

Review

Stimuli responsive ion gels based on polysaccharides and other polymers prepared using ionic liquids and deep eutectic solvents



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ABSTRACT

Ion gels and self-healing gels prepared using ionic liquids (ILs) and deep eutectic solvents (DESs) have been largely investigated in the past years due to their remarkable applications in different research areas. Herewith we provide an overview on the ILs and DESs used for the preparation of ion gels, highlight the preparation and physicochemical characteristics of stimuli responsive gel materials based on co-polymers and biopolymers, with special emphasis on polysaccharides and discuss their applications. Overall, this review summarizes the fundamentals and advances in ion gels with switchable properties prepared using ILs or DESs, as well as their potential applications in electrochemistry, in sensing devices and as drug delivery vehicles.

1. Introduction

Stimuli-responsive polymeric materials, especially gel like materials, are receiving considerable attention from the scientific community due to their potential applications for drug delivery, as biosensors, shape memory materials, coating and textiles (Stuart et al., 2010; Yang and Urban, 2013). Almost all polymeric gels, irrespective of their synthetic or bio-based origin, show both liquid like flow and elastic behaviour. These characteristics make them good candidates for the fabrication of functional materials. Self-repairing is one of the most important functionalities of gelling materials, being investigated by many researchers. Among the numerous approaches to introduce the self-repairing ability in gels, one of the most popular is based on the addition of cross-linkers (Urban, 2012). There are several reports of self-healing polymeric gel systems fabricated mainly by cross-linking with groups containing the $-NH-CO-$ moiety capable of forming reversible covalent bonds (Hager, Greil, Leyens, van der Zwaag, & Schubert, 2010; Kushner, Vossler, Williams, & Guan, 2009; Phadke et al., 2012). The formation of these self-healing materials involves the sharing of electrons among the host and the guest molecules leading to the formation of covalent bonds. However, in biological living systems, reversible noncovalent molecular interactions play an important role, for instance in the replication of DNA, in the folding of

proteins into intricate three-dimensional forms, and in the detection of molecular signals (Berg, Tymoczko, & Stryer, 2002).

The design of stimuli responsive-healing polymeric systems involves the encapsulation of effective healing agents in desired polymeric systems followed by activation employing external stimuli, such as heating, which is a popular way to regain the structural integrity in structurally damaged polymers (Cho, Kim, Oh, & Chung, 2010). After heating, the healing agent moves to the damaged part and promotes the self-healing by initiating suitable polymeric entanglements. In such physically induced healing processes, heating promotes the movement of polymeric chains and diffusion. In such cases the polymeric material is usually heated above its glass transition temperature (T_g) (Prager et al., 1981). The heating above T_g promotes surface rearrangement, followed by wetting, diffusion and re-entanglement of the polymer chains (Kim & Wool, 1983).

Smart polymeric materials are materials that are responsive to different stimuli, such as pH, temperature, light, solvent, magnetic field, redox and mechanical stress. Such materials have potential interest for various fields of applications (Klaikherd, Nagamani, & Thayumanavan, 2009; Balu et al., 2014; Zhuang, Gordon, Ventura, Li, & Thayumanavan, 2013), such as in drug delivery (Li et al., 2014; Liu, Zhou, Guan, Su, & Dong, 2014; Lee, Lee, & Park, 2014), imaging (Sundaresan, Menon, Rahimi, Nguyen, & Wadajkar, 2014), catalysis (Deng et al.,

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2014), coatings (Zhao et al., 2014), and sensors (Kavanagh, Byrne, Diamond, & Fraser, 2012; Zhang, Jin, Zheng, & Duan, 2014; Li, Xiao, Lin, & Wang, 2012; Yan et al., 2012). Several authors have reviewed stimuli responsive polymeric gels functionalized with metals (Weng, Fang, Zhang, Peng, & Lin, 2013), carbon nanotubes, graphene and multi-responsive complexes (Tang, Kang, Wei, Guo, & Zhang, 2013).

In recent years, ionic liquids (ILs) emerged as unique platforms for materials design (Noro, Matsushita, & Lodge, 2008; Smiglak et al., 2014) and as suitable solvent media for the dissolution of several polysaccharides, including cellulose, starch, chitin and DNA (Swatloski, Spear, Holbrey, & Rogers, 2002; Isik, Gracia et al., 2014; Isik, Sardon, & Mecerreyes, 2014; Payal, Bejagam, Mondal, & Balasubramanian, 2015; Wilpiszewska & Szychaj 2011; Prasad, Izawa, Kaneko, & Kadokawa, 2009; Prasad, Murakami et al., 2009; Mondal, Sharma, Mukesh, Gupta, & Prasad, 2013; Sharma, Mondal, Mukesh, & Prasad, 2013a; Sharma, Mondal, Mukesh, & Prasad, 2013b). Among these, DNA draws special attention due to its molecular recognition, biocompatibility, biodegradability and mechanical flexibility features, making it suitable for the design of functional materials useful in molecular sensing in the form of DNA nanomachines and intelligent drug delivery and programmable chemical syntheses (Bath & Turberfield, 2007). DNA based hybrid materials and hydrogels were proposed for applications in targeted drug delivery, tissue engineering bioanalysis, biomedicine and as stimuli-responsive materials (Lee et al., 2012; Um et al., 2006; Peng et al., 2013). Further, due to the responsiveness of DNA towards pH and salt addition, it is also considered as a suitable precursor for designing bio-artificial muscles (Costa, Miguel, & Lindman, 2007; Besteman, Eijk, & van Lemay, 2007). However, from the DNA based ion gel point of view, there is only one report on the preparation of gelatin and DNA based gel polymer electrolytes by treating them with acetic acid and LiClO₄, leading to the formation of ion gels with high ionic conductivity (Pawlicka et al., 2009). There are also limited reports on the preparation of ion gels by the combination of DNA and ionic liquids (ILs) or deep eutectic solvents (DESs). However, ILs are extensively used as suitable substrates for the preparation of other ion gels (Isik, Gracia et al., 2014; Isik, Sardon et al., 2014; Seki et al., 2005; Ueki and Watanabe, 2008).

The preparation of thermo-responsive synthetic polymers, such as polymethyl methacrylates and poly (*N*-isopropylacrylamide) in [C₂mim][N(Tf₂)] (Fig. 1) was first described by Ueki in 2014. Multi stimuli responsive polymers with switchable wettability functionalized with imidazolium based ILs were synthesised and proposed by Döbbelin et al. in 2009. Apart from the preparation of stimuli-responsive materials comprising polymers in ILs, polymerizable ILs (PILs) were also proposed as suitable substrates for the preparation of functional stimuli-responsive materials and ion gels suitable for gas separations (Cowan, Gin, & Noble, 2016; Kausar, 2017). Well-defined triblock copolymers, namely polystyrene-block-poly(methyl methacrylate)-block-polystyrene (SMS), were used to prepare viscoelastic ion gel with [C₂mim][N(Tf₂)] (Fig. 1) with tetrahydrofuran, displaying high ionic conductivity (Imaizumi, Kokubo, & Watanabe, 2012).

Up to date the research on functional materials has mainly focused on synthetic thermosetting, thermoplastic and elastomeric polymers based on reversible Diels-Alder reactions. Very less attention has however been given to the preparation of “smart” materials based on renewable/natural polymers, which are of particular significance in line with the principles of ‘green chemistry’ and sustainability (Höfer & Bigorra, 2008).

An overview of the current smart ion gels materials prepared using co-polymers, biopolymers or polysaccharides and ILs or DES, as well as their potential applications, are described and discussed below. The following section is presented according to the response of the ion gels to external stimuli, namely pH, heat, light and magnetism. The chemical structure of different ILs, DESs, and polymers, copolymers,

biopolymers and polysaccharides investigated for the preparation of such materials are shown in Figs. 1 and 2.

2. pH-responsive ion gels

pH or proton (H⁺) responsive ion gels show different behaviour upon changes in the pH of the system (Noro et al., 2008; Mukesh, Bhatt, & Prasad, 2014; Hashimoto, Fujii, Nishi, Sakai, & Shibayama, 2016; Xie, Huang, & Taubert, 2014). Towards the development of such ion gels, Xie et al. (2014) have reported dye-IL based proton responsive transparent, ion-conducting, and flexible ion gels, which exhibit reversible colour change depending on the concentration of protons or hydroxide ions. Researchers first prepared the imidazolium based IL having methyl orange [C₄mim][MO] as counter ion (Fig. 1A), followed by the addition of poly(methylmethacrylate) (PMMA) and another IL, namely [C₄mim][N(Tf₂)] (Fig. 1A), in the presence of acetone. Uniformity and absence of defects in the ion gels were confirmed by scanning electron microscopy (SEM), FT-IR spectroscopy and thermo gravimetric (TGA) studies. Moreover, no significant shifts in FT-IR bands after the IL incorporation were observed, indicating that the interactions between the IL and PMMA are weak and may led to the IL leaching from the gel matrix. Recently, Hashimoto et al. (2016) have disclosed the preparation of tetra-armed polyethylene glycol based ion gels with high-toughness using imidazolium based aprotic ILs ([C₂mim][N(Tf₂))] with buffering properties (Hashimoto et al., 2016). The authors showed that by controlling the pH, the properties of the ion gel can be manipulated. An ideal and homogenous polymer network was formed when pH was controlled by adding aprotic ILs with buffering characteristics, whereas the ion gel system without buffering ILs showed discrete polymer network with irregular cross-linking (Hashimoto et al., 2016).

In order to fulfil the requirements of biomedical applications, efforts have been made on the development of new stimuli-responsive materials using biodegradable and biocompatible molecules. Chitosan is considered as one of the most widely explored polysaccharide for a wide number of applications (Roy, Cambre, & Sumerlin, 2010; Stuart et al., 2010). In order to prepare a suitable pH and electric responsive material for drug delivery applications, chitosan films loaded with ILs or salts, such as choline chloride and choline dihydrogenphosphate, and dexamethasone sodium phosphate, an anticancer drug, were prepared, followed by studies on the drug release kinetics at different pH values (Dias et al., 2013). The drug release kinetics showed that the release of dexamethasone sodium phosphate does not occur by simple diffusion or swelling; it is instead controlled by the interactions occurring between the chitosan film, dexamethasone sodium phosphate and choline dihydrogenphosphate (Fig. 3).

In a similar line of research, DESs were explored to synthesize self-polymerizable ion gels for pH responsive drug release. In this work, self-polymerization of 2-hydroxyethylmethacrylate (HEMA) in a DES, namely ChCl-Fruc 2:1 (Fig. 1B), in the presence of indomethacin (anti-inflammatory drug) led to the formation of a drug-immobilized nontoxic ion gel with hemocompatible features. The ion gel thus obtained showed a pH responsive release of indomethacin. Moreover, the drug immobilized in the gel matrices can be stored at room temperature for a long period (up to 6 months) without degradation (Mukesh, Upadhyay et al., 2016; Mukesh, Gupta et al., 2016). Self polymerization of HEMA in ChCl-Or 1:1.5 (Fig. 1B) resulting in the formation of highly stretchable ion gel with good capacitance behaviour was obtained (Mukesh, Upadhyay et al., 2016; Mukesh, Gupta et al., 2016). The use of DESs for the preparation of pH responsive DNA based ion gels was also explored by Mukesh & Prasad (2015). The formation of three different morphologies of DNA was observed in a DES composed of ChCl-EG 1:2, which is known to solubilize high concentrations of DNA (Mondal et al., 2013). In

(A)	Cations	Anions	Name	Abbreviation	Reference
			1-Ethyl-3-methylimidazolium bis (trifluoro methanesulphonyl)amide	[C ₂ mim][N(Tf ₂)]	Hashimoto et al., 2016 ; Imaizumi et al., 2012; Noro et al., 2008 ; Noro et al., 2013; Noro et al., 2014
			1-Ethylimidazolium ethyl sulphate	[C ₂ im][EtSO ₄]	Benito-Lopez et al., 2014
		Cl ⁻	1-butyl-3-methylimidazolium chloride	[C ₄ mim]Cl	Sharma et al., 2013 ; Sharma et al., 2014; Prasad et al., 2009
		CH ₃ COO ⁻	1-butyl-3-methylimidazolium acetate	[C ₄ mim]CH ₃ COO ⁻	Trivedi et al., 2015
			1-Butyl-3-methylimidazolium bis(trifluoro methanesulphonyl)amide	[C ₄ mim][N(Tf ₂)]	Xie et al., 2014
			1-Butyl-3-methylimidazolium Methylorange	[C ₄ mim][MO]	Xie et al., 2014
	R = H, CH ₃ ; R ₁ = CH ₃ CH ₂ ; CH ₃ CH ₂ CH ₂ CH ₂				
			Trihexyltetradecylphosphonium bis (trifluoro methanesulphonyl)amide	[P _{6,6,6,14}][N(Tf ₂)]	Benito-Lopez et al., 2010 ; Kavanagh et al., 2012
			Trihexyltetradecylphosphonium dicyanoamide	[P _{6,6,6,14}][dca]	Kavanagh et al., 2012
			Trihexyltetradecylphosphonium dodecyl benzene sulphonate	[P _{6,6,6,14}][dbsa]	Benito-Lopez et al., 2010 ; Kavanagh et al., 2012
			Choline Acrylate	[Ch][acrylate]	Mukesh et al., 2014
			1-Ethylamino-3-butyl-3-(triethoxysilyl) propyl isocyanate	[NH ₂ -C ₄ im]Br	Ru et al., 2013

Fig. 1. Chemical structure, abbreviation and references reporting on ionic liquids (A) and deep eutectic solvents (B) used to prepare ion gels.

(B)	Hydrogen Bond acceptors	Hydrogen Bond donors	Name	Abbreviation	Reference
			Choline Chloride : Ethylene glycol (1:2)	ChCl-EG 1:2	Mukesh et al., 2015
			Choline Chloride : Fructose (2:1)	ChCl-Fruc 2:1	Mukesh et al., 2016
			Choline Chloride : Orcinol (1: 1.5)	ChCl-Or 1:1.5	Mukesh et al., 2016

this work, DNA was converted into pH reversible ion gels, comprising aggregated DNA structures (pH 2.98), spheroid shaped DNA micro-structured assemblies, and pH responsive DNA micro-hydrogels (pH 7.30). The chemical and structural stability of DNA in all the formats

were confirmed. The micro-sized DNA assemblies as well the micro-hydrogels are useful for applications in targeted gene or drug delivery.

Besides the use of co-polymers for the preparation of pH responsive ion gels, recently, pH responsive polymerized bio-ionic liquid based

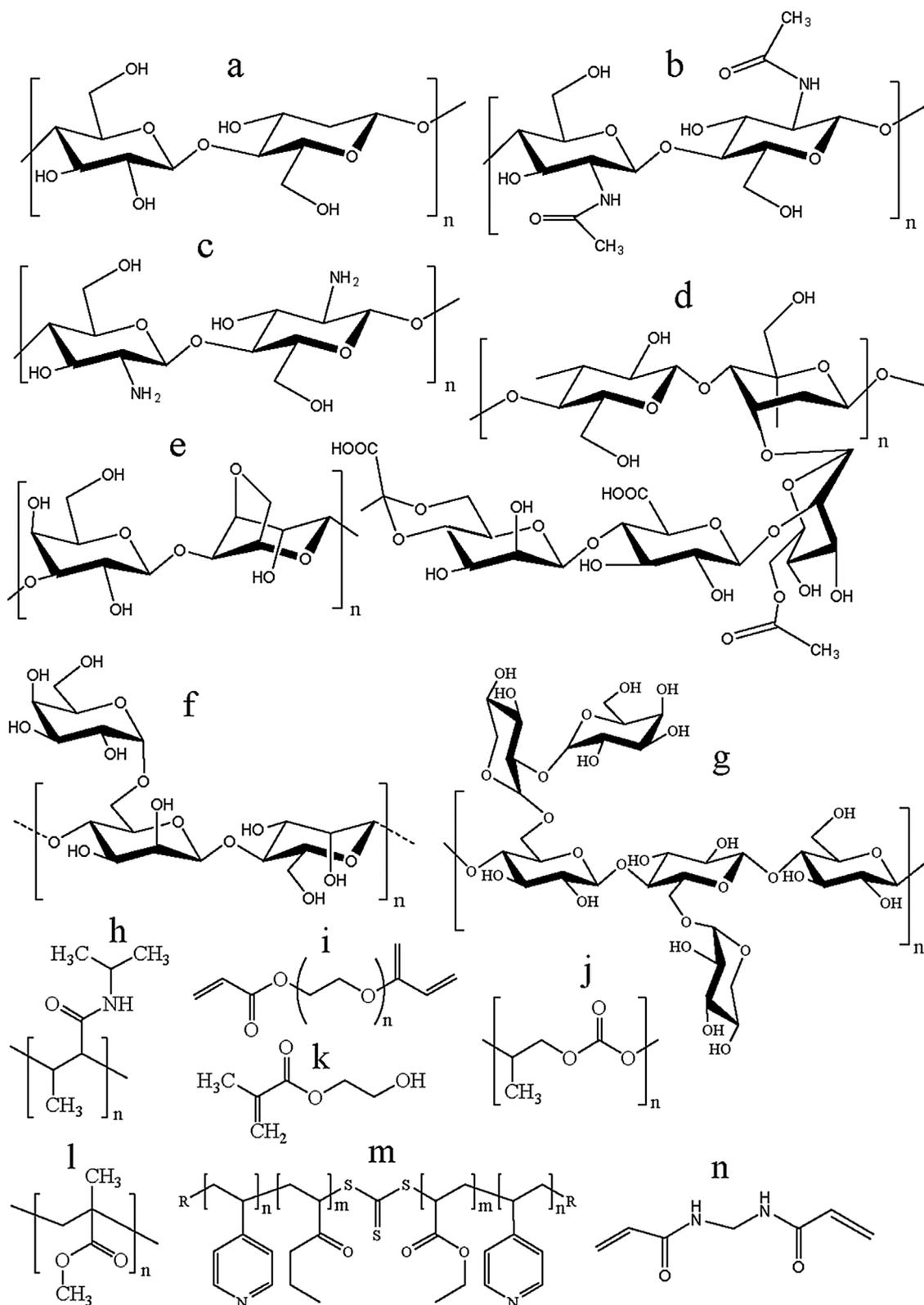


Fig. 2. Chemical structure of monomer units of polysaccharides and other polymers used for the preparation of stimuli responsive ion gels (a) cellulose (b) chitin (c) chitosan (d) xanthan gum (e) agarose (f) guar gum (g) tamarind gum (h) poly(N-isopropylacrylamide) (i) poly(ethylene glycol)diacrylate (j) poly(propylene carbonate) (k) (Hydroxyethyl)methacrylate, (l) poly(methylmethacrylate) (m) P4VP-PEA-P4VP triblock copolymer, and (n) N,N-bisacrylamide.

nanogel matrices were proposed for the delivery of an anticancer drug (Mukesh et al., 2014). pH-responsive nanogel systems with an average hydrodynamic size of 41 ± 15 nm were developed by the simultaneous polymerization and cross-linking of a polymerizable bio-based ionic liquid [Ch][acrylate] (Fig. 1A). The nanogel thus obtained showed

prolonged drug delivery (10 days) for an anticancer drug (5-fluorouracil) at pH 1.2 (stomach pH) at the physiological human body temperature (37 °C). Remarkably, no substantial drug delivery was observed at pH values of 5 and 7.4. The prolonged drug release profile makes the reported nanogel system a potential candidate as drug

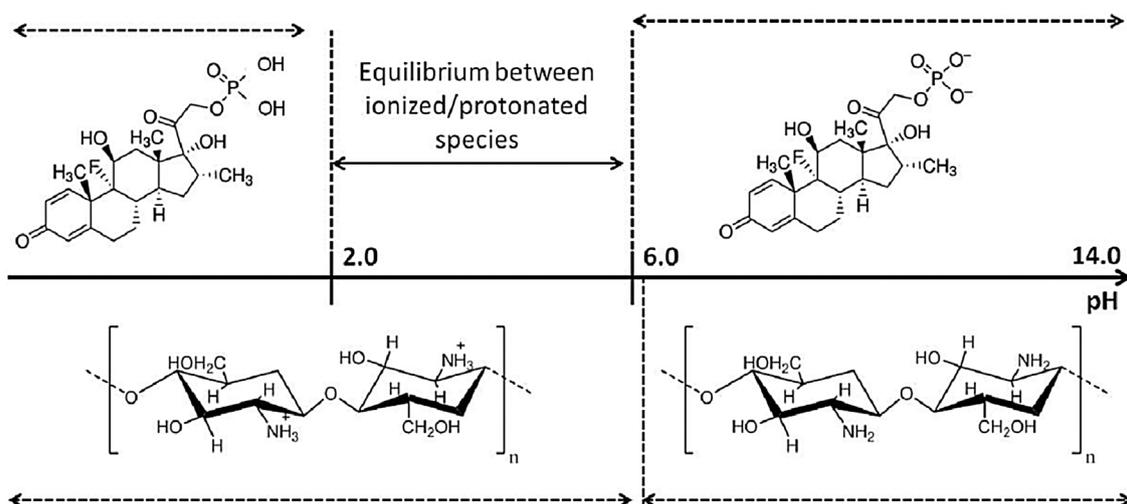


Fig. 3. Prevalence of ionic charges on chitosan and dexamethasone sodium phosphate according to the pH.

nanocarrier vehicles for the in vivo delivery of stomach specific therapeutic agents.

3. Thermo-responsive ion gels

Ion gels in which their properties can be tuned by temperature as external stimuli are known as thermo-responsive ion gels. Such ion gels have several potential applications, such as in reversible water uptake, actuators, optical sensors, and in flexible optical devices (Noro, Matsushima, He, Hayashi, & Matsushita, 2013; Noro et al., 2008; Benito-Lopez, Antonana-Diez, Curto, Diamond, & Castro-Lopez, 2014; Ru, Wang, Zhang, Yu, & Li, 2013; Mine, Prasad, Izawa, Sonoda, & Kadokawa, 2010).

Temperature responsive viscoelastic properties of supramacromolecular ion gels were prepared in an IL, $[C_2mim][N(Tf_2)]$ (Fig. 1A), via H-bonding between the end blocks of a triblock copolymer, namely poly(2-vinylpyridine)-*b*-poly(ethyl acrylate)-*b*-poly(2-vinylpyridine) (P2VP-PEA-P2VP) (Fig. 2), and a homopolymer (Noro et al., 2008). The prepared ion gel showed reversible gel like properties up to 141.5 °C; above this temperature it behaves like a viscous liquid. The authors have also showed that the relaxation time of the system increases by ~11 times on cooling from the gel point (141.5 °C) down to 30 °C. The IL was found to maintain good solvent conditions over a wide range of temperatures. Ru et al. (2013) have explored IL-modified alkoxyisilane based thermally reversible, flexible, and luminescent ion gels in presence of lanthanide ions (Eu^{3+} and Tb^{3+}). An amino-functionalized ionic liquid ($[NH_2-C_4im]Br$) (Fig. 1A) was used for the study. The thermal reversibility of the ion gels was tested by a heating-cooling process, whereas the material showed fluid nature at 60 °C, and upon cooling down to room temperature the ion gel property was restored and the process was shown to be repeatable for several times. Such thermo-responsive luminescent materials have potential application towards the development of flexible optical devices. Thermo-reversible supramolecular polymer ion gels were also prepared by Noro et al. (2013). The reported ion gels were prepared by mixing a poly(4-vinylpyridine)-*b*-poly(ethyl acrylate)-*b*-poly(4-vinylpyridine) (P4VP-PEA-P4VP), a triblock copolymer (Fig. 2) and zinc chloride in presence of the IL $[C_2mim][N(Tf_2)]$ (Fig. 1A). The authors have showed that the metal-ligand coordination between zinc and pyridine group in the presence of IL was the driving force towards the formation of gel as confirmed by FT-IR spectroscopy. Heating-cooling experiments showed that the material exhibited thermo-reversible viscoelastic properties between a gel-like state and a liquid-like state.

Benito-Lopez et al. (2014) explored a thermo-responsive ion gel with improved actuation behaviour in comparison to its hydrogel counterpart. This ion gel was prepared by encapsulating $[C_2mim]$

$[EtSO_4]$ into a cross-linked poly(*N*-isopropylacrylamide) matrix. The authors showed that the ion gel has temperature responsive reversible swelling and shrinking behaviours, whereas the corresponding hydrogel did not show any of such behaviours.

Apart from the use of polymers and copolymers of synthetic origin for designing thermo-reversible ion gels, ion gels based on biopolymers were also reported. Guar gum (GG) is a galactomannan extracted from the seeds of the leguminous shrub *Cyamopsis tetragonoloba*, and chemically made up of (1,4)-linked β -D-mannopyranose main chains with a branched α -D-galactopyranose unit at C-6 (Fig. 2). $[C_4mim]Cl$ (Fig. 1A) was used for the gelation of GG (15% w/w) by a heating-cooling process followed by protic solvent treatment to obtain hard gel materials. The obtained hard material was compressed (ca. 10 MPa) to get stable thin films. These films showed a fracture stress of 17 MPa with a fracture strain of 18.2% under tensile mode and became hard on heating, meaning that they could be arranged to a target shape at higher temperatures (Fig. 4). This high temperature shapeability was essentially due to the switching of crystalline GG at higher temperatures to amorphous GG at room temperature (Prasad, Izawa et al., 2009; Mine et al., 2010). The same ionic liquid, i.e. $[C_4mim]Cl$, was used to prepare functional ion gels of xanthan gum (Izawa and Kadokawa, 2010). The ion gels thus obtained showed good mechanical properties and thermally induced shape-memory effect. The specific association of the IL in the gels and interaction of the imidazolium cation with xanthan gum chains were suggested as the main reasons behind the production of such unique functional gels. Another IL, namely $[C_4mim]CH_3COO$ (Fig. 1), was used as solvent media to produce acetylated and carbanilated agarose, which was found to be thermoreversible. Furthermore, the researchers were able to prepare self-healing ion gels of agarose using mixture of ILs (Trivedi, Bhattacharjya, Yu, & Kumar, 2015).

4. Solvent-responsive ion gels

Guar gum (GG) ion gels and their nanocomposite gels incorporating multiwalled carbon nanotubes (MWCNT) with self and solvent responsive healing abilities were explored by our group (Sharma et al., 2013a, 2013b). In this work, ion gels in $[C_4mim]Cl$ were prepared in three different concentrations of GG (3, 5 and 10% w/v) by a heating-cooling process. The gels were bisected and kept one upon another or aligned horizontally with each other in close vicinity at room temperature (30 °C). It was observed that the ion gel with 10% w/v of GG was self-healed after 6 h of standing (Fig. 5A). Further, a composite gel was prepared in presence of 0.2% MWCNT with respect to $[C_4mim]Cl$, and the self-healing of the gel was observed after 5 h of standing at room temperature. The unified gel structure was bisected and kept one

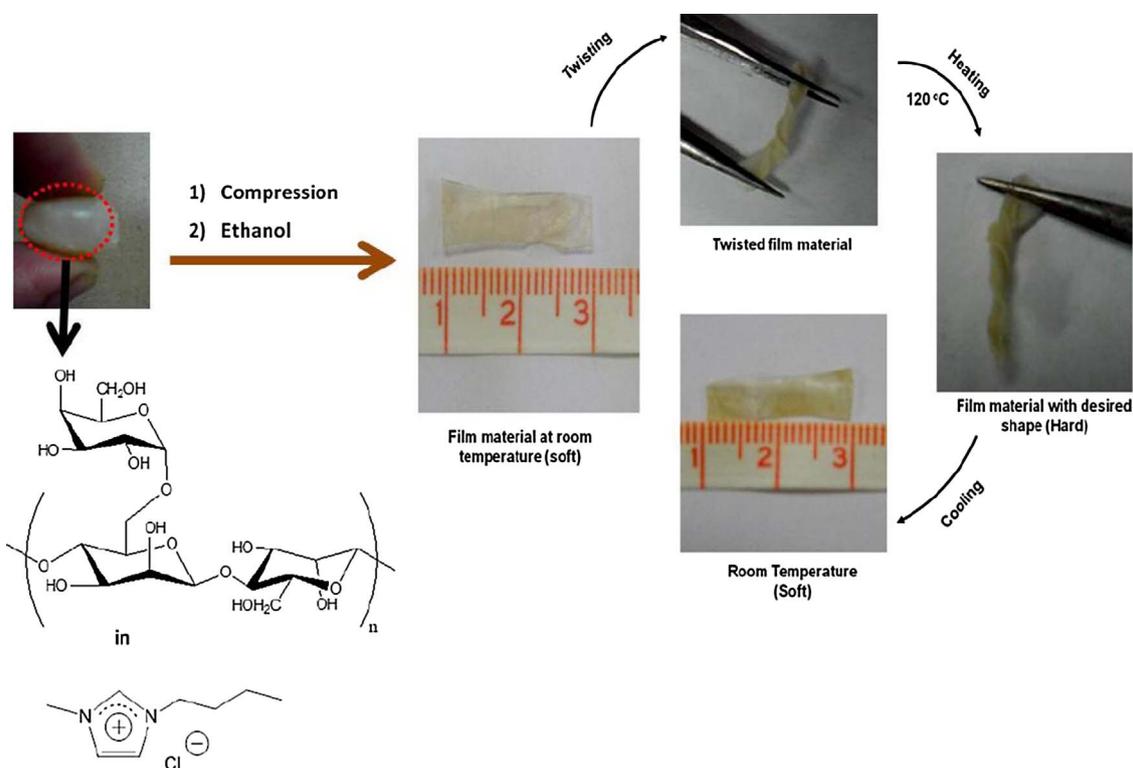


Fig. 4. Temperature induced shapeability in guar gum ion gel film.

upon another. The gel pieces self-healed and the process was repeated for 3 consecutive cycles. No more cycles were achieved, may be due to the loss of the IL mobility. [C₄mim]Cl was used with a dual functionality since it behaves as a solvent and as a junction promoter that ties guar gum chains leading to the formation of network structures similar to physical gels. These cross-linking structures are not regular but rather form extended junction zones due to cooperative effects. The three dimensional network upon application of mechanical strain (higher shear rate) was disturbed, but upon release of the force, reconstitution of the three dimensional structure took place responsible for the self-healing of the gels. The area of the hysteresis loop formed for the GG-[C₄mim]Cl gel was 2.33×10^5 Pa/s, which is lower than that of GG-[C₄mim]Cl/MWCNT (7.9×10^5 Pa/s), explaining the quicker response

of the later to mechanical strain towards self-healing. The area of the hysteresis loop after three consecutive cycles was almost the same, indicating the ability of the materials to self-heal after bisections for three times.

The prepared GG ion gels in [C₄mim]Cl were bisected and aligned horizontally with each other in close vicinity at room temperature, followed by placing the gel pieces in polar aprotic solvents, namely acetone, DMSO, DMF and acetonitrile. The ion gel with 10% w/v of GG healed after 1.5 h of exposure to acetone, DMSO and DMF (Fig. 5B); however, no healing was observed in acetonitrile. It should be noted that the ion gels of other polysaccharides, such as agarose, κ -carrageenan and xanthan gum did not show healing behaviour in these polar aprotic solvents. It was proposed that the branched

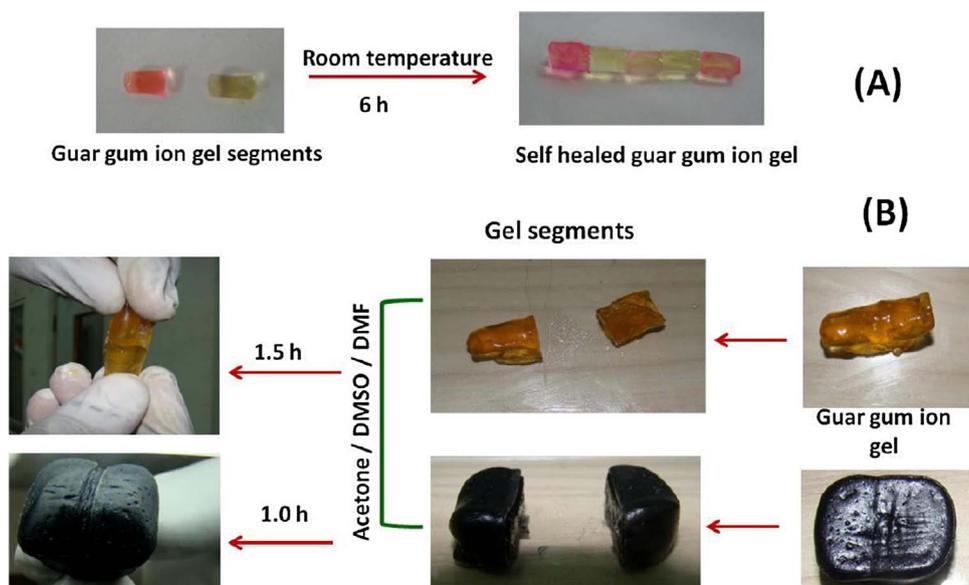


Fig. 5. Self and solvent responsive healing ability for guar gum ion gel. Reproduced with permission from the Royal Society of Chemistry.

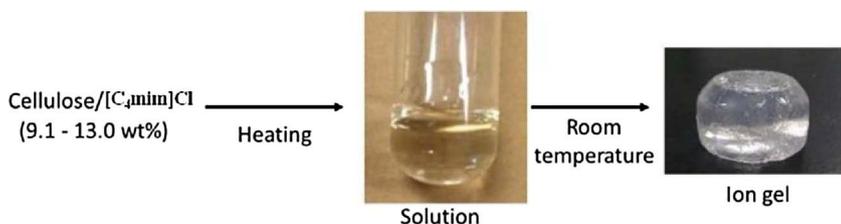


Fig. 6. Preparation of cellulose ion gel in [C₄mim]Cl. Reproduced with permission from authors.

galactopyranose unit of GG may play an important role in the healing process. All the other polysaccharides mentioned above are straight chain polysaccharides, with the exception of xanthan gum which consist of bulky side chain. The bulky side chain possibly did not favour the physical cross-linking required for gelation (xanthan gum side chain: C₂₄H₃₆O₁₈; GG side chain: C₆H₁₂O₆). On the other hand, the nano-composite ion gel prepared with MWCNT healed upon 1 h of exposure to the same aprotic solvents.

5. Shear-responsive ion gels

Shear responsive ion gels based on Tamarind gum and IL were reported by us (Sharma, Mondal, Mukesh, & Prasad, 2014). Tamarind gum (TG) is a natural polysaccharide, extracted from the endosperm of the seeds of *Tamarindus indica* Linn (Glicksman, 1986) (Fig. 2). Chemically TG is composed of β-(1,4)-D-glucan backbone substituted with side chains of α-(1,4)-D-xylopyranose and (1,6) linked [β-D-galactopyranosyl-(1,2)-α-D-xylopyranosyl] to glucose residues, where glucose, xylose, and galactose units are present in the ratio of 2.8: 2.25: 1.0 as the monomer units (Gidley et al., 1991). TG is widely used as a thickening, stabilizing, emulsifying and gelling agent in the food and pharmaceutical industries (Zhang, Zeng, Zhang, Wang, & Wang, 2006). Stable TG ion gel was obtained for 10% w/w TG in [C₄mim]Cl (Sharma et al., 2013a, 2013b).

In order to investigate the recovery of storage modulus (\dot{G}) of the ion gels upon relaxation, the gels were fractured employing high strain followed by relaxation. The ion gel prepared in [C₄mim]Cl was initially subjected to 1% strain at 1 Hz frequency for 300 s and \dot{G} and \dot{G} were monitored during the process and by fracturing the gels employing a high strain at 1 Hz for 100 s. The storage modulus for TG-[C₄mim]Cl gel recovered the original value upon relaxation. The cycle could be repeated for 10 consecutive times. On the other hand, the hydrogel did not show structure recovery upon relaxation indicating absence of thixotropic nature.

6. Magnet-responsive ion gels

Magnetically responsive ion gels have potential applications due to their inherent magnetic behaviour (Yuan, Venkatasubramanian, Hein, & Misra, 2008). In general, magnetic ion gel materials are prepared by the incorporation of magnetic substances onto to polymer matrix or use of magnetic ILs (Ziółkowski et al., 2012; Xie et al., 2010). Ziółkowski et al. (2012) reported the synthesis of magnetic ion gels using organosilane-coated iron oxide nanoparticles, N-isopropylacrylamide and a phosphonium-based IL. The authors showed that after modification of magnetic nanoparticles with silane, the ion gel became homogenous and also prevents the leaching of nanoparticles from the gel matrix. Furthermore, the IL imparted optimal mechanical strength and healing properties to the gel. Such magnetic ion gels with improved mechanical stability and flexibility respond differently to external permanent magnets and therefore have potential to be employed as soft magnetic actuators.

The same research group have also studied the suitability of an iron-containing magnetic IL, [C₄mim][FeCl₄], towards the formation of transparent, ion-conducting and paramagnetic ion gels by mixing it with suitable amounts of polymethyl methacrylate in acetone (Xie

et al., 2010). The authors have studied the structural changes of the IL by UV-vis spectroscopy upon incorporation into the polymer matrix and showed that the coordination around the Fe (III) ion slightly changed upon incorporation; nevertheless, the magnetic properties were similar to the pure IL. Such magnetic ion gels are exciting prototypes for flexible and mechanically stable materials for various applications.

In addition to the stimuli responsive ion gels discussed above, other functional ion gels based on polysaccharides were prepared by various researchers. Cellulose and [C₄mim]Cl are amongst the most studied polysaccharides and ILs respectively, to prepare ion gels. It was shown that high concentrations of the polysaccharide (15% w/w) in the IL can lead to the formation of a transparent ion gel upon standing (Kadokawa, Murakami, & Kaneko, 2008; Takada & Kadokawa, 2015) (Fig. 6).

The ion gels prepared using guar gum and [C₄mim]Cl or any polysaccharide based ion gels prepared using ILs have an inherent problem – the leaching of the IL from the polymer matrices. Zhang et al. (2017) have recently overcame this situation by preparing a self-standing stable guar gum film using [C₄mim]Cl and an imidazolium based polymerisable ionic liquid (PIL), namely poly-(1-[2-acryloyl-ethyl]-3-methylimidazolium bromide). The combination of GG and the PIL provided an excellent dimensional stability to the ion gels with no expulsion of the IL, even after long term standing. Such ions gels could also display high thermal stability and electric conductivity. PILs were also used to prepare chitin/cellulose thin films by solubilising a mixture of polysaccharides in [C₄mim]Cl, followed by the addition of PIL monomers. The free radical polymerization of the later resulted in the formation of thermally stable thin films (Setoyama, Kato, Yamamoto, & Kadokawa, 2013).

7. Conclusions and future prospects

In this review, stimuli responsive ion gels prepared using polymers, co-polymers, biopolymers and polysaccharides in ILs or DESs are overviewed and discussed, particularly ion gels responsive to external stimuli, such as pH, temperature, stress, magnetism and solvents, and self-healing gels. In most of the reported studies, ILs have been used as gelling media to provide high ionic conductivity and high temperature stability and flexibility. On the other hand, in spite of having promising features, less attention has been given to DESs for designing such functional ion gels. DESs are considered as more benign alternatives over ILs due to the possibility of their formation using bio-based starting materials. Due to the remarkable properties of ILs or DESs to prepare stimuli responsive ion gels, other and wider stimuli responsive properties, for instance multi-stimulus and bio-stimulus responsive, deserve to be investigated in the near future. The unique characteristics of the reported stimuli-responsive ions gels based on ILs or DESs make of them remarkable materials for applications in electrochemistry, in sensing devices and as drug delivery vehicles, for which deeper investigations on their potential applications and their scale-up still stand out as issues to accomplish.

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References

- Balu, R., Dutta, N. K., Choudhury, N. R., Elvin, C. M., Lyons, R. E., Knott, R., et al. (2014). An16-resilin: An advanced multi-stimuli-responsive resilin-mimetic protein polymer. *Acta Biomaterialia*, *10*, 4768–4777.
- Bath, J., & Turberfield, A. J. (2007). DNA nanomachines. *Nature Nanotechnology*, *2*, 275–284.
- Benito-Lopez, F., Antonana-Diez, M., Curto, V. F., Diamond, D., & Castro-Lopez, V. (2014). Modular microfluidic valve structures based on reversible thermoresponsive ionogel actuators. *Lab on a Chip*, *14*, 3530–3538.
- Berg, J. M., Tymoczko, J. L., & Stryer, L. (2002). *Chemical bonds in biochemistry* (5th ed.).
- Besteman, K., Eijk, K., & van Lemay, S. G. (2007). Charge inversion accompanies DNA condensation by multivalent ions. *Nature Physics*, *3*, 641–644.
- Cho, S.-Y., Kim, J.-G., Oh, S.-Y., & Chung, C.-M. (2010). Heat-induced crack healing in a perfluorocyclobutane-containing polymer. *Macromolecular Research*, *18*, 212–214.
- Costa, D., Miguel, M. G., & Lindman, B. (2007). Responsive polymer gels: Double-stranded versus single-stranded DNA. *Journal of Physical Chemistry B*, *111*, 10886–10896.
- Cowan, M. G., Gin, D. L., & Noble, R. D. (2016). Poly(ionic liquid)/ionic liquid ion-gels with high free ionic liquid content: platform membrane materials for CO₂/light gas separations. *Accounts in Chemical Research*, *49*, 724–732.
- Döbbelin, M., Tena-Zaera, R., Marcilla, R., Iturri, J., Moya, S., Pomposo, J. A., et al. (2009). Multiresponsive PEDOT-Ionic liquid materials for the design of surfaces with switchable wettability. *Advanced Functional Materials*, *19*, 3326–3333.
- Deng, J., Liu, X., Shi, W., Cheng, C., He, C., & Zhao, C. (2014). Light-triggered switching of reversible and alterable biofunctionality via β -cyclodextrin/azobenzene-based host–Guest interaction. *ACS Macro Letters*, *3*, 1130–1133.
- Dias, A. M. A., Cortez, A. R., Barsan, M. M., Santos, J. B., Brett, C. M. A., & De Sousa, H. C. (2013). Development of greener multi-responsive chitosan biomaterials doped with biocompatible ammonium ionic liquids. *ACS Sustainable Chemistry & Engineering*, *1*, 1480–1492.
- Gidley, M. J., Lillford, P. J., Rowlands, D. W., Lang, P., Dentini, M., & Crescenzi, V. (1991). Structure and solution properties of tamarind-seed polysaccharide. *Carbohydrate Research*, *214*, 299–314.
- Tamarind seed gum. In M. Glucksman (Vol. Ed.), *Food hydrocolloids: Vol. 3*, (pp. 191–202). Florida: CRC Press.
- Höfer, R., & Bigorra, J. (2008). Biomass-based green chemistry: Sustainable solutions for modern economies. *Green Chemistry Letters and Reviews*, *1*, 79–97.
- Hager, M. D., Greil, P., Leyens, C., van der Zwaag, S., & Schubert, U. S. (2010). Self-healing materials. *Advanced Materials*, *22*, 5424–5430.
- Hashimoto, K., Fujii, K., Nishi, K., Sakai, T., & Shibayama, M. (2016). Nearly ideal polymer network ion gel prepared in pH-buffering ionic liquid. *Macromolecules*, *49*, 344–352.
- Imazumi, S., Kokubo, H., & Watanabe, M. (2012). Polymer actuators using ion-gel electrolytes prepared by self-assembly of ABA-triblock copolymers. *Macromolecules*, *45*, 401–409.
- Isik, M., Gracia, R., Kollnus, L. C., Tome, L. C., Marrucho, I. M., & Mecerreyes, D. (2014). Cholinium lactate methacrylate: ionic liquid monomer for cellulose composites and biocompatible ion gels. *Macromolecular Symposia*, *342*, 21–24.
- Isik, M., Sardon, H., & Mecerreyes, D. (2014). Ionic liquids and cellulose: Dissolution, chemical modification and preparation of new cellulosic materials. *International Journal of Molecular Science*, *15*, 11922–11940.
- Izawa, H., & Kadokawa, J. (2010). Preparation and characterizations of functional ionic liquid-gel and hydrogel materials of xanthan gum. *Journal of Material Chemistry*, *20*, 5235–5241.
- Kadokawa, J., Murakami, M., & Kaneko, Y. (2008). A facile preparation of gel materials from a solution of cellulose in ionic liquid. *Carbohydrate Research*, *343*, 769–772.
- Kausar, A. (2017). Research progress in frontiers of poly(ionic liquid)s: A review. *Polymer-Plastics Technology and Engineering*. <http://dx.doi.org/10.1080/03602259.2017.1289410>.
- Kavanagh, A., Byrne, R., Diamond, D., & Fraser, K. J. (2012). Stimuli responsive ionogels for sensing applications-an overview. *Membranes (Basel)*, *2*, 16–39.
- Kim, Y. H., & Wool, R. P. (1983). A theory of healing at a polymer-polymer interface. *Macromolecules*, *16*, 1115–1120.
- Klaikherd, A., Nagamani, C., & Thayumanavan, S. (2009). Multi-stimuli sensitive amphiphilic block copolymer assemblies. *Journal of the American Chemical Society*, *131*, 4830–4838.
- Kushner, A. M., Vossler, J. D., Williams, G. A., & Guan, Z. (2009). A biomimetic modular polymer with tough and adaptive properties. *Journal of American Chemical Society*, *131*, 8766–8768.
- Lee, J. B., Peng, S., Yang, D., Roh, Y. H., Funabashi, H., Park, N., et al. (2012). A mechanical metamaterial made from a DNA hydrogel. *Nature Nanotechnology*, *7*, 816–820.
- Lee, S. Y., Lee, H., & Park, S. Y. (2014). pH/redox/photo responsive polymeric micelle via boronate ester and disulfide bonds with spiropyran-based photochromic polymer for cell imaging and anticancer drug delivery. *European Polymer Journal*, *57*, 1–10.
- Li, S., Xiao, T., Lin, C., & Wang, L. (2012). Advanced supramolecular polymers constructed by orthogonal self-assembly. *Chemical Society Review*, *41*, 5950–5968.
- Li, J., Zhang, X., Chen, S., You, Q., He, R., Shi, J., et al. (2014). Multi-responsive drug release from hydrogen-bonding multilayers containing PEGylated nanoparticles and azobenzenes. *Journal of Material Chemistry B*, *2*, 4422–4425.
- Liu, G., Zhou, L., Guan, Y., Su, Y., & Dong, C. M. (2014). Multi-responsive polypeptide-some: characterization, morphology transformation, and triggered drug delivery. *Macromolecular Rapid Communications*, *35*, 1673–1678.
- Mine, S., Prasad, K., Izawa, H., Sonoda, K., & Kadokawa, J. (2010). Preparation of guar gum-based functional materials using ionic liquid. *Journal of Material Chemistry*, *20*, 9220–9225.
- Mondal, D., Sharma, M., Mukesh, C., Gupta, V., & Prasad, K. (2013). Improved solubility of DNA in recyclable and reusable bio-based deep eutectic solvents with long-term structural and chemical stability. *Chemical Communications*, *49*, 9606–9608.
- Mukesh, C., & Prasad, K. (2015). Formation of multiple structural formats of DNA in a bio-deep eutectic solvent. *Macromolecular Chemistry & Physics*, *216*, 1061–1066.
- Mukesh, C., Bhatt, J., & Prasad, K. (2014). Polymerizable bio-ionic liquid based nanogel: A new nanocarrier for an anticancer drug. *Macromolecular Chemistry and Physics*, *215*, 1498–1504.
- Mukesh, C., Gupta, R., Srivastava, D. N., Nataraj, S. K., & Prasad, K. (2016). Preparation of a natural deep eutectic solvent mediated self polymerized highly flexible transparent gel having super capacitive behaviour. *RSC Advances*, *6*, 28586–28592.
- Mukesh, C., Upadhyay, K. K., Devkar, R. V., Chudasama, N. A., Rao, G. G., & Prasad, K. (2016). Preparation of a nontoxic hemocompatible ion gel by self-polymerization of HEMA in a green deep eutectic solvent having long term drug immobilization and pH stability efficiency. *Macromolecular Chemistry & Physics*, *217*, 1899–1906.
- Noro, A., Matsushita, Y., & Lodge, T. P. (2008). Thermoreversible supramacromolecular ion gels via hydrogen bonding. *Macromolecules*, *41*, 5839–5844.
- Noro, A., Matsushita, S., He, X., Hayashi, M., & Matsushita, Y. (2013). Thermoreversible supramolecular polymer gels via metal–Ligand coordination in an ionic liquid. *Macromolecules*, *46*, 8304–8310.
- Pawlicka, A., Firmino, A., Vieira, D., Sentanin, F., Grote, J. G., & Kajzar, F. (2009). *Gelatin- and DNA-based ionic conducting membranes for electrochromic devices*, Vol. 7487 [74870J-74870J-74812].
- Payal, R. S., Bejagam, K. K., Mondal, A., & Balasubramanian, S. (2015). Dissolution of cellulose in room temperature ionic liquids: Anion dependence. *Journal of Physical Chemistry B*, *119*, 1654–1659.
- Peng, L., Wu, C. S., You, M., Han, D., Chen, Y., Fu, T., et al. (2013). Engineering and applications of DNA–Grafted polymer materials. *Chemical Science*, *4*, 1928–1938.
- Phadke, A., Zhang, C., Arman, B., Hsu, C. C., Mashelkar, R. A., Lele, A. K., et al. (2012). Rapid self-healing hydrogels. *Proceeding of the National Academy of Science of the United States of America*, *109*(12), 4383–4388.
- Prager, T. C., Wilson, D. J., Avery, G. D., Merritt, J. H., Garcia, C. A., Hopen, G., et al. (1981). Vitreous fluorophotometry: Identification of sources of variability. *Investigative Ophthalmology and Visual Science*, *21*(6), 854–864.
- Prasad, K., Izawa, H., Kaneko, Y., & Kadokawa, J. (2009). Preparation of temperature-induced shapeable film material from guar gum-based gel with an ionic liquid. *Journal of Material Chemistry*, *19*, 4088–4090.
- Prasad, K., Murakami, M., Kaneko, Y., Takada, A., Nakamura, Y., & Kadokawa, J. (2009). Weak gel of chitin with ionic liquid, 1-allyl-3-methylimidazolium bromide. *International Journal of Biological Macromolecules*, *45*, 221–225.
- Roy, D., Cambre, J. N., & Sumerlin, B. S. (2010). Future perspectives and recent advances in stimuli-responsive materials. *Progress in Polymer Science*, *35*, 278–301.
- Ru, Q. R., Wang, Y. G., Zhang, W. J., Yu, X. Y., & Li, H. R. (2013). Thermally reversible, flexible, transparent, and luminescent ionic organosilica gels. *European Journal of Inorganic Chemistry*, *2013*(13), 2342–2349.
- Seki, S., Susan, M. A., Kaneko, T., Tokuda, H., Noda, A., & Watanabe, M. (2005). Distinct difference in ionic transport behavior in polymer electrolytes depending on the matrix polymers and incorporated salts. *Journal of Physical Chemistry B*, *109*, 3886–3892.
- Setoyama, M., Kato, T., Yamamoto, K., & Kadokawa, J. (2013). Preparation of chitin/cellulose films compatibilized with polymeric ionic liquids. *Journal of Polymers and the Environment*, *21*, 795–801.
- Sharma, M., Mondal, D., Mukesh, C., & Prasad, K. (2013a). Solvent responsive healing of guar gum and guar gum–Multiwalled carbon nanotube nanocomposite gels prepared in an ionic liquid. *RSC Advances*, *3*, 16509–16515.
- Sharma, M., Mondal, D., Mukesh, C., & Prasad, K. (2013b). Self-healing guar gum and guar gum–multiwalled carbon nanotubes nanocomposite gels prepared in an ionic liquid. *Carbohydrate Polymers*, *98*, 1025–1030.
- Sharma, M., Mondal, D., Mukesh, C., & Prasad, K. (2014). Preparation of tamarind gum based soft ion gels having thixotropic properties. *Carbohydrate Polymers*, *102*, 467–471.
- Smiglak, M., Pringle, J. M., Lu, X., Han, L., Zhang, S., Gao, H., et al. (2014). Ionic liquids for energy, materials and medicine. *Chemical Communications*, *50*, 9228–9250.
- Stuart, M. A., Huck, W. T. S., Genzer, J., Müller, M., Ober, C., Stamm, M., et al. (2010). Emerging applications of stimuli-responsive polymer materials. *Nature Materials*, *9*, 101–113.
- Sundaresan, V., Menon, J. U., Rahimi, M., Nguyen, K. T., & Wadajkar, A. S. (2014). Dual-responsive polymer-coated iron oxide nanoparticles for drug delivery and imaging applications. *International Journal of Pharmaceutics*, *466*, 1–7.
- Swatoski, R. P., Spear, S. K., Holbrey, J. D., & Rogers, R. D. (2002). Dissolution of cellulose with ionic liquids. *Journal of the American Chemical Society*, *124*, 4974–4975.
- Takada, A., & Kadokawa, J. (2015). Fabrication and characterization of polysaccharide ion gels with ionic liquids and their further conversion into value-added sustainable materials. *Biomolecules*, *5*, 244–262.
- Tang, Z., Kang, H., Wei, Q., Guo, B., & Zhang, L. (2013). Incorporation of graphene into

- polyester/carbon nanofibers composites for better multi-stimuli responsive shape memory performances. *Carbon*, 64, 487–498.
- Trivedi, T. J., Bhattacharjya, D., Yu, J.-S., & Kumar, A. (2015). Functionalized agarose self-healing ionogels suitable for supercapacitors. *ChemSusChem*, 8, 3294–3303.
- Ueki, T., & Watanabe, M. (2008). Macromolecules in ionic liquids: Progress, challenges and opportunities. *Macromolecules*, 41, 3739–3749.
- Ueki, T. (2014). Stimuli-responsive polymers in ionic liquids. *Polymer Journal*, 46, 646–655.
- Um, S. H., Lee, J. B., Park, N., Kwon, S. Y., Umbach, C. C., & Luo, D. (2006). Enzyme-catalysed assembly of DNA hydrogel. *Nature Materials*, 5(10), 797–801.
- Urban, M. W. (2012). Dynamic materials: The chemistry of self-healing. *Nature Materials*, 4, 80–82.
- Weng, W., Fang, X., Zhang, H., Peng, H., & Lin, Y. (2013). Multiresponsive supramolecular gels constructed by orthogonal metal–Ligand coordination and hydrogen bonding. *European Polymer Journal*, 49, 4062–4071.
- Wilpiszewska, K., & Spychaj, T. (2011). Ionic liquids: Media for starch dissolution, plasticization and modification. *Carbohydrate Polymers*, 86, 424–428.
- Xie, Z.-L., Jelicic, A., Wang, F.-P., Rabu, P., Friedrich, A., Beuermann, S., et al. (2010). Transparent, flexible, and paramagnetic ionogels based on PMMA and the iron-based ionic liquid 1-butyl-3-methylimidazolium tetrachloroferrate(III) [Bmim][FeCl₄]. *Journal of Material Chemistry*, 20, 9543–9549.
- Xie, Z.-L., Huang, X., & Taubert, A. (2014). Dye ionogels: Proton-responsive ionogels based on a dye-ionic liquid exhibiting reversible color change. *Advanced Functional Materials*, 24, 2837–2843.
- Yan, X., Xu, D., Chi, X., Chen, J., Dong, S., Ding, X., et al. (2012). A multiresponsive, shape-persistent: and elastic supramolecular polymer network gel constructed by orthogonal self-assembly. *Advanced Materials*, 24, 362–369.
- Yang, Y., & Urban, M. W. (2013). Self-healing polymeric materials. *Chemical Society Review*, 42, 7446–7467.
- Yuan, Q., Venkatasubramanian, R., Hein, S., & Misra, R. D. K. (2008). A stimulus-responsive magnetic nanoparticle drug carrier: Magnetite encapsulated by chitosan-grafted-copolymer. *Acta Biomaterialia*, 4, 1024–1037.
- Zhang, J., Zeng, J., Zhang, S., Wang, Y., & Wang, Y. (2006). Immobilization of α -galactosidase on tamarind gum and chitosan composite microspheres. *Journal of Bioactive and Compatible Polymers*, 21, 415–432.
- Zhang, M.-L., Jin, F., Zheng, M.-L., & Duan, X.-M. (2014). Inverse opal hydrogel sensor for the detection of pH and mercury ions. *RSC Advances*, 4, 20567–20572.
- Zhang, B., Sudre, G., Quintard, G., Serghei, A., David, L., Bernard, J., et al. (2017). Guar gum as biosourced building block to generate highly conductive and elastic ionogels with poly(ionic liquid) and ionic liquid. *Carbohydrate Polymers*, 157, 586–595.
- Zhao, Q., Dunlop, J. W., Qiu, X., Huang, F., Zhang, Z., Heyda, J., et al. (2014). An instant multi-responsive porous polymer actuator driven by solvent molecule sorption. *Nature Communications*, 5, 4293.
- Zhuang, J., Gordon, M. R., Ventura, J., Li, L., & Thayumanavan, S. (2013). Multi-stimuli responsive macromolecules and their assemblies. *Chemical Society Review*, 42(17), 7421–7435.
- Ziółkowski, B., Bleek, K., Twamley, B., Fraser, K. J., Byrne, R., Diamond, D., et al. (2012). Magnetic ionogels (MagIGs) based on iron oxide nanoparticles, poly (N-isopropylacrylamide), and the ionic liquid trihexyl(tetradecyl)phosphonium dicyanamide. *European Journal of Inorganic Chemistry*, 2012, 5245–5251.