoparticles or networks into polymer materials can greatly improve the polymer composite mechanical strength and thermal stability,¹⁸⁻²⁶ which strongly supported our findings. The mechanical properties of our new materials will be examined in the future studies.

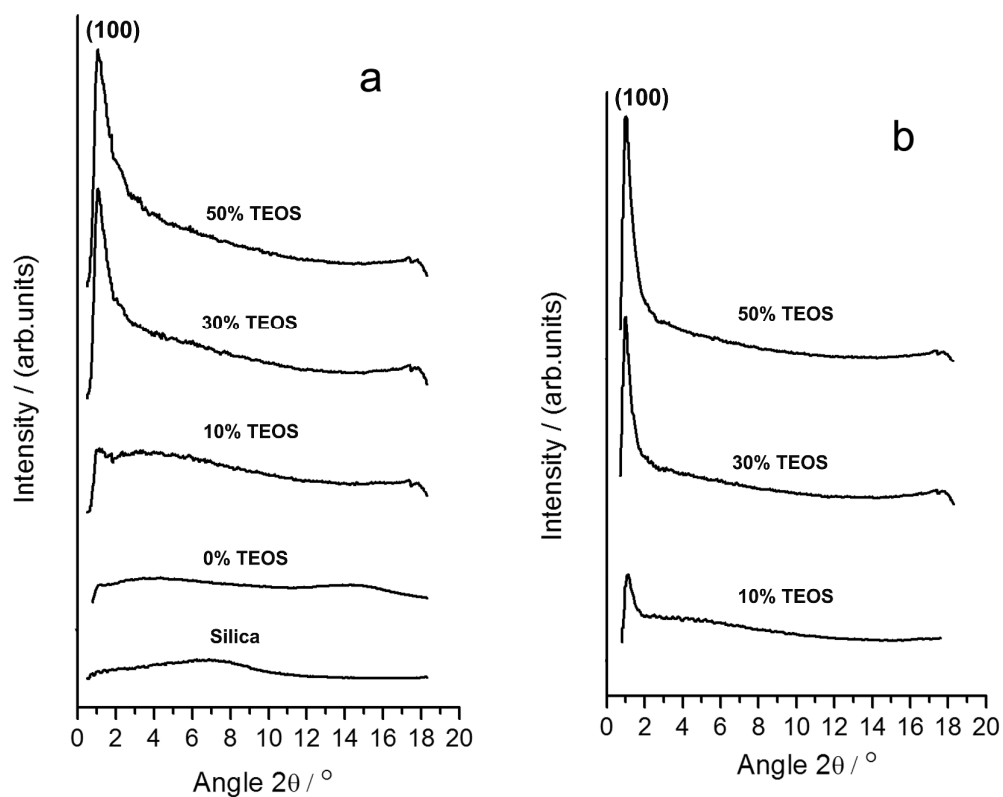


Figure 6 XRD spectra for dried samples with different TEOS loadings: a) without heat treatment, and b) with heat treatment at 140 °C for 2 hours.

Table 2 Silica obtained in final purified cross-linked PEGDA gels calculated from TGA test.

Dried samples with different TEOS loading	Silica content (%)	
	Without heat treatment	With heat treatment
10%	1.1	2.2
30%	6.6	8.3
50%	14.0	15.2

3.3 Silica content and dispersion

To confirm the silica network formed in the cross-linked PEGDA gels, Figure 7 shows the FTIR spectra of the dried samples without heat treatment. Compared with the spectra of the sample without TEOS loading, the appearance of peaks at 795 cm^{-1} and 442 cm^{-1} associated with the symmetric vibration of Si-O for the samples with TEOS loading indicates the incorporation of silica into the polymer matrix, and the intensity of these peaks increases with the increasing TEOS loading.

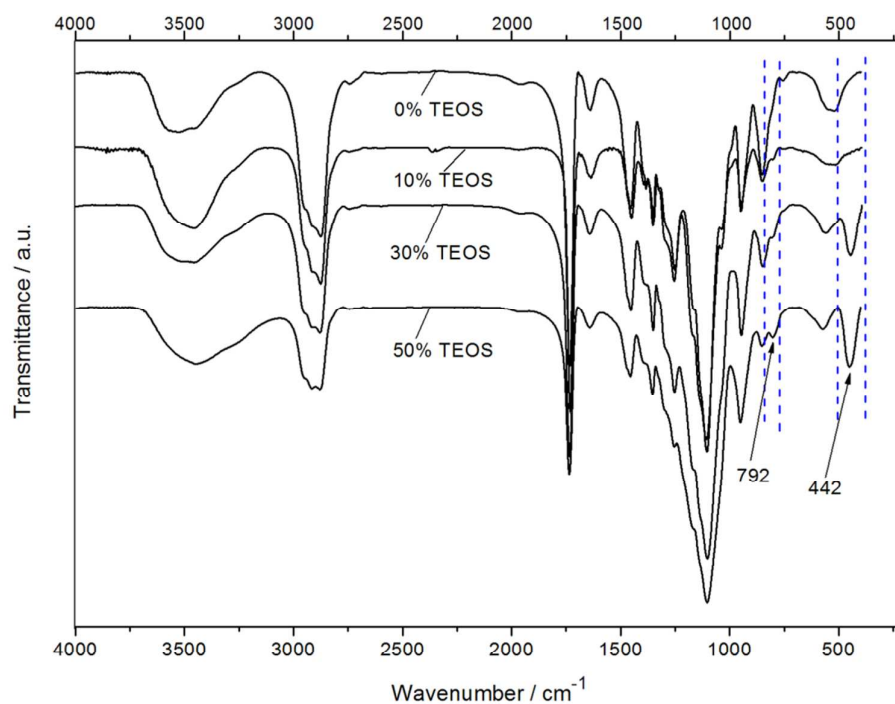


Figure 7 FTIR transmittance spectra of dried samples with and without TEOS loading.

A mapping technique was employed to elucidate the distribution of the silica network in the cross-linked PEGDA. Figure 8 shows a silicon map and EDX chemical analysis of the surface

of a dried sample with 30% TEOS. The results in Figure 8 were similar for samples with or without heat treatment. The white spots represent the silica network, which is uniformly dispersed throughout the polymer matrix in all samples (10%, 30%, and 50% TEOS).

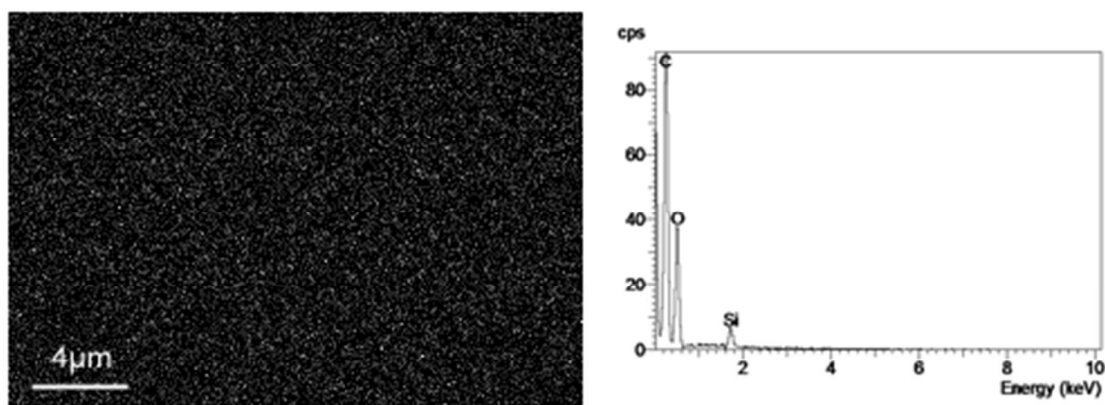


Figure 8 Silicon mapping (left) and SEM-EDX (right) of the surface of a dried sample containing 30% TEOS.

The higher the TEOS loading, the higher the content of silica in the dried samples (Table 2), which is in agreement with FTIR results. It is postulated that the heat treatment improves the degree of silica condensation as the samples with heat treatment have higher silica content than that of the samples without heat treatment.

3.4 Thermal properties

The thermal properties of the samples with different content of TEOS were studied by DSC and TGA. The T_g of samples increases with increasing TEOS loading (Figure 9), possibly due to restricted polymer chain mobility due to the silica network formed across the polymer matrix.^{43,44}

After heat treatment, within experimental errors, the same T_g values were observed for all samples (Figure 9). This result is probably due to the stress relaxation between the cross-linked polymer gel and silica network during the heat treatment at 140 °C for 2 hours.

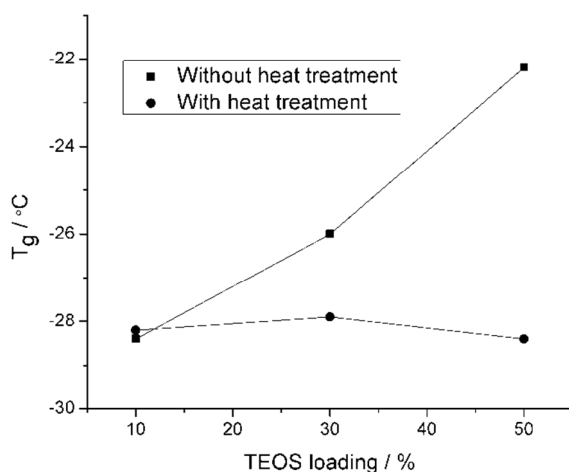


Figure 9 DSC results of dried samples with different TEOS loadings.

Figures 10 show the TGA results of samples without and with heat treatment. The majority of weight loss occurs in the range of 300 – 450 °C. The samples with higher content of TEOS appear slightly more stable. However the addition of a silica network does not significantly affect the thermal stability of the templated PEGDA gel.

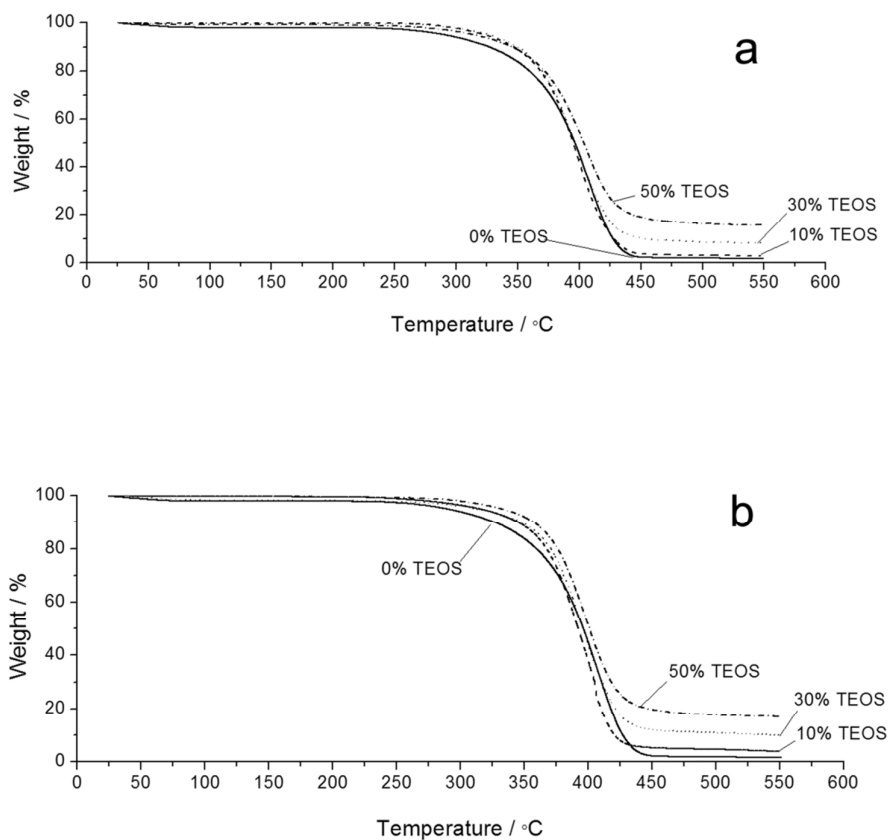


Figure 10 TGA tests of dried samples with different TEOS loading: a) without heat treatment, and b) with heat treatment at 140 °C for 2 hours.

3.5 Hydrophilicity analysis

The contact angle measurements were performed to measure the surface hydrophilicity and the results are shown in Table 3. The introduction of silica network significantly improves the material hydrophilicity. With an increasing TEOS loading, the contact angle becomes significantly lower. As can be seen, a contact angle of 59.1° was measured for sample without TEOS compared to 38.6°, 32.5° and 27.4° for samples with 10%, 30% and 50% TEOS

loading without heat treatment and 29.8°, 28.9° and 24.8° for samples with 10%, 30% and 50% TEOS loading with heat treatment.

Table 3 Contact angles of water on templated samples with different TEOS loading.

Dried samples with different TEOS loading	Contact angle (°)	
	Without heat treatment	With heat treatment
0	59.1±0.1	-
10%	38.6±2.0	29.8±1.8
30%	32.5±1.0	28.9±1.8
50%	27.4±2.5	24.8±1.9

4 Conclusions

The retention of the hexagonal LLC template structure in polymer gels has been achieved by the introduction of a silica network into the cross-linked PEGDA gel in order to stabilize the hexagonal structure. The hexagonal phase was successfully formed for samples with different content of TEOS as a silica precursor, before polymerization. The d -spacing (d_{100}) and the center to center distance are increased with increasing TEOS content. However, due to the condensation of TEOS and the cross linking of PEGDA, the hexagonal arrays become more compact after polymerization. After surfactant removal and drying, the samples with 30% and 50% TEOS loading either without heat treatment or with heat treatment preserve the hexagonal LLC structure, indicating that a well dispersed silica network of sufficient loading in PEGDA gels contributes to the retention of original LLC structures by resisting the surface tension during drying. The introduction of silica network significantly improved the material hydrophilicity.

Acknowledgement

The project has been supported by a Deakin University postgraduate scholarship and a CSIRO top-up scholarship from the National Research Flagship Water for a Healthy Country. SAXS was performed on the SAXS beamline at the Australian Synchrotron, Victoria, Australia.

References

- (1) J. D. Clapper, C. A. Guymon, *Macromolecules*, 2007, **40**, 1101.
- (2) B. J. Elliott, W. B. Willis, C. N. Bowman, *J. Membrane Sci.*, 2000, **168**, 109.
- (3) Y. Y. Liang, T. W. Jensen, E. J. Roy, C. Y. Cha, R. J. DeVolder, R. E. Kohman, B. Z. Zhang, K. B. Textor, L. A. Rund, L. B. Schook, Y. W. Tong, H. Kong, *Biomaterials*, 2011, **32**, 2004.
- (4) H. Q. Lin, E. Van Wagner, B. D. Freeman, L. G. Toy, R. P. Gupta, *Science*, 2006, **311**, 639.
- (5) G. P. Ma, D. Z. Yang, Q. Z. Li, K. M. Wang, B. L. Chen, J. F. Kennedy, J. Nie, *Carbohydr. Polym.*, 2010, **79**, 620.
- (6) E. M. Smoak, M. M. Henricus, I. A. Banerjee, *J. Appl. Polym. Sci.*, 2010, **118**, 2562.
- (7) G. D. Kang, Y. M. Cao, H. Y. Zhao, Q. Yuan, *J. Membrane Sci.*, 2008, **318**, 227.
- (8) B. J. Hinds, N. Chopra, T. Rantell, R. Andrews, V. Gavalas, L. G. Bachas, *Science*, 2004, **303**, 62.
- (9) J. K. Holt, H. G. Park, Y. M. Wang, M. Stadermann, A. B. Artyukhin, C. P. Grigoropoulos, A. Noy, O. Bakajin, *Science*, 2006, **312**, 1034.
- (10) M. Antonietti, R. A. Caruso, C. G. Goltner, M. C. Weissenberger, *Macromolecules*, 1999, **32**, 1383.
- (11) M. A. DePierro, K. G. Carpenter, C. A. Guymon, *Chem. Mater.*, 2006, **18**, 5609.
- (12) L. Sievens-Figueroa, C. A. Guymon, *Polymer*, 2008, **49**, 2260.
- (13) J. D. Clapper, L. Sievens-Figueroa, C. A. Guymon, *Chem. Mater.*, 2008, **20**, 768.
- (14) J. Zhang, Z. Xie, A. J. Hill, F. H. She, A. W. Thornton, M. Hoang, L. X. Kong, *Soft Matter*, 2012, **8**, 2087.
- (15) H. Namatsu, *J. Photopolym. Sci. Tec.*, 2002, **15**, 381.
- (16) H. Namatsu, K. Yamazaki, K. Kurihara, *Microelectron. Eng.*, 1999, **46**, 129.
- (17) Y. C. Zhang, Q. N. Li, *Adv. Building Mater., Pts 1-3*, 2011, **168-170**, 258.
- (18) Z. Hosgor, N. Kayaman-Apohan, S. Karatas, Y. Menciloglu, A. Gungor, *Prog. Org. Coat.*, 2010, **69**, 366.
- (19) A. Valles-Lluch, G. G. Ferrer, M. M. Pradas, *Eur. Polym. J.*, 2010, **46**, 910.
- (20) R. L. Guo, X. C. Ma, C. L. Hu, Z. Y. Jiang, *Polymer*, 2007, **48**, 2939.
- (21) H. Palza, R. Vergara, P. Zapata, *Compos. Sci. Technol.*, 2011, **71**, 535.

-
- (22)H. Palza, R. Vergara, P. Zapata, *Macromol. Mater. Eng.*, 2010, **295**, 899.
- (23)S. S. Ray, M. Okamoto, *Prog. Polym. Sci.*, 2003, **28**, 1539.
- (24)F. Zoukrami, N. Haddaoui, C. Vanzeveren, M. Sclavons, J. Devaux, *Polym. Int.*, 2008, **57**, 756.
- (25)M. Z. Rong, M. Q. Zhang, Y. X. Zheng, H. M. Zeng, R. Walter, K. Friedrich, *Polymer*, 2001, **42**, 167.
- (26)E. Kontou, M. Niaounakis, *Polymer*, 2006, **47**, 1267.
- (27)Y. Liu, M.Kontopoulou, *Polymer*, 2006, **47**, 7731.
- (28)M. Asomoza, M. P. Dominguez, S. Solis, T. Lopez, *Mater. Lett.*, 1997, **33**, 153.
- (29)C. Kang, E. Kim, H. Baek, K. Hwang, D. Kwak, Y. Kang, E. L. Thomas, *J. Am. Chem. Soc.*, 2009, **131**, 7538.
- (30)S. Sakka, K. Kamiya, *J. Non-Cryst. Solids*, 1982, **48**, 31.
- (31)C.-J. Chen, H.-T. Lu, W.-Y. Tseng, I. H. Tseng, S.-L. Huang, M.-H. Tsai, *J. Appl. Polym. Sci.*, 2011, **122**, 648.
- (32)S. H. Wang, Z. Ahmad, J. E. Mark, *Polym. Bull.*, 1993, **31**, 323.
- (33)P. Falcaro, S. Costacurta, G. Mattei, H. Amenitsch, A. Marcelli, M. C. Guidi, M. Piccinini, A. Nucara, L. Malfatti, T. Kidchob, P. Innocenzi, *J. Am. Chem. Soc.*, 2005, **127**, 3838.
- (34)B. Su, X. M. Lu, Q. H. Lu, *J. Am. Chem. Soc.*, 2008, **130**, 14356.
- (35)S. A. El-Safy, F. Mizukami, T. Hanaoka, *J. Phys. Chem. B*, 2005, **109**, 9255.
- (36)C. G. Goltner, B. Berton, E. Kramer, M. Antonietti, *Adv. Mater.*, 1999, **11**, 395.
- (37)D. Liu, J. H. Lei, L. P. Guo, X. D. Du, K. Zeng, *Micropor. Mesopor. Mat.*, 2009, **117**, 67.
- (38)M. R. Porter, *Handbook of surfactants*; Blackie & Son Ltd.: New York, 1991.
- (39)J. F. Hulvat, S. I. Stupp, *Angew. Chem. Int. Edit.*, 2003, **42**, 778.
- (40)C. L. Lester, C. D. Colson, C. A. Guymon, *Macromolecules*, 2001, **34**, 4430.
- (41)H. Tang, S. P. Jiang, *J. Phys. Chem. C*, 2008, **112**, 19748.
- (42)K. Uosaki, Y. Shen, T. Kondo, *J. Phys. Chem. _US*, 1995, **99**, 14117.
- (43)M. Pishvaei, F. F. Tabrizi, *Iran. Polym. J.*, 2010, **19**, 707.
- (44)A. P. Zhu, A. Y. Cai, Z. Y. Yu, W. D. Zhou, *J. Colloid Interf. Sci.*, 2008, **322**, 51.

Table 1 XRD results of samples with different content of TEOS loading before surfactant removal.

Dried samples with different TEOS loading	Before		After		After heat	
	polymerization		polymerization		treatment	
	d_{100} (Å)	α (Å)	d_{100} (Å)	α (Å)	d_{100} (Å)	α (Å)
0%	31.1	36.0	33.7	39.0	-	-
10%	31.8	36.8	31.1	36.0	35.9	41.5
30%	34.4	39.8	29.9	34.6	35.3	40.8
50%	39.9	46.1	28.6	33.1	34.2	39.5

d_{100} : d-spacing of the primary (100) reflection

α : center to center distance

Table 2 Silica obtained in final purified cross-linked PEGDA gels calculated from TGA test.

Dried samples with different TEOS loading	Silica content (%)	
	Without heat	With heat
	treatment	treatment
10%	1.1	2.2
30%	6.6	8.3
50%	14.0	15.2

Table 3 Contact angles of water on templated samples with different TEOS loading.

Dried samples with different TEOS loading	Contact angle (°)	
	Without heat	With heat
	treatment	treatment
0	59.1±0.1	-
10%	38.6±2.0	29.8±1.8
30%	32.5±1.0	28.9±1.8
50%	27.4±2.5	24.8±1.9

Figure captions

Figure 1 LLC templating process with silica network reinforcement for nanostructure retention in PEGDA.

Figure 2 Polarized light microscopy (PLM) images for the hexagonal phases with different TEOS loading: (a) before and (a1) after polymerization without TEOS; (b) before and (b1) after polymerization with 10% TEOS; (c) before and (c1) after polymerization with 30% TEOS; (d) before and (d1) after polymerization with 50% TEOS.

Figure 3 XRD profiles of samples with different content of TEOS a) before and b) after polymerization.

Figure 4 XRD profiles of samples after heat treated at 140 °C for 2 hours and before surfactant removal.

Figure 5 Synchrotron SAXS profiles of samples after heat treated at 140 °C for 2 hours and before surfactant removal.

Figure 6 XRD profiles of dried samples with different TEOS loadings: a) without heat treatment, and b) with heat treatment at 140 °C for 2 hours.

Figure 7 FTIR transmittance spectra of dried samples with and without TEOS loading.

Figure 8 Silicon mapping (left) and SEM-EDX (right) of the surface of a dried sample containing 30% TEOS.

Figure 9 DSC results of dried samples with different TEOS loadings.

Figure 10 TGA tests of dried samples with different TEOS loading: a) without heat treatment, and b) with heat treatment at 140 °C for 2 hours.