

Thermal and mechanical properties of poly(*N*-isopropylacrylamide)-based hydrogels as a function of porosity and medium change

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ABSTRACT: Poly(*N*-isopropylacrylamide) (PNIPAAm) has been a well-known stimuli-responsive material and has been used in multiple novel applications. One of the key attributes to make the hydrogel more attractive is to control the response time and temperature. This work focused on comparing the physical properties, such as response time, transition temperature, heat of fusion, and mechanical strength, of macroporous and microporous PNIPAAm hydrogels, respectively. It was found that the macroporous hydrogels synthesized from a low-temperature polymerization with addition of tetramethyl orthosilicate exhibited a faster response time and superior mechanical strength. Furthermore, to modulate the transition temperature, both the macroporous and microporous hydrogels were subjected to different qualities of media by introducing a cosolvent (methanol) or an anionic surfactant (sodium dodecyl sulfate). Interestingly, addition of a cosolvent demonstrated a more pronounced effect on the macroporous hydrogel, whereas the surfactant resulted in a more pronounced effect on the microporous hydrogel. Such results revealed that based on their porosity; there were appreciable differences when the PNIPAAm hydrogels interacted with media molecules. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2015, 132, 42776.

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INTRODUCTION

Since Heskins and Guillet first conducted systematic temperature–response studies of poly(*N*-isopropylacrylamide) (PNIPAAm) in 1968,¹ PNIPAAm and its copolymer derivatives have been extensively used as environmentally responsive hydrogels in diverse engineering applications such as drug delivery,^{2,3} actuators,⁴ sensors,^{5,6} and smart devices.^{7,8} The key reason for its wide applicability could be attributed to the existence of lower critical solution temperature (LCST) of 32°C, at which a discontinuous volume change occurs. The desire for fast response to environmental stimulus, that is, fast swelling and deswelling along with the capacity of controlling the transition temperature, plays a crucial role in increasing the suitability of hydrogels for practical usage.

Conventional hydrogels, however, demonstrate slow response due to the diffusion dominated solvent uptake process, which directly depends on the surface area of the hydrogel. Furthermore, due to the “skin effect,” an outer periphery of the hydrogel shrinks and further retards the deswelling rate of larger gel

pieces.⁹ Previously, this issue has been tackled by increasing the pore size of the hydrogels through introducing external porogens during the synthesis,^{10,11} or by developing structural inhomogeneity inside the hydrogel network.^{12,13} Such approaches have been instrumental in accelerating the hydrogel swelling and deswelling characteristics through capillary effect and convective transport for solvent absorption instead of conventional diffusion mechanism as discussed above.^{14–16} However, the mechanical properties, particularly the compressive modulus and toughness of such porous hydrogels can be significantly lower than hydrogels with lower porosity. Thus, there are fine balances of improving the mechanical properties of the porous hydrogels versus response rates.

Along with the desire for development of fast responsive hydrogels, the ability for modulation of the transition temperatures is also critical for wider applicability of environmentally responsive hydrogels. Controlling the process of hydrogen bond formation and dissociation by alteration of the media quality, for example, through addition of an organic cosolvent or surfactant

results in a change of LCST. Previously, common solvents such as methanol and tetrahydrofuran have been used to alter the LCST of linear PNIPAAm polymers in dilute solutions.^{17,18} Although independently the solvents act as excellent media for the PNIPAAm polymers, when mixed with water, they demonstrate interesting effects on the LCST due to presence of dominant solvent–solvent interaction termed as consolvency.^{19–22} Surfactants, conversely, modify the LCST of PNIPAAm polymers by specifically targeting the hydrophobic isopropyl groups on the PNIPAAm chain, thereby stabilizing the coil–globule transition when heated.^{23,24} These works are important in understanding the behavior of PNIPAAm molecules, however, most of these pertain to linear PNIPAAm polymers in dilute solutions and do not offer considerable insight on the effect of these additives on the behavior of crosslinked PNIPAAm-based hydrogels. Also previous studies have mostly focused on molecular level interaction of hydrogel polymer with surfactant molecules such as Fourier transform infrared spectroscopy (FTIR), which do not reveal much information at the bulk level.^{25,26} A combination of rheology and differential scanning calorimetry (DSC) could offer a more effective combination to understand the bulk level effect of addition of additive molecules to the media. Furthermore, this work is interesting as it highlights the properties of less-studied large porosity PNIPAAm hydrogels which in many cases could be more attractive than the conventional low porosity hydrogels on account of their faster response behavior.

In this work, macroporous gels that are postulated to have faster response characteristics due to larger pore size (greater than 10 μm) are developed by adopting low temperature polymerization with addition of tetramethyl orthosilicate (TMOS) during the synthesis. These hydrogels were further compared with lower porosity hydrogels termed as microporous hydrogels with a pore size less than 1 μm . The microporous hydrogels were synthesized at room temperature and without the addition of TMOS during the synthesis. Both the macroporous and microporous hydrogels were characterized using microscopy techniques such as scanning electron microscope (SEM) and confocal laser scanning microscope. Apart from the morphological analysis, the effect of additives such as cosolvent (methanol) or surfactant (sodium dodecyl sulfate [SDS]) on the macroporous and microporous hydrogels was studied using differential scanning calorimetry and rheometer. The results reveal interesting differences between the interaction of crosslinked hydrogels and media additives; viz. surfactant and cosolvent on the basis of porosity.

METHODOLOGY

Materials

N-isopropylacrylamide (NIPA), *N,N'*-methylenebisacrylamide (MBAAm), ammonium persulfate (APS), *N,N,N',N'*-tetramethylethylenediamine (TEMED), TMOS, SDS, and anhydrous methanol were purchased from Sigma-Aldrich Chemicals and used as supplied.

Synthesis of PNIPAAm Hydrogels

The macroporous hydrogel synthesis started with mixing 600 mg (5.30 mmol) of NIPA with 12.6 mg (0.082 mmol) MBAAm in 5.354 g (297.44 mmol) of deionized (DI) water,

and purged with nitrogen in a water bath maintained at 10°C. Subsequently, 23 μL (0.15 mmol) of TEMED and 208 μL (1.40 mmol) of TMOS was added and mixed well. After 10 min. of degassing, 1084 μL of APS solution (1%; 0.05 mmol) was added to the mixture. After waiting for 3 more minutes, the polymeric solution was then cooled down and maintained at -15°C for 24 h. The frozen gel samples were subsequently thawed and immersed in DI water to remove any unpolymerized monomers. For microporous hydrogels, the synthesis started with mixing 600 mg (5.3 mmol) of NIPA with 12.6 mg (0.082 mmol) MBAAm and 23 μL (0.15 mmol) of TEMED in 5.354 g (297.44 mmol) of DI water, and purged with nitrogen in a water bath maintained at 25°C. After 10 min of degassing, 1084 μL of APS solution (1%; 0.05 mmol) was added to the mixture. The reaction was allowed to proceed at room temperature for 24 h.

Preparation of Media

Modification of response temperature of hydrogels was done by equilibrating the freeze-dried samples of macroporous and microporous hydrogel in different concentration of SDS (0–30 mM) and methanol (0–0.6 vol. fraction).

Characterization

Scanning Electron Microscopy. The surface morphology of the hydrogels was studied using a SEM (XL Series-30, Philips). Specimens were initially freeze-dried and then glued to the brass holders followed with gold sputtering for 100 s using a sputter machine (JFC-1200 Fine coater) prior to the SEM examination.

Confocal Laser Scanning Microscopy. The structure of the hydrogels was investigated using a Leica SP5-X Confocal Microscope. Alexa Fluor 488 fluorescent dyes were absorbed by the hydrogels to differentiate between the polymeric network and intermittent pores. An Argon laser (488 nm) was used to image these materials.

Instron. The compressive stress–strain curves of both macroporous and microporous hydrogels were obtained by conducting tests on a MTS servo hydraulic test system with a load cell of 500 g. Tests were run in displacement control in longitudinal direction at a loading rate of 1 mm/min.

Rheometry. A TA rheometer (TA Instruments AR-G2) was used to perform a temperature sweep on both the macroporous and microporous PNIPAAm hydrogels. The temperature responsive hydrogel samples were first equilibrated in water or the appropriate media and then subjected to a ramp rate of 0.25°C/min and frequency of 1 rad/s. The upper and lower temperatures for the temperature sweep tests were decided depending on the media.

Dynamic Mechanical Analysis (DMA). The dry films of hydrogels were tested for their glass transition temperature using a TA dynamic mechanical analyzer (TA Instruments Q 800). The films were attached to tensile testing grips and subjected to a temperature ramp condition of 3°C/min from 25°C to 220°C at a frequency of 1 Hz.

Differential Scanning Calorimetry (DSC). A TA differential scanning calorimeter (TA Instruments Q-20) was used to

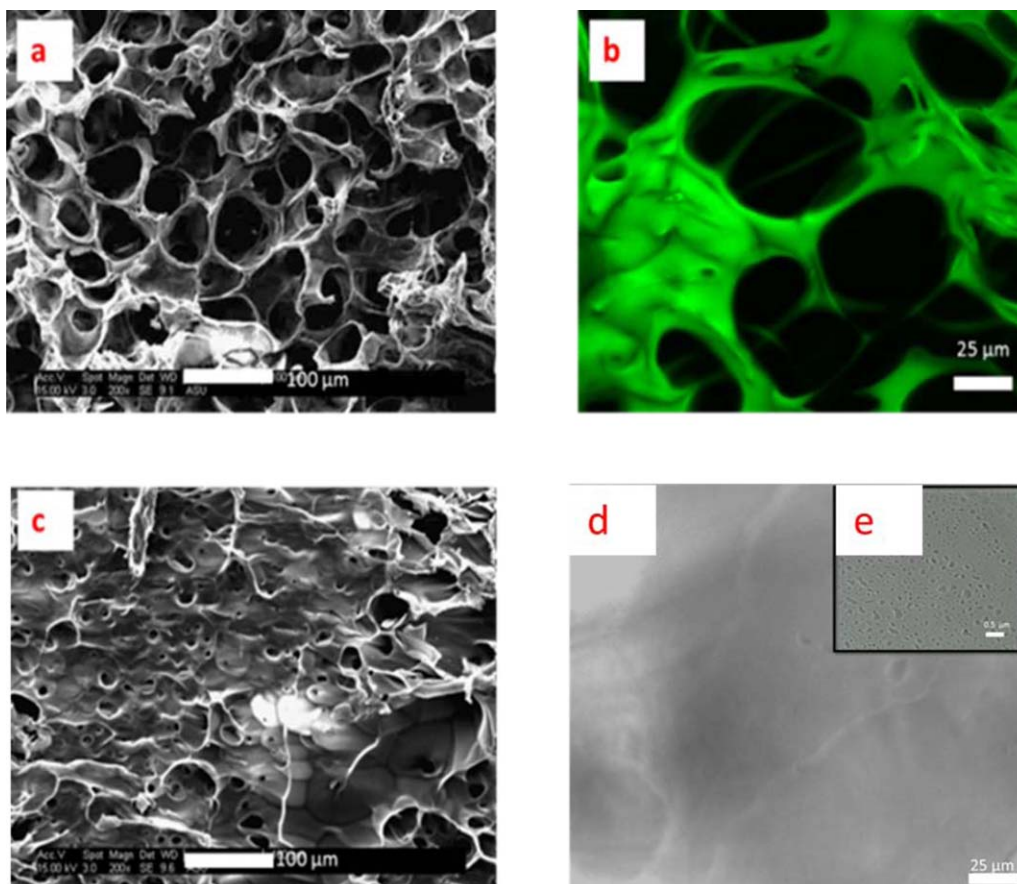


Figure 1. SEM and confocal microscopy for morphology studies of PNIPAAm hydrogel: (a), (b) macroporous hydrogel with average pore length of $65.08 \pm 10.7 \mu\text{m}$; (c)–(e) microporous hydrogel with average pore length less than $1 \mu\text{m}$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

characterize the transition temperature of the thermoresponsive hydrogels. First, the dry gels were equilibrated with HPLC water or the appropriate media and then analyzed with respect to same solvent as reference. The upper and lower temperatures for the DSC experiments were decided depending on the media with a heating rate of $3^\circ\text{C}/\text{min}$.

Reswelling and Swelling Ratio Measurements. The swelling ratios of the hydrogels were measured gravimetrically after wiping off the excess water from hydrogel surface. The hydrogel was incubated in a particular media for 24 h at room temperature. The reswelling ratio measurements were calculated as $S_r = W_t/W_D$ where W_t is the net weight of the equilibrated hydrogel after the solvent is reabsorbed and W_D is the weight of the hydrogel after transition. Similarly, the swelling ratio was calculated as $S_D = W_t/W_o$ where W_t is the weight of equilibrated hydrogel after is solvent absorbed by the hydrogel and W_o is the weight of dry hydrogel.

RESULTS AND DISCUSSION

Comparison of Morphology and Mechanical Properties of Macroporous and Microporous PNIPAAm Hydrogels

Figure 1 shows the significant difference in morphology of PNIPAAm hydrogels synthesized using different procedures. For the

hydrogels demonstrated in Figure 1(a,b), the reaction temperature of the monomeric mixture was maintained below the freezing point of water, which resulted in the formation of large ice crystals in the system and provided framework for the formation of macroporous PNIPAAm hydrogels. Additionally, to ensure uniform growth of the ice crystals, the synthesis process was divided into two stages. In the first stage, the monomeric solution was initially mixed at a temperature of approximately 10°C in an inert environment for a few minutes. Following this, the mixture was placed in a freezer maintained at -15°C . The initial step of low temperature equilibration facilitated in uniform nucleation and growth of ice crystals in the system. Previously Zhang and Zhuo²⁷ and Strachotova *et al.*²⁸ have highlighted the importance of such a two-step temperature reduction process. Importantly, a temperature of lower than -20°C in the freezer would not be conducive for formation of macroporous hydrogel as this would result in the formation of smaller and larger number of solvent crystals, which would lead to smaller pore sizes.^{29,30} The hydrogels were thawed after the polymerization step was completed, which allowed the ice crystals inside the hydrogel to melt. This facilitated in creating a three-dimensional (3D) interconnected porous network, as depicted in both the SEM [Figure 1(a)] and confocal images of the macroporous hydrogels [Figure 1(b)]. In contrast, the

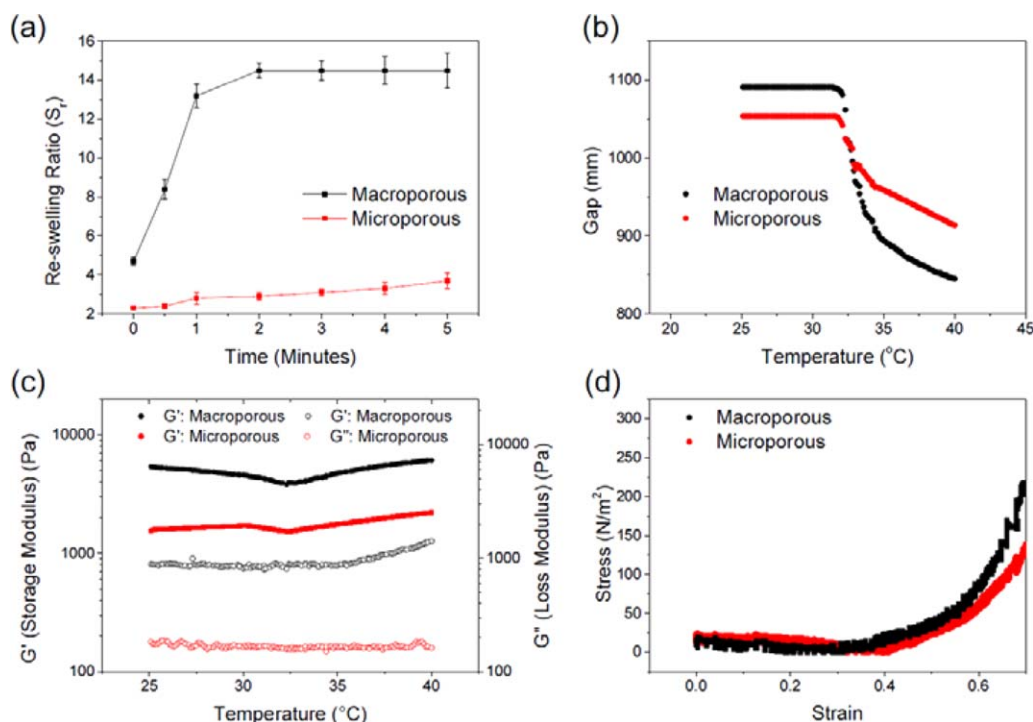


Figure 2. Comparison of solvent uptake and mechanical properties of macroporous and microporous hydrogel: (a) comparison of reswelling rate of the hydrogels; (b) gap change in rheometer for macroporous and microporous hydrogels; (c) rheometer analysis of macroporous and microporous hydrogels; (d) instron compressive analysis of water saturated hydrogels. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

microporous hydrogels shown in Figure 1(c,d), were synthesized at room temperature without any change in monomeric or initiator composition except the omission of TMOS. A visual comparison from the micrographs clearly revealed that the low-temperature polymerization process is useful in obtaining a uniform 3D and interconnected porous network. Furthermore, such a technique was proven to have faster reswelling rate due to solvent absorption by capillary action and convective flow of fluid media into the porous network as opposed to the slower and surface area-dependent diffusion process in the microporous hydrogel [Figure 2(a)].

Although low-temperature synthesis successfully assists in the formation of the desired three dimensional large porous polymeric hydrogel system, it also results in lowering of the mechanical properties and structural integrity, which is an adverse effect of such synthesis.¹⁰ One of the facile ways of achieving faster responsive PNIPAAm hydrogels is by copolymerizing NIPAM with siloxane compounds, such as TMOS, which creates a porous network.¹⁶ In the macroporous hydrogel synthesis, an *in situ* silicate network was incorporated by a hydrolysis reaction of TMOS with water. The silica network provides an additional backbone for the PNIPAAm hydrogel by stabilizing the pores and channels, thereby delivering improved reswelling rates over conventional microporous hydrogel as previously discussed in Figure 2(a). Interestingly, as discussed later, apart from improving the solvent absorption capabilities, the additional silica network also improves the mechanical properties by complementing the softer polymer gel network.

The postulated improved swelling and deswelling response rate and better mechanical properties of the fast responsive macroporous hydrogel were further quantified and confirmed by a viscoelasticity–temperature study on both hydrogels (macroporous and microporous) with a rheometer. The gap change information acquired from such temperature sweep studies revealed that the macroporous hydrogels had a steeper slope, suggesting a quicker deswelling behavior when compared to microporous hydrogels [Figure 2(b)]. The rheological data also demonstrated that the storage modulus and the loss modulus of the macroporous gels were much higher than the microporous gels [Figure 2(c)]. A separate compressive stress analysis on the saturated hydrogels using an Instron instrument revealed that the macroporous gels were 1.33 times tougher than the microporous gels [Figure 2(d)]. Both the rheometer and Instron results validated the important hypothesis that the silicate network played a decisive role in strengthening the framework of the gels. Compared to other techniques of preparing macroporous hydrogels such as incorporation of surfactants during the hydrogel preparation,^{31,32} hydrogel preparation during the LCST,^{33–35} or hydrogel preparation by a freeze drying and hydration process,³⁶ the present method of macroporous hydrogel synthesis is much simpler and efficient.

Figure 3(a,b) demonstrates the DMA data to analyze the glass-transition temperatures (T_g) of the macroporous and microporous hydrogels, respectively, using $\tan \delta$, which is a ratio of the loss modulus (G'') to the storage modulus (G'). Interestingly, the glass-transition temperatures of the dry macroporous

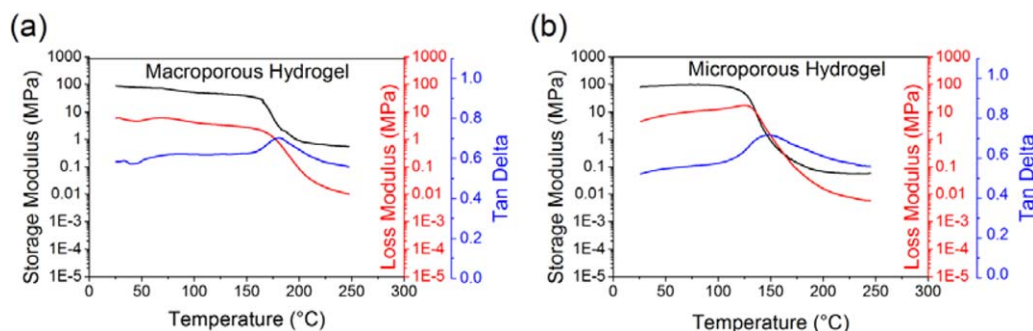


Figure 3. DMA analysis of dry hydrogel: (a) Macroporous PNIPAAm hydrogel and (b) Microporous PNIPAAm hydrogel. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

hydrogel ($T_g = 181.7^\circ\text{C}$) is significantly higher than the microporous hydrogel ($T_g = 149.7^\circ\text{C}$). As we already know, the glass transition corresponds to the temperature at which there is substantial mobility of the polymeric chains. If the interactions among polymer chains are strong, a higher temperature would be needed to promote this chain mobility. In the case of macroporous hydrogels due to addition of the silicate network, there might be slowing down of chain mobility which subsequently results in a higher T_g .

Controlling the Transition Temperature of Macroporous and Microporous PNIPAAm Hydrogels

Effect of Cosolvent. Figure 4(a,b) demonstrates the DSC thermograms depicting the transition temperature of macroporous and microporous PNIPAAm-based hydrogels, respectively, with

addition of an organic solvent (methanol) in the media. Conventionally, the transition temperature is referred to the endothermic peak in the DSC thermogram.²⁷ Both the macroporous and microporous hydrogels demonstrate a significant shift in the transition temperature as the concentration of the methanol is varied [Figure 4(c)]. This observation is in good agreement with experiments done initially by Winnik *et al.* to study the effect of methanol as a cosolvent for linear PNIPAAm polymers in dilute aqueous solutions.¹⁷ This rare and interesting occurrence of consolvency is quite different from cosolvency in which a mixture of two or more solvents acts as a solvent for a particular compound, such as a polymer, when independently both the solvents are inept in solubilizing the third component.³⁷ In this case, PNIPAAm demonstrates consolvency, as both methanol and water are excellent solvents for it, however,

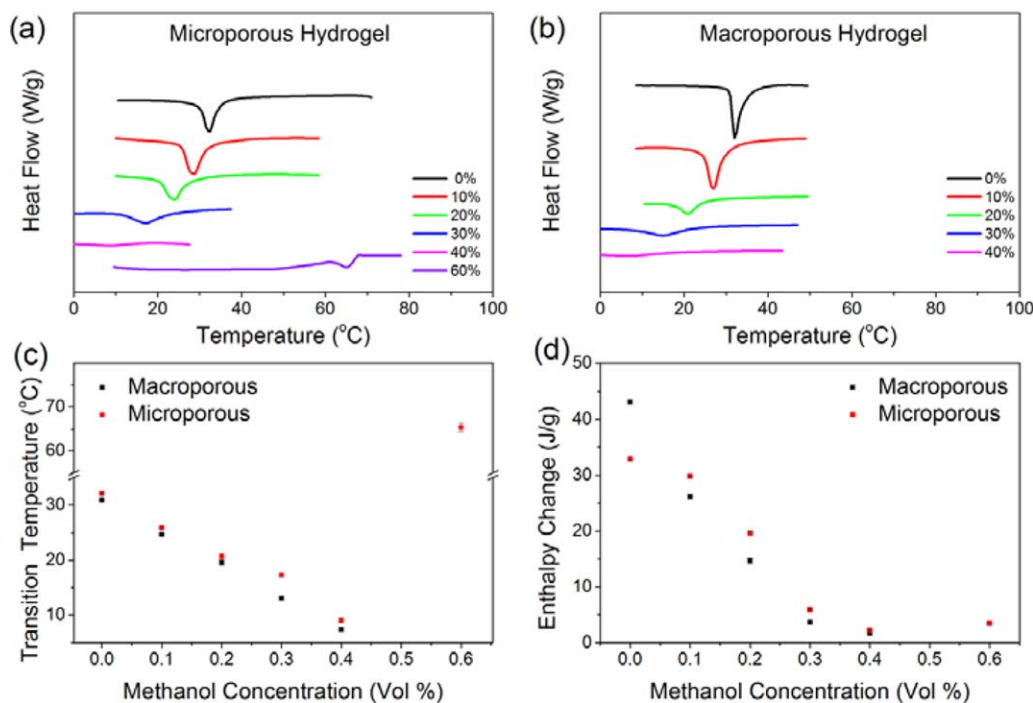


Figure 4. Effect of methanol on the transition temperature and enthalpy change of macroporous and microporous PNIPAAm hydrogel: (a) DSC thermograms of macroporous hydrogel; (b) DSC thermograms of microporous hydrogel; (c) Comparison of LCST with change in porosity and change of solvent (standard deviation <2% over 3 separate runs); (d) Comparison of heat of fusion with change in porosity and change of solvent (standard deviation <5% over 3 separate runs). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

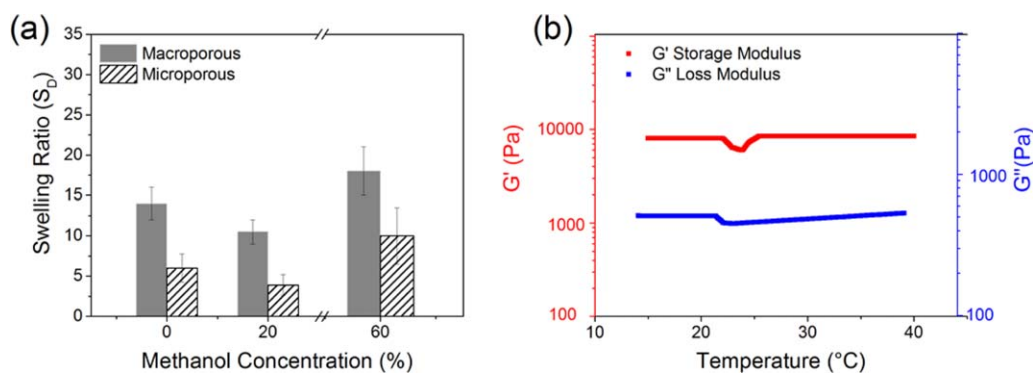


Figure 5. Effect of methanol concentration on the swelling ratio and rheological properties (a) comparison of swelling ratio between macroporous and microporous hydrogel under different methanol concentration; (b) rheometer analysis of macroporous hydrogel equilibrated with 20% methanol concentration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

when mixed together the LCST of PNIPAAm shifts, suggesting marked decrease in the solubility. This case is different from the linear PNIPAAm polymer chains as both the macroporous and microporous hydrogels discussed here are crosslinked.

In the past, there have been competing explanations for the presence of cononsolvency. The first one suggests the complexation between water and methanol induced by the presence of the PNIPAAm network.^{38,39} But such an argument had difficulty in explaining the re-entrant swelling behavior in an extremely dilute solution with linear PNIPAAm polymers.^{40–42} The second theory postulates, the presence of “competitive” absorption between PNIPAAm–water and PNIPAAm–methanol.^{43,44} But such an argument also does not hold ground based on its initial hypothesis that the solvent–solvent interaction is insignificant, which has been subsequently contested by other work.^{45,46} Finally, the theory initially proposed by Zhang and Wu,^{20,47} explains quite well the peculiar behavior of PNIPAAm polymer in the presence of methanol. It suggests the formation of stoichiometric compounds between the solvent and PNIPAAm polymer molecules which results in decreased solubility at certain concentration.

Figure 4(d) depicts the change in the enthalpy value associated with the phase transition of macroporous and microporous hydrogels by integrating the peaks obtained from the DSC thermograms. For the macroporous hydrogel, the enthalpy value (water as the solvent) is higher than the microporous hydrogel, suggesting that for a given temperature increase above the transition temperature, the amount of water released is higher. This is because the freed water within the heterogeneous macroporous hydrogel is able to diffuse outward more easily than from the microporous hydrogel. Such an analysis is in accordance with the faster reswelling and deswelling rate of macroporous hydrogel discussed in the previous section [Figure 2(a,b)] and with earlier reported results on other macroporous hydrogel synthesized using a mixed solvent synthesis technique.¹⁵

The rise in the methanol percentage in the media induced a sharp decrease in the enthalpy value during the phase transition, as evident from Figure 4(d). Such a decrease highlights the limited affinity of such a media for both the macroporous and microporous hydrogels. This depression in enthalpy content and

transition temperature is followed by an abrupt increase of both these values as the media became more methanol rich, and therefore, more suitable for hydrogen bonding with the hydrogels, as deduced earlier by Winnik *et al.*¹⁷ The effect of higher concentrations of methanol on the macroporous hydrogel could not be perceived by the DSC resulting in a disappearance of endothermic peak for methanol concentration at 60% by volume.

Both the macroporous and microporous hydrogels demonstrated a decrease in swelling ratio at concentrations of methanol when the transition temperature had decreased, and increased again as the methanol concentration rises over certain percentages [Figure 5(a)]. The decrease in the swelling ratio suggests the limited absorption of methanol–water mixture by both macroporous and microporous hydrogels which as discussed before decreases the enthalpy change during phase transition as well as the transition temperature. However, as the methanol percentage is increased over 50% the swelling ratio recovers suggesting suitable media for hydrogen bond formation and lower water–methanol interaction. Moreover, the presence of methanol induces greater change in swelling ratio for microporous gels for both below and above 50% methanol concentration. The possible reason for lesser effect of methanol on the swelling ratio of macroporous hydrogel is the larger pore size, which allows more solvent molecules to penetrate into the hydrogel and thereby induces lesser abrupt swelling pattern.

Apart from the differences in swelling ratio, there is also effect on the mechanical properties due to the presence of methanol in the media. At 20% methanol concentration by volume in the media the macroporous hydrogel demonstrated a slight increase in the storage modulus (G') and loss modulus (G'') when compared to similar experiment results in the previous section using a rheometer and pure water media [Figures 2(c) and 5(b)]. The increase of the mechanical properties could be deduced to the lower solvent uptake and the shrunken nature of the macroporous hydrogel in presence of methanol. Along with the increase of the mechanical properties the increase of the G' at approximately 20°C suggests the transition temperature and validates the DSC results signifying the depression of the transition temperature due to the presence of methanol in the media.

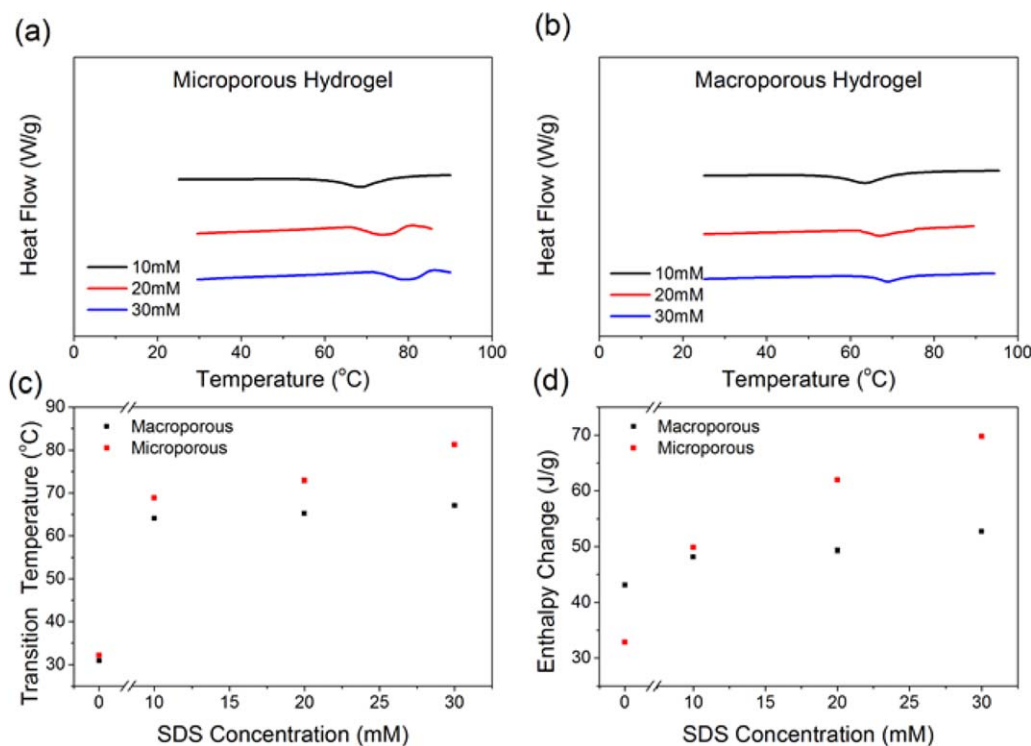


Figure 6. Effect of SDS on the transition temperature and enthalpy change of macroporous and microporous PNIPAAm hydrogel: (a) DSC thermograms of macroporous hydrogel; (b) DSC thermograms of microporous hydrogel; (c) comparison of transition temperature with change in porosity and change of surfactant concentration (standard deviation <2% over 3 separate runs); (d) comparison of heat of fusion with change in porosity and change of surfactant concentration (standard deviation <2.5% over 3 separate runs). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Effect of Surfactant. Figure 6(a,b) depict the effect on the transition temperature of the microporous and macroporous hydrogel, respectively, as a function of increase in the concentration of anionic surfactant, SDS. SDS has been chosen as it has been previously reported that anionic surfactants interact more strongly with nonionic polymers like PNIPAAm when compared to cationic surfactants.^{48,49} The results are also in good agreement with the first observed effects of surfactants on the coil-globule transition of linear PNIPAAm polymers.⁵⁰

The effect of surfactant on the transition temperature of PNIPAAm has been attributed to alterations in the hydrophobic interactions of PNIPAAm with water due to the presence of charged moieties in the media. Various earlier works have deduced that the hydrophobic part of surfactant binds locally with the isopropyl group of PNIPAAm hydrogels.^{51–53} This converts the intrinsically nonionic nature of the PNIPAAm polymeric network to polyelectrolyte type. Thus, these additional acquired charges on the PNIPAAm polymer network directly influences the transition temperature of the PNIPAAm hydrogels by balancing the hydrophobic forces brought about by the disruption of the hydrogen bond with water or other media when the temperature is raised. This explanation is also similar to the observed increase of the transition temperature of ionic hydrogels and microgels. For example, poly(*N*-isopropylacrylamide-co-acrylic acid) hydrogel has a higher transition temperature than simple PNIPAAm hydrogel due to the ionized carboxylic acid group (–COOH) presence on the polymeric

chain,⁵⁴ which subsequently increases the hydrophilic nature of the polymeric network and counters the hydrophobic nature of PNIPAAm molecule above a certain temperature.

The compiled effect of the transition temperature as a function of porosity is represented in Figure 6c. These results when compared to the earlier section, that is, effect of methanol on the transition temperature due to cononsolvency, seems different [Figure 4(c)], as the alterations due to surfactant on the transition temperature could be ascertained as of increasing nature only, unlike methanol, where both increase and decrease of transition temperature occurs depending on the methanol percentage in the media. The effect of the presence of the surfactant molecules in the media can be better analyzed through changes in the enthalpy value during transition [Figure 6(d)]. The macroporous and microporous hydrogels both demonstrated an increase in the enthalpy change during transition with increasing surfactant concentrations. This occurrence is explained through higher stability of the PNIPAAm due to local binding of surfactant molecules on the PNIPAAm chain as discussed earlier, thereby suggesting that the transition process here is more thermal energy intensive owing to the stronger surfactant interaction with the polymeric network. Also interestingly the microporous hydrogels recorded higher heat flow at transition when compared to the macroporous hydrogels, particularly at higher SDS concentrations (>10 mM). These results could point to the fact that due to the lower pore size in the microporous hydrogels, the proximity of neighboring polymeric

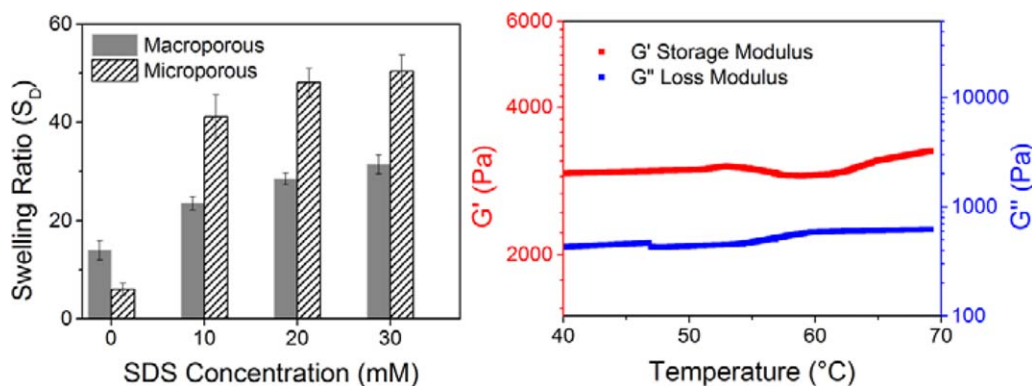


Figure 7. Effect of SDS concentration on the swelling ratio and rheological properties (a) comparison of swelling ratio between macroporous and microporous hydrogel under different SDS concentration (b) rheometer analysis of macroporous hydrogel equilibrated with 10-mM concentration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

chains is closer which subsequently increase the effect of the surfactant molecules and lead to higher interactions between the electrolytic charges of the surfactant molecules locally bound on the polymer network. The higher interaction of the electrolytic charges possibly causes greater charge repulsion and expansion of polymer network and results in increase of polymer network stabilization with respect to temperature.

Such observations could be attributed to the increased osmotic pressure due to adhering of hydrophobic part of the surfactant molecules on the polymer chains.⁵² More interestingly, the microporous hydrogel demonstrated greater than sixfold increase in the swelling ratio when the surfactant concentration in the media was 10 mM or higher, while the macroporous hydrogels showed a maximum increase of approximately 1.6 times increase in the swelling ratio. One probable hypothesis to such an observation might be due to increased density of the polymer network in microporous hydrogels over macroporous hydrogels. The difference in network density may provide higher surfactant molecules interaction resulting in increase in the swelling ratio. Furthermore, the effect on mechanical properties due to presence of surfactant in the media was studied with the help of the rheometer. The decrease of the storage modulus (G') and loss modulus (G'') when compared to pure water media indicates the increase in the swelling ratio in such an environment [Figures 2(c) and 7(b)]. The rheometer results also validate the increase of transition temperature as analyzed by DSC due to the presence of surfactant in the media.

CONCLUSION

In summary, two types of PNIPAAm-based hydrogels, namely macroporous and microporous, were prepared by adopting different synthesis techniques. The structure–property relationship studies of these hydrogels were performed through various characterization techniques such as DSC and rheometer. These studies offered useful insight into the difference of the mechanical and thermal properties of PNIPAAm hydrogels as a function of pore size. The precise measurement of the transition temperature and the enthalpy changes during the phase transition furthered the understanding of the effect of the additives such as a cosolvent (methanol) and an ionic surfactant (SDS) in the

media. Such results reveal that there are appreciable differences in interaction of PNIPAAm-based hydrogels with media molecules based on their porosity. The comprehensive studies would enhance the present knowledge of both fast responsive PNIPAAm and conventional hydrogels and help them to be more extensively used in advanced applications.

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