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Influence of imidazolium based green solvents on volume phase transition temperature of crosslinked poly(N-isopropylacrylamide-co-acrylic acid) hydrogel

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The volume phase transition temperature (VPTT) of crosslinked poly(N-isopropylacrylamide-co-acrylic acid) (PNIPAM-co-AA) hydrogel in water in the presence of five imidazolium based ionic liquids (ILs) was studied. The VPTT of PNIPAM-co-AA hydrogel can be modulated to different extents by the addition of different amounts of ILs. The modulations in VPTT values can be attributed to the IL-induced alterations in hydrophobic, hydrophilic and hydrogen bonding interactions of PNIPAM-co-AA hydrogel with neighboring solvent and molecular chains. The influence of ILs, having a common cation, 1-butyl-3-methylimidazolium cation ([Bmim]) and different anions such as, Iodide (I^-), tetrafluoroborate (BF_4^-), chloride (Cl^-), acetate (CH_3COO^-) and hydrogen sulfate (HSO_4^-), on the phase transition of PNIPAM-co-AA hydrogel was monitored by the aid of differential scanning calorimetry (DSC), dynamic light scattering (DLS) and Fourier transform infrared (FT-IR) spectroscopy. Further, the interfacial properties between aqueous IL and polymer surface were scrutinized with the help of contact angle (CA) measurements. The overall specific ranking of ILs in preserving the hydration layer around the PNIPAM-co-AA hydrogel in water was [Bmim][I]> [Bmim][BF_4]> [Bmim][Cl]> [Bmim][Ac] > [Bmim][HSO_4]. The trend of these ILs followed the well-known Hofmeister series. Interestingly, PNIPAM-co-AA hydrogel in water shows abnormal salting-out property in the presence of [Bmim][BF_4] at higher concentration and this abnormal behavior can be explained based on the lack of sufficient binding sites on the macromolecule for higher number of [Bmim][BF_4] at higher concentration.

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1. Introduction

Thermoresponsive polymer, particularly poly(N-isopropylacrylamide) (PNIPAM), exhibits coil-to-globule phase transition in water at its lower critical solution temperature (LCST) in response to external stimuli, and thus has attracted considerable attention from the research community.[1-5] This coil-to-globule phase transition of PNIPAM chains is governed by hydrogen bonds and hydrophobic interactions in water. Further, introduction of cross linkers or comonomers at various amounts into the PNIPAM results in different kinds of PNIPAM-based hydrogels with different volume phase transition temperatures (VPTT).[6-8] For instance, the phase transition temperature of PNIPAM is increased with the addition of hydrophilic group, acrylamide; by contrast, the phase transition temperature was decreased with the addition of hydrophobic group, *N*-butylacrylamide.[9] The applications of given polymer with fixed feed ratios of constituents in a given area may require a specific transition temperature and, therefore, tuning of transition temperature of a thermosensitive polymers is an important research subject.[10]

In spite of common practice for altering the phase transition temperature by controlling the feed ratios of hydrophilic or hydrophobic constituents, the controlling of feed ratios during polymerization reaction is a complex process and time consuming. Further, excess or low amounts of hydrophilic or hydrophobic groups in a polymer may lead to the undesired products. Moreover, the fixed feed ratios of constituents of a polymer may not produce a desired phase transition temperature. In this concern, changing of solvent quality for a desired phase transition temperature becomes a prominent alternative in the area of smart polymers.

Addition of salts,[11-13] surfactants,[14,15] urea,[16,17] sugars,[18,19] into the solvent of polymer is an alternative active approach for changing the solvent quality and thereby, governing the transition temperature of smart polymers. The use of ionic liquids (ILs) in controlling the transition temperature of smart polymers came into limelight in recent years.[20-23] ILs, are a class of materials that have a considerable potential to provide advances in a variety of scientific fields.[24,25] Consisting entirely of ions, these semi-Coulomb materials offer unique properties of particular interest including low flammability, inert nature, low volatility, low vapor pressure, low melting point, wide liquid range, and solvating properties for diverse substances.[26]

Although extensive studies have been devoted to explore the tuning of phase transition temperature of thermoresponsive polymers in water, these studies have largely focused on the effects of ionic salts and surfactants. Till date, only a few reports have been devoted to explain the role of ILs in tuning the transition temperature of thermoresponsive polymers.[20-23] However, these reports are seldom seen in open literature. Moreover, to the best of our knowledge, thermoresponsive hydrogel, with superior biocompatibility, have never been studied in water in the presence of biocompatible ILs. Further, in view of the growing importance of ILs and polymer matrixes in various scientific fields, it is desirable to systematize the ILs effect on transition temperature of thermoresponsive polymer. In this connection, we have put our efforts to understand the effects of various ILs with common cation, 1-butyl-3-methylimidazolium, ([Bmim]) and commonly used anions such as I^-, BF_4^-, Cl^-, $CH_3COO^-$and HSO_4^- on VPTT of PNIPAM-co-AA hydrogel in water. Our sophisticated experimental results such as differential scanning calorimetry (DSC), dynamic light scattering (DLS), Fourier transform infrared spectroscopy (FT-IR) and contact angle (CA) unveil that the extent of the response of hydrogel to solute IL was found to be consistent with the Hofmeister series, being [Bmim][HSO_4] was structure maker, while [Bmim][I] was structure breaker for the hydration layer around the PNIPAM-co-AA hydrogel in water. The current study is apparently the first report of CA measurements to evaluate the interaction between ILs and PNIPAM based hydrogel.

2. Experimental section

Materials and sample preparation

All the chemicals were received from different sources and used without further purification as they were provided in highest purity. N-Isopropylacrylamide (NIPAM), acrylic acid (AA) and [Bmim][Cl] were purchased from King Ming Chemical Co., Ltd. *N,N,N′,N′*-tetramethylethylenediamine (TEMED), ammonium persulfate (APS) and *N,N′*-methylenebisacrylamide (MBAA) (cross-linker) were obtained from the Sigma chemical co. ILs such as [Bmim][I], [Bmim][BF_4], [Bmim][CH_3COO] and [Bmim][HSO_4] were purchased from the Uni-onward Corp. Water with resistivity of 18.2 MΩ cm was obtained from a Roda purification system (Te Chen Co. Ltd.) and used for all the samples preparation. The concentration of PNIPAM-co-AA hydrogel in water was maintained at 1% (w/v) for all the measurements, while IL concentrations vary from 0.5 M to 1.5 M.

Synthesis of PNIPAM-co-AA hydrogel

PNIPAM-co-AA hydrogel was prepared by following the procedure in previous literature.[27] In brief, NIPAM, AA and MBAA dissolved in phosphate buffered saline (PBS) in three necked flask and stirred for 30 min under N_2 atmosphere at room temperature. The catalyst, TEMED was added to the solution in the three necked flask and the solution was mechanically stirred at 200 rpm under nitrogen for 19 h at room temperature. The synthetic route for PNIPAM-co-AA hydrogel has given in Scheme 1. The pH of PBS buffer was maintained at 6.8 for avoiding the ionization of acidic groups in polymer during synthesis. The obtained hydrogel was freeze-dried before the use. The synthesized polymer was characterized by the FT-IR spectroscopy. The absence of carbon-carbon double bond has confirmed the complete polymerization of monomers, NIPAM and AAc. The feed ratio of [NIPAM]/[AA]/[APS]/[MBAA] in PNIPAM-co-AA hydrogel is $4.77\times10^{-5}/6.24\times10^{-6}/1.97\times10^{-7}/5.84\times10^{-8}$ mol L^{-1}, respectively.

Differential scanning calorimetry (DSC) measurements

Each sample weighted about 10-15 mg and was sealed in aluminum pan. DSC analysis were carried out on a TA-MDSC-2920 (TA Instruments, New Castle, DE, USA). At the beginning of measurement, each sample was equilibrated at 20 °C for 5 min to ensure thermal equilibrium.

Thermo-analytical curves of each sample obtained by heating the sample at the rate of 10 °C/min. Standard procedure was followed to calibrate the temperature scale to ensure reliability of the data obtained. The uncertainties in temperature and heat flow readings are ± 0.02 °C and ± 0.1%, respectively. Each DSC thermogram reported here is an average of three measurements. All the experiments were performed in a nitrogen atmosphere.

Dynamic light scattering (DLS) measurements

The hydrodynamic diameter (d_H) was measured by dynamic light scattering (DLS) on a Coulter N4-Plus Submicron Particle Sizer (Beckman Coulter) at a fixed angle of 90°. The light source of the instrument is a 4.10 mW He - Ni with a fixed wavelength of λ= 632.8 nm. The Coulter N4 Plus uses a photon correlation spectroscopy-based technique employing autocorrelation spectroscopy of scattered laser light to determine its time-dependent fluctuations resulting from the Brownian motion of particles in suspension. A bubble free sample was introduced in a glass cuvette and a teflon-coated screw cap was placed at the mouth of cell to secure from dust. Then the airtight sample cell was placed in the sample chamber of DLS instrument. The correlation functions of scattering data were analyzed via the CONTIN method to obtain the distribution of diffusion coefficients (D) of the solutes. The apparent d_H was deduced from D by the Stokes−Einstein equation, $d_H = kT/3\pi\eta D$, where k is the Boltzmann constant, T is the absolute temperature, and η is the solvent viscosity. All the DLS measurements were performed at room temperature.

Contact angle (CA) measurements

The contact angle measurements were performed on a contact angle meter (CAM-100, Creating-Nanotech Co.) equipped with controlled liquid dispenser at a room temperature. The average CA was obtained using the software Euresys (Easy Grab Multicam for Picolo Version 3.8.3). In a typical measurement, a fixed volume of sample droplet (water having IL) was placed on the flat surface of dry hydrogel and started obtaining CA after allowing drop to held in place for ca. 5 sec.

Fourier transform infrared spectroscopy (FT-IR) measurements

FT-IR spectra were recorded at room temperature on a FT/IR-460 plus (JASCO, USA). The samples were placed between two ZnSe tablets. Each IR spectrum reported here was an average of 32 scans using a spectral resolution of 4 cm^{-1} for an acceptable signal-to-noise ratio. Analyses of the spectra were performed by using spectroscopic software (Spectra Manager). A background spectrum of the solvent was measured directly before each sample containing PNIPAM-co-AA hydrogel.

3. Results and discussion

Fig. 1 shows typical DSC thermograms of PNIPAM-co-AA hydrogel in water in the absence and presence of different ILs at 0.5 M concentration. Further, these thermograms were used to obtain the VPTT values of PNIPAM-co-AA hydrogel in water in the absence and presence of ILs. The VPTT is defined as the temperature corresponding to the initial break point of the DSC thermogram. The PNIPAM-co-AA hydrogel in water undergo LCST type phase transition at around 38.9 °C. Below the VPTT, hydrogen bonds between water molecules and hydrophilic groups of hydrogel are dominated and leads to the swollen state of the hydrogel. When the external temperature is increased to the VPTT, the hydrophobic interactions among the hydrophobic groups of hydrogel overwhelm the hydrogen bonds between hydrogel and water.[28-30] Surprisingly, the VPTT value of PNIPAM-co-AA hydrogel in water is decreased to 37.5 and 28.8 °C in the presence of 0.5 M [Bmim][Ac] and [Bmim][HSO_4], respectively. On the other hand, PNIPAM-co-AA hydrogel in water did not show volume phase transition in the presence of [Bmim][I] and [Bmim][Cl]. Whereas, PNIPAM-co-AA hydrogel in water shows volume phase transition at 40.4 °C in the presence of [Bmim][BF_4]. From these results, one can understand that [Bmim][I], [Bmim][BF_4] and [Bmim][Cl] ILs behave as "*constructers*" for the hydration layer around the PNIPAM-co-AA hydrogel. Whereas, [Bmim][Ac] and [Bmim][HSO_4] act as "*destroyers*" for the hydration layer around the PNIPAM-co-AA hydrogel, as smaller VPTT values (37.5 °C in the case of [Bmim][Ac], 28.8 °C in the case of [Bmim][HSO_4]) were observed in the presence of these ILs.

The influence of concentrations (1M and 1.5 M) of ILs on the VPTT of PNIPAM-co-AA hydrogel in water was also measured. The change in VPTT was monitored by the addition of different concentrations of IL. For the sake of brevity we have not presented all the DSC thermograms in the presence of various kinds of ILs. It is clear that the VPTT of PNIPAM-co-AA hydrogel in water is significantly influenced by the addition of ILs, and can be modulated to different extent by the addition of different ILs at different concentrations. The complete profile of VPTT values of PNIPAM-co-AA hydrogel in water in the presence of different kinds of ILs at various concentrations was given in table 1 and the same was presented in Fig. 2. As can be seen from table 1 and Fig. 2, ILs, [Bmim][Ac] and [Bmim][HSO_4] significantly depress the VPTT of PNIPAM-co-AA hydrogel in water as increasing the concentration, while [Bmim][I] significantly elevates the VPTT. On the other hand, ILs, [Bmim][Cl] and [Bmim][BF_4] show anomalous behavior on VPTT of PNIPAM-co-AA hydrogel in water. At low concentrations (0.5 and 1 M), [Bmim][Cl] and [Bmim][BF_4] elevates the VPTT of PNIPAM-co-AA hydrogel in water. However, with further increase in concentration of these ILs, the VPTT value was appreciably decreased from 45.5 °C (in the presence of 1 M [Bmim][BF_4]) and 40.9 °C (in the presence of 1 M [Bmim][Cl]) to 38.1 (in the presence of 1.5 M [Bmim][BF_4]) and 35 °C (in the presence of 1.5M [Bmim][Cl]). From these aforesaid results we can come to the following inferences.

The ILs, [Bmim][Ac] and [Bmim][HSO_4], behave as "*destroyers*" for the hydration layer of PNIPAM-co-AA hydrogel in water at all concentrations, make the well swollen PNIPAM-co-AA hydrogel into shrunken collapsed globular structure by "*salting out*" mechanism. This phenomenon can be visualized from Fig. 3. As shown in Fig. 3, in the presence of 1.5 M [Bmim][Ac] the PNIPAM-co-AA hydrogel in water exhibits shrunken behavior as the resulting solution become cloudy. The shrunken behavior of PNIPAM-co-AA hydrogel in water further intensified in the presence of 1.5 M [Bmim][HSO_4] as evidenced from the optical image shown in the Fig. 3. The increased hydrophobic interactions among polymer chains would drive the water out and cause the chains to collapse and entangle at lower temperature in the presence of [Bmim][HSO_4]. Thus, a solid like aggregated state would form.[29] This behavior is in agreement with the normal Hofmeister series, addition of the kosmotropic salts leads to the hydrophobic collapse of polymer and thereby decrease the VPTT value.[13] Moreover, the hydrophobic collapse of PNIPAM-co-AA hydrogel in water can be correlated to the ability of salting out of ILs, which is further regulated by the entropy of hydration of strongly hydrated/kosmotropes.[31] The addition of [Bmim][HSO_4] at higher concentrations leads to the formation of large aggregates. On the other hand, [Bmim][I] exhibits the significant "*salting in*" effect that is embodied by the increase of VPTT at all concentrations. Indeed, the chaotropic ions apparently bind to the amine and carbonyl groups of macromolecule at lower concentration. The elevated VPTT values in the presence of chaotropic ions can be attributed to the binding interactions, between chaotropic ions and polar groups of macromolecule, which will increase the charge on the macromolecule and thereby inhibit hydrophobic collapse of macromolecule.[32]

While, the remaining two ILs, [Bmim][BF_4] and [Bmim][Cl] surprisingly show mixed behavior of "*salting in*" and "*salting out*" based upon the concentrations. At low and moderate concentrations (0.5 and 1 M), these ILs act as "*constructers*" for hydration layer around the PNIPAM-co-AA hydrogel, while act as "*destroyers*" at high concentration (1.5 M). Interestingly, the binding interactions between chaotropic ion and polar groups of macromolecule and destabilization of hydrophobic hydration waters around polymer carbon chain come into action depend upon the chaotropic ion concentration. At lower concentration of [Bmim][BF_4] and [Bmim][Cl], the binding interactions between chaotropic ion and polar groups of macromolecule are dominated, while destabilization of hydrophobic hydration of polymer carbon chain is true at higher concentration. Moreover, the cooperative binding interactions between chaotropic ion and polar groups of macromolecule become anti cooperative at higher concentrations as larger numbers of anions to the same polymer chain increasingly difficult to bind at higher concentration.[33] This should be the case because the binding of one anion repels the binding of additional anions by electrostatics and thereby enhances the surface tension at polymer carbon chain and hydration layer interface, which ultimately leads to the hydrophobic collapse of polymer.

However, the mixed behavior of [Bmim][BF_4] for PNIPAM-co-AA hydrogel in water is quite opposite to its mixed behavior for PNIPAM in water, where it acted as "*destroyer*" and "*constructer*" at lower and higher concentrations, respectively [20]. Here, it is worth enough to compare the phase transition temperature behavior of PNIPAM homopolymer in water with that of PNIPAM-co-AA hydrogel in water in the presence of [Bmim][BF_4]. As shown in *Ref.* 20, PNIPAM in water exhibits phase transition at around 31 °C in the presence of 0.4 M [Bmim][BF_4]. In contrast to this, PNIPAM-co-AA hydrogel in water exhibits phase transition around 40.4 °C in the presence of 0.5 M [Bmim][BF_4]. The elevated phase transition temperature for PNIPAM-co-AA hydrogel is mainly attributed from the more number of binding sites than that of PNIPAM homopolymer. The higher number of binding sites led to the cooperative interactions between tetrafluoroborate anion and polar groups on the PNIPAM-co-AA hydrogel and thereby enhances the solubility of PNIPAM-co-AA hydrogel shows swollen behavior. However, with the increase of concentration of [Bmim][BF_4], all the binding sites of PNIPAM-co-AA hydrogel are occupied by anions and the excess anions start increasing surface tension between hydration layer and polymer, and this obviously led to the salting out phenomenon. On the other hand, since the number of binding sites are less in PNIPAM homopolymer, the surface tension phenomena dominates over cooperative binding between anion and polar groups of polymer even at lower concentration of [Bmim][BF_4] and thereby, polymer undergo hydrophobic collapse. This complete mechanism can be understood from the scheme 2.

In order to get more insight on the effect of ILs on the hydration layer around the PNIPAM-co-AA hydrogel and VPTT values in water, the DLS measurements were performed at room temperature. Since the DLS experiments were performed at room temperature the changes occurred in the hydration layer is solely contributed from the ILs. Fig. 4 shows the intensity distribution graphs of PNIPAM-co-AA hydrogel in water in the absence and presence of different kinds of ILs at the concentration of 0.5 M. The intensity distribution graphs of PNIPAM-co-AA hydrogel in water at higher concentrations (1 and 1.5 M) of ILs have been shown in supporting information (Fig. S1 and S2). As shown in Fig. 4, the PNIPAM-co-AA hydrogel shows intensity peak corresponding to the higher d_H values in pure water. These higher d_H values symbolize that the PNIPAM-co-AA hydrogel is in swollen form and there is no aggregation of polymer chain. Further, there is no noticeable change in hydrodynamic diameter (d_H) of PNIPAM-co-AA hydrogel in water with the addition of [Bmim][I], [Bmim][BF_4] and [Bmim][Cl] ILs. This reflects that these ILs act as constructers for the hydration layer around the polymer and thereby induce the further swelling of polymer. On the other hand, addition of [Bmim][Ac] and [Bmim][HSO_4] to the PNIPAM-co-AA hydrogel in water, brings the PNIPAM-co-AA hydrogel into shrunken state and thereby, obviously leads to the lower d_H values as shown in the Fig. 4. With the addition of ILs with kosmotropes to PNIPAM-co-AA hydrogel in water, all the water molecules, that surrounded the amide groups of polymer, are pulled by the anions of ILs. Because of this effect, inter- and intra- molecular hydrogen bonds among the amide groups on the PNIPAM-co-AA hydrogel become dominate and thereby PNIPAM-co-AA hydrogel becomes shrunken. Moreover, ILs with kosmotropic anions increase the hydrophobic collapse of PNIPAM-co-AA hydrogel and help for the shrinking of polymer. This hydrophobic collapse is more pronounced at higher concentration of kosmotropic anions. This phenomenon is further evidenced from the optical image (Fig. 3), where PNIPAM-co-AA hydrogel completely aggregated in the presence of 1.5 M of [Bmim][HSO_4]. These large aggregates can be attributed to the observed high d_H values as shown in Fig. S2 (Supporting Information). With this inference, one can conclude that the ILs, [Bmim][Ac] and [Bmim][HSO_4] act as “destroyers” for the hydration layer around the PNIPAM-co-AA hydrogel. These findings are strongly consisting with our DSC results.

Now turning to the CA measurements analysis, surfaces grafted with thermoresponsive polymers, such as PNIPAM based and elastin-like polypeptides (ELPs) are known to reversibly switch between hydrophilic and hydrophobic states in response to external changes.[4,34-38] CA measurements are known to play vital role to elucidate the behavior of polymer surface in response to external stimuli.[4,38] By keeping these advantage in mind, in our present study we have performed the CA measurements by applying the aqueous solutions of ILs, at 1.5 M concentration, on flat surface of dried PNIPAM-co-AA hydrogel. However, it was not possible to measure the CA at lower concentrations of IL, as aqueous solutions of ILs would penetrate through the dry hydrogel. The modulations in wettability of dried PNIPAM-co-AA hydrogel in response to IL type are elucidated in Fig. 5, in terms of CA. As shown in Fig. 5, the contact angles varies from 52° (in the presence of water) to 32° (in the presence of [Bmim][I]) and 67°, 77°, 87° and 98° (in the presence of [Bmim][BF_4], [Bmim][Cl], [Bmim][Ac], and [Bmim][HSO_4], respectively). This indicates that the surface of dried PNIPAM-co-AA hydrogel behaves reversibly either hydrophilic or hydrophobic depending on the identity of the IL in the water. Further, these changes in CA can be understood from the “salting in” and “salting out” in the presence of ILs. As [Bmim][I] is known for salting in behavior, the surface of PNIPAM-co-AA hydrogel can act as a hydrophilic and thereby observed lower CA in the presence of [Bmim][I] (chaotropes). On the other hand, the surface of PNIPAM-co-AA hydrogel can act as a hydrophobic in the presence of [Bmim][HSO_4] (kasmotrope), as it is known for salting out mechanism. The extent of change in CA to aqueous IL is found to be consistent with the Hofmeister series and with associated changes in surface roughness which result from varying degrees of polymer swelling in response to solute ion identity. The present results are corroborating with the existing results,[38] where the CA values were altered at the interface of PNIPAM graft on a PEI modified PE films by the addition of aqueous solution of sodium salts.

. To probe the molecular-level mechanism, for changes in the VPTT of PNIPAM-co-AA hydrogel in water in the presence of ILs that were observed in DSC experiment, FTIR spectroscopy experiments were conducted at a constant temperature of 25 °C (room temperature), which is well below to the VPTT of the PNIPAM-co-AA hydrogel. Since the FTIR measurements were performed well below to the VPTT value, the role of ILs on the swelling and shrinking behavior of PNIPAM-co-AA hydrogel in water can be understood more accurately. In the present study the spectral region in 1674–1572 cm^{-1} was mainly considered to probe the molecular-level mechanism behind the volume phase transition of PNIPAM-co-AA hydrogel in water in the presence of ILs. Such amide bands in 1674–1572 cm^{-1} can provide valuable insight for the molecular mechanism of swelling and shrinking behavior of PNIPAM-co-AA hydrogel in water.[8]

As shown in Fig. 6, the wavenumber of the amide group of NIPAM in PNIPAM-co-AA hydrogel experiences a blue shift with addition of ILs with Kosmotropic anions. The blue shift in amide region is indicative for the transformation of well hydrated amide groups to dehydrate. Similar type of blue shift was observed, when the PNIPAM based polymers heated to above their phase transition temperature due to dehydration of amide group.[39-41] As the current FTIR study performed at room temperature, instead of at various temperatures, the blue shift in amide region is due to dehydration that is triggered by the presence of IL with kosmotrope anions. The intensity of the amide band decreases with the addition of ILs with kosmotrope anions. The shift in an amide region towards higher frequency is further intensified with higher concentration (1M) of IL with kosmotrope anions as shown in supporting information (Fig. S3). However, it was not possible to measure the FTIR spectra at higher concentration (1.5 M) of ILs as PNIPAM-co-AA hydrogel turned into large aggregates as shown in Fig. 3 and thereby, we have not performed FTIR at higher concentration of ILs. In contrast to this, there is no shift in amide region in the presence of ILs with chaotropes anions, and symbolizes that the hydration layer of amide groups is well protected in the presence ILs with chaotropes and thereby there is no shift in the wavenumber of amide region. The spectral intensity increase and decrease in the presence of chaotropes and kosmotropes, respectively, can be attributed to the hydrated (or) swollen and dehydrated (or) shrunken states of PNIPAM-co-AA hydrogel, respectively. As shown in Fig. 6, the broad band in the range 1900 to 2400 cm^{-1} was attributed to the water.[42]

Conclusions

The volume phase transition of a PNIPAM-co-AA hydrogel in water was greatly influenced by the addition of different kinds of ILs. The sophisticated DSC, DLS, FTIR and CA measurements results unveil that the ILs with kosmotropic anions such as CH_3COO^- and HSO_4^- greatly depress the VPTT of PNIPAM-co-AA hydrogel, while reverse was true in the presence of ILs with chaotropic anions. The decrease in VPTT of PNIPAM-co-AA hydrogel in water in the presence of ILs with kosmotropes was mainly due to the "*salting out*" of polymer, which was attributed to the water structuring ability of kosmotropes. The water structuring ability of kosmotropes can be understand from the shift in FTIR amide bands towards higher wavenmuber due to the dehydration of polymer which was triggered by the kosmotropes. On the other hand, the elevation of VPTT of PNIPAM-co-AA hydrogel in water in the presence of ILs with chaotropes was mainly due to the "*salting in*" behavior of polymer, which was attributed from the water breaking ability of chaotropes. However, the IL with BF_4^- shows anomalous behavior on volume phase transition of PNIPAM-co-AA hydrogel in water. Being a chaotrope at lower concentrations, [Bmim][BF_4] elevates the VPTT of PNIPAM-co-AA hydrogel in water, while depress that of PNIPAM-co-AA hydrogel at higher concentration acting as a kosmotrope. This abnormal behavior attributed from the availability of binding sites on the PNIPAM-co-AA hydrogel. There are enough binding sites on PNIPAM-co-AA hydrogel for tetrafluoroborate anion at lower concentration, while the binding sites on PNIPAM-co-AA hydrogel become less at higher concentration and thereby surface tension effect come into play and finally leads to the hydrophobic collapse of PNIPAM-co-AA hydrogel. One should not ignore the role of cation, 1-butyl-3-methyl-imidazolium on phase transition of PNIPAM-co-AA hydrogel and currently these studies are under progress in our laboratory. In the creation of new materials, sensor devices, and novel self-assembled structures of polymers by applying the ILs, the knowledge from the current study may certainly helpful.

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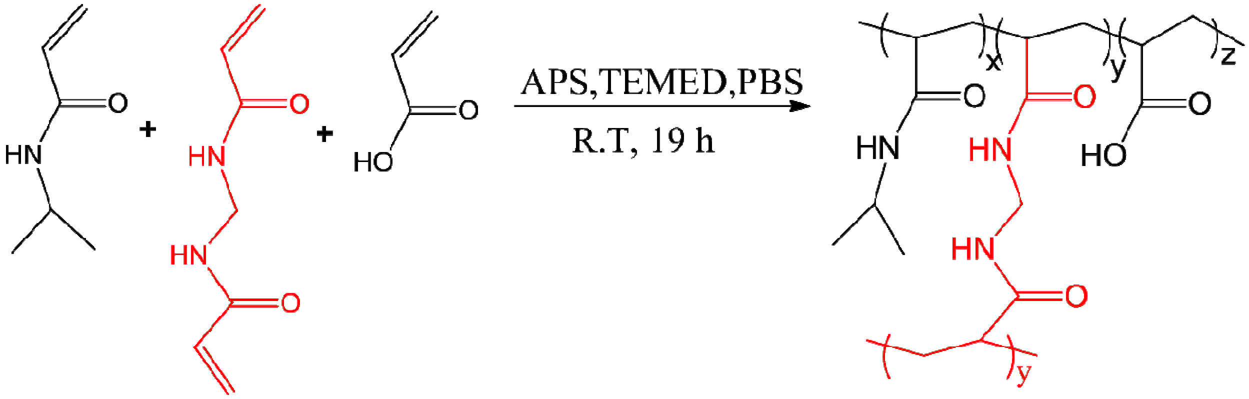
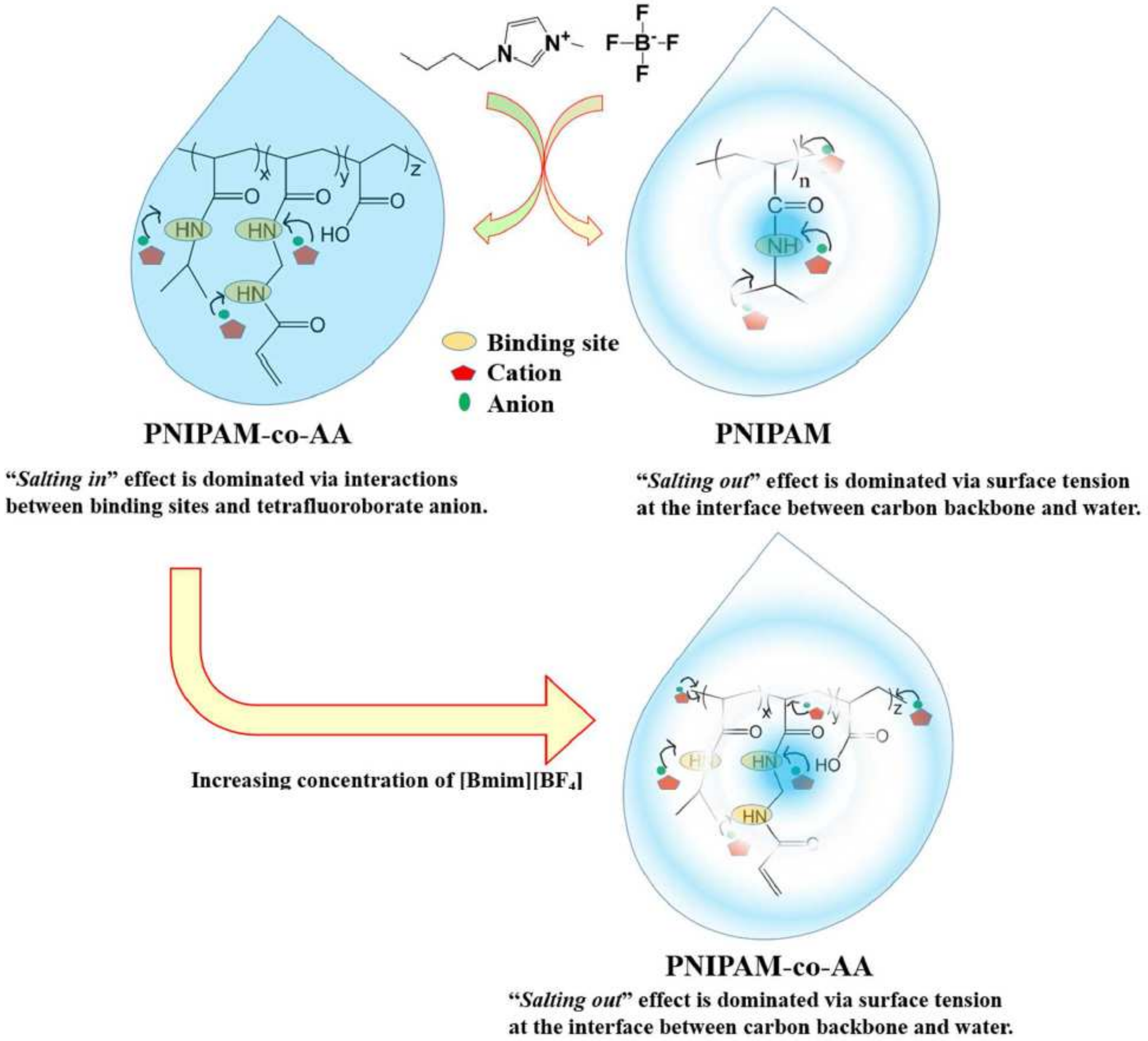


Scheme 1. Synthetic route for PNIPAM-co-AA hydrogel.



Scheme 2. Schematic illustration of effect of [Bmim][BF$_4$] on the phase transition of PNIPAM and PNIPAM-co-AA hydrogel.

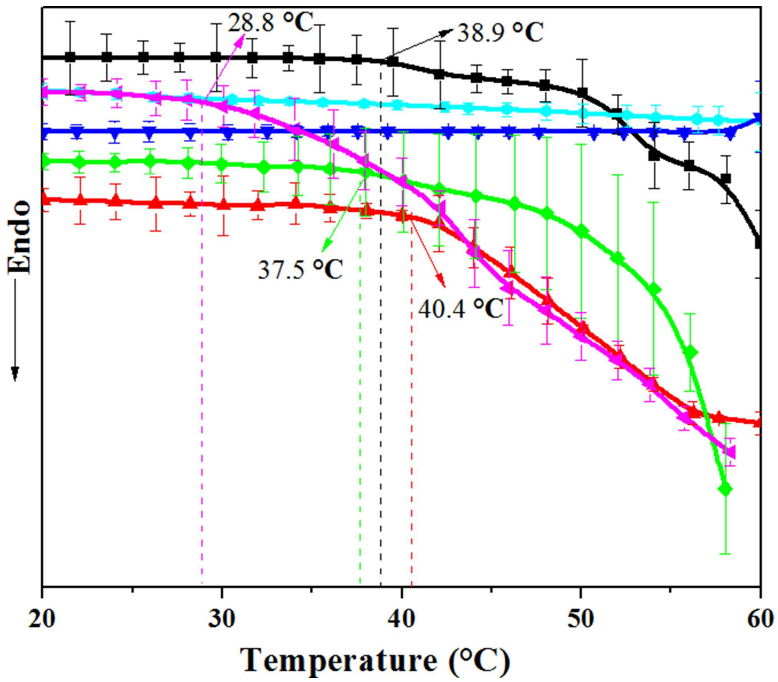


Fig. 1 DSC curves of PNIPAM-co-AA hydrogel (black color line) recorded in the presence of different kinds of ILs, [Bmim][I] (cyan color line), [Bmim][BF$_4$] (red color line), [Bmim][Cl] (blue color line), [Bmim][Ac] (green color line) and [Bmim][HSO$_4$] (magenta color line) at concentration of 0.5 M.

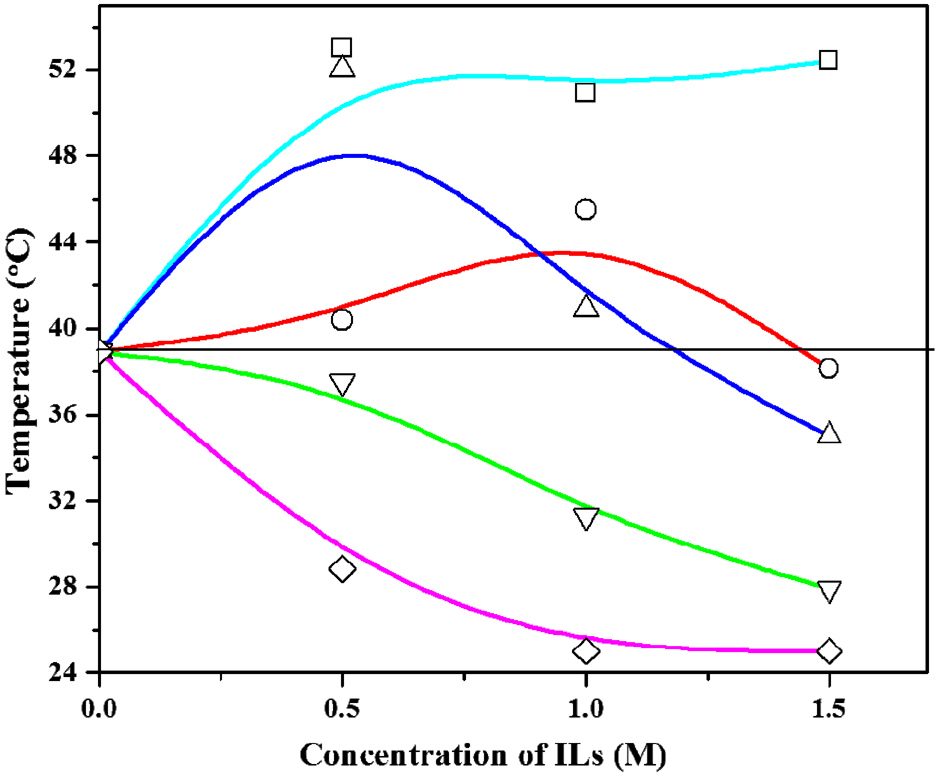


Fig. 2 VPTT values of 1 wt% PNIPAM-co-AA hydrogel in water in the presence of different ILs at different concentrations. [Bmim][I] (□, cyan color line), [Bmim][BF_4] (o, red color line), [Bmim][Cl] (Δ, blue color line), [Bmim][Ac] (∇, green color line) and [Bmim][HSO_4] (◊, magenta color line).

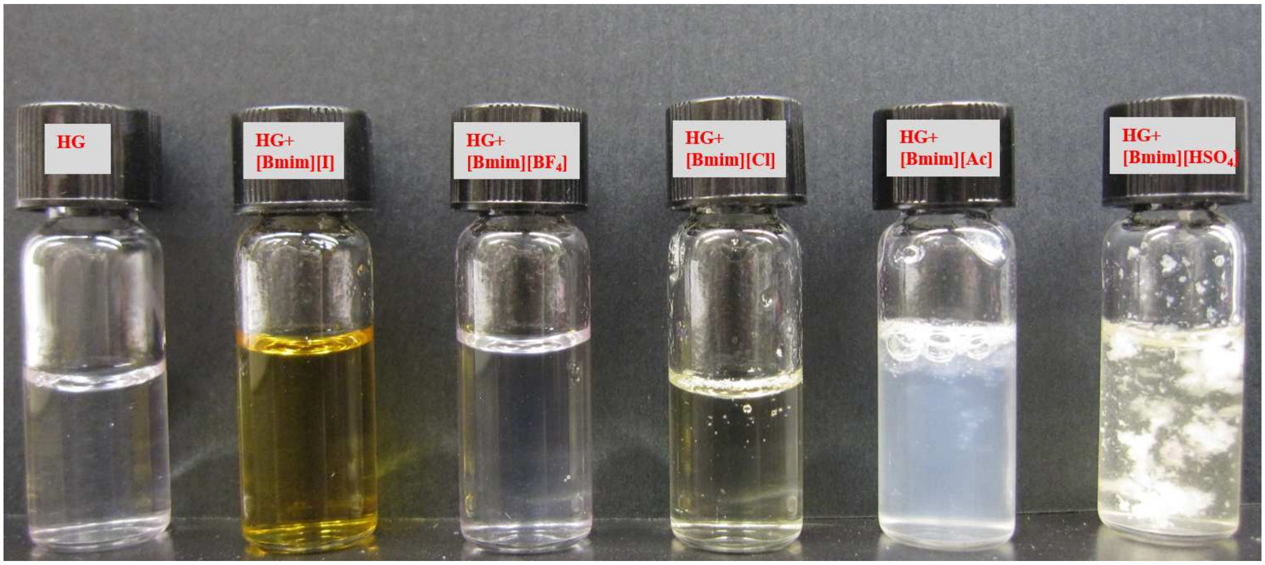


Fig. 3 Optical image for 1 wt% PNIPAM-co-AA hydrogel in water in the presence of different kinds of ILs at the concentration of 1.5 M.

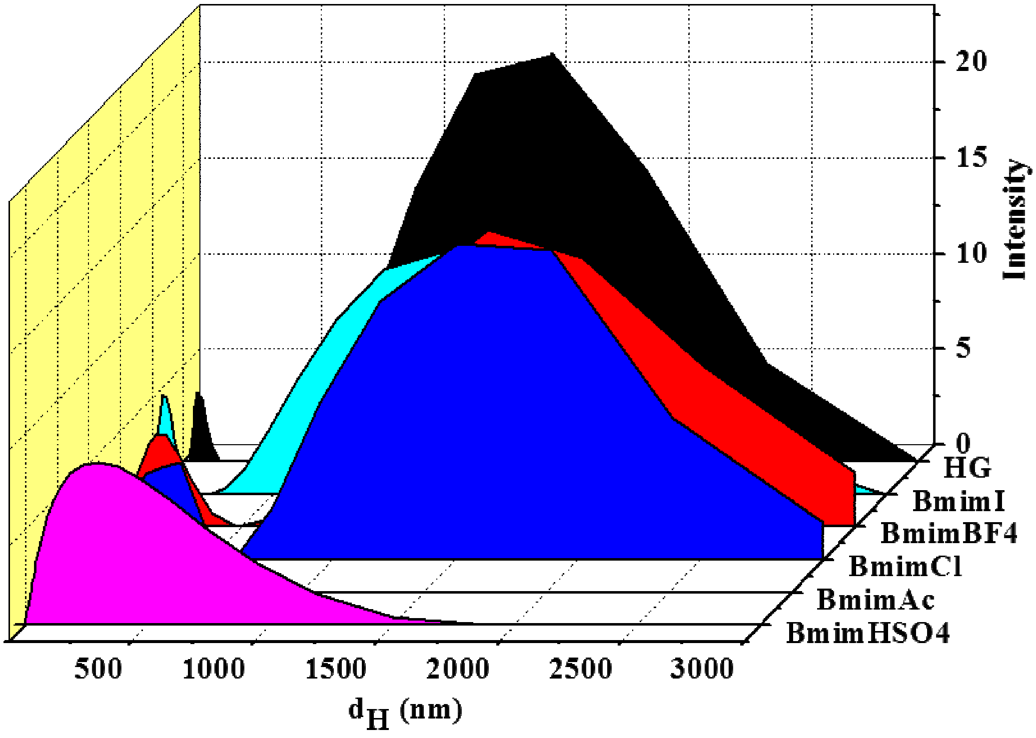


Fig. 4 PNIPAM-co-AA hydrogel (1 wt%) size distribution in the presence of different ILs at the concentration of 0.5 M.

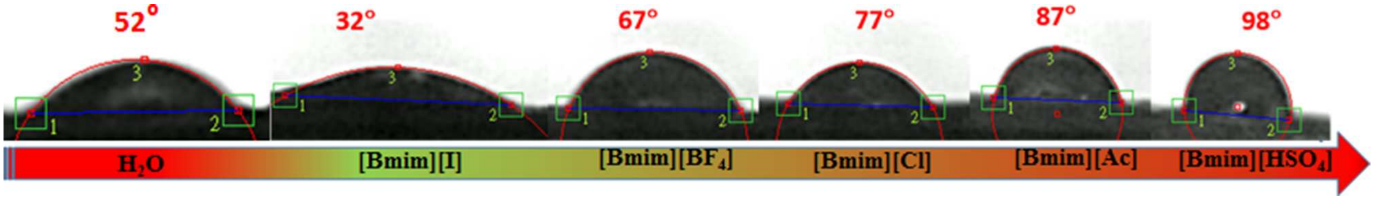


Fig. 5 Contact angles for aqueous solutions of different ILs on the flat surface of dry PNIPAM-co-AA hydrogel. The concentration of ILs is 1.5 M.

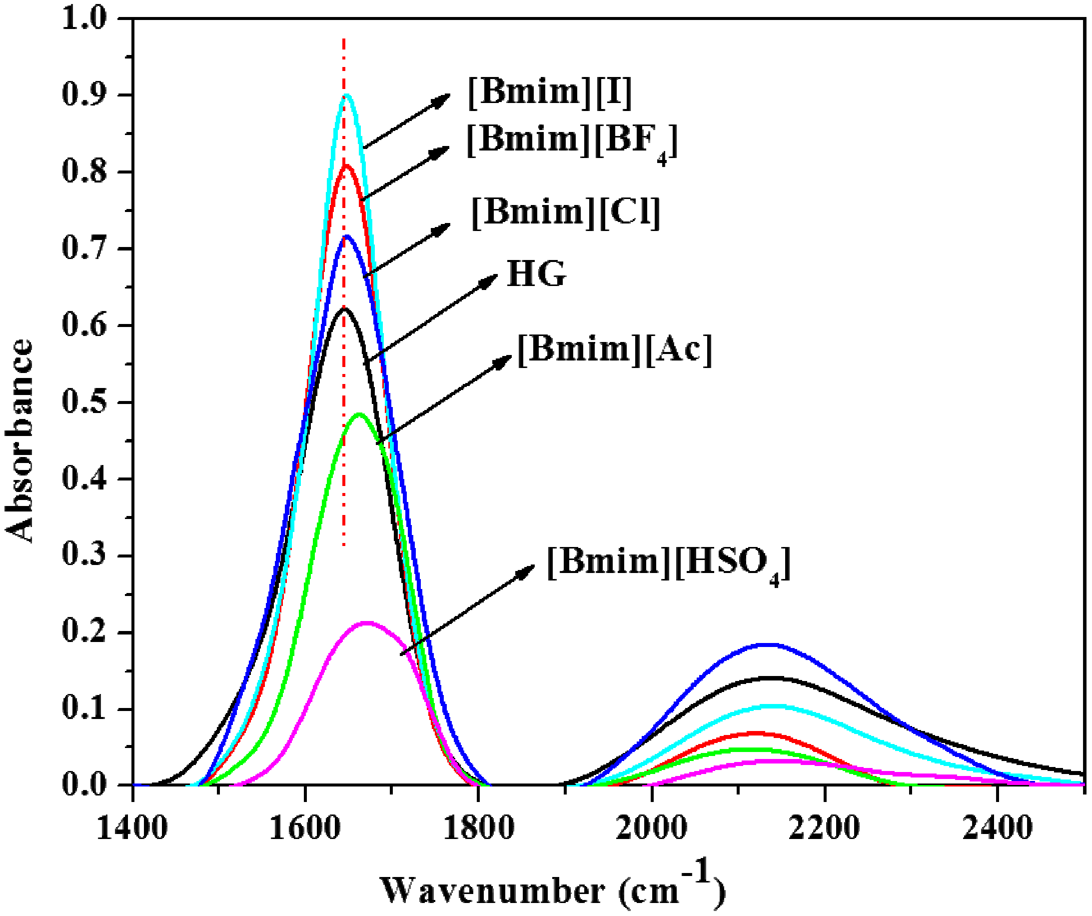


Fig. 6 FT-IR spectra for the PNIPAM-co-AA hydrogel (1 wt%) in the absence and presence of different kinds of ILs at room temperature. The concentration of ILs is 0.5 M.

Table 1 VPTT values of PNIPAM-co-AA hydrogel, in the presence of different kinds of ILs at different concentrations, were obtained from the DSC thermograms.

Type of IL	VPTT **(°C)**		
	0.5 M	**1 M**	**1.5 M**
[Bmim][I]	No phase transition	49.0	51.4
[Bmim][BF_4]	40.4	45.5	38.1
[Bmim][Cl]	No phase transition	40.9	35.0
[Bmim][Ac]	37.5	31.3	27.9
[Bmim][HSO_4]	28.8	25.0	25.0

Table of content (TOC)

Influence of imidazolium based green solvents on volume phase transition temperature of crosslinked poly(N-isopropylacrylamide-co-acrylic acid) hydrogel

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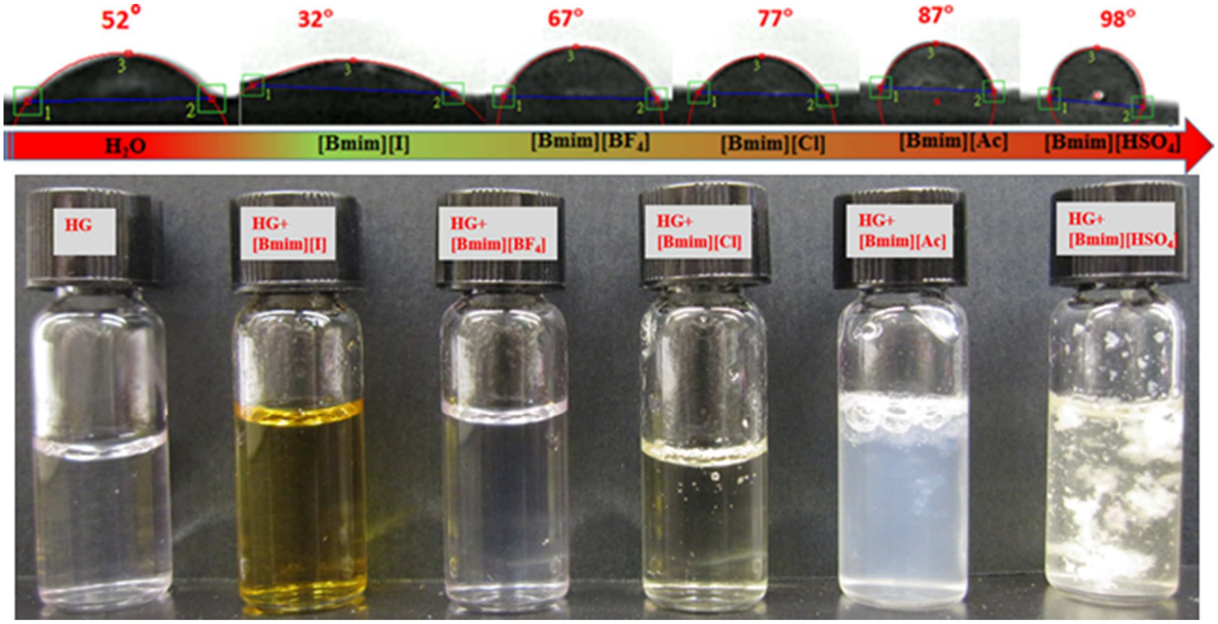

Ionic liquids, known as green solvents, can be used effectively to obtain the desired phase transition temperature for a given stimuli responsive polymeric material.