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Synthesis and Characterization of Ionic Liquid based Polyampholyte Hydrogels

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Synthesis and Characterization of Ionic Liquid based Polyampholyte Hydrogels



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The future belongs to those who prepare for it today

Malcolm X

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Abstract

The development of new research areas on ionic liquids (ILs) is due to their unique properties, which justify that over the years remarkable work has been done in order to develop IL based materials that can fulfill the present and future needs. The potential application areas are extremely vast, including extraction systems (stationary phases for chromatography) or reaction and synthesis media (electrolytes in electrochemistry and polymerization processes and as a new generation of solvents). However, there is still a lot to study and develop, especially because of the massive variety of ILs currently available, which opens a wide range of opportunities ready to be explored. The aim of this work was to develop and characterize 2-hydroxyethyl methacrylate (HEMA) based superabsorbent ionic hydrogels synthesized by free radical vinyl polymerization. These ionic hydrogels were designed to contain different cationic and anionic molar ratios provided by the vinyl monomers 1-butyl-3-vinylimidazolium chloride (BVI_mCl) and 3-sulphopropyl-acrylate potassium (SPAK), respectively. The resulting hydrogels are, by definition, polyampholytes, which will have numerous applications. The prepared polyampholytes were characterized according to several techniques. Elemental analysis, transmission FTIR and SEM permitted to confirm the homogeneity of the samples and that poly(HEMA) was indeed modified with the cationic and anionic functional groups; thermo-mechanical properties, evaluated by thermogravimetric analysis, DSC and tensile tests, showed that the hydrogels have a relatively high thermal stability and that the neutral polyampholytes present interesting mechanical properties due to the ionic crosslinking that is established between cationic and anionic groups existing in the hydrogel network; the water swelling capacity results revealed that superabsorbent poly(HEMA) based hydrogels can be obtained by the applied strategy. Cationic and anionic polyelectrolytes exhibited particularly high water swelling degree and were able to increase 100 times their own dry weight when immersed in water. Moreover these hydrogels are very sensitive to changes in the ionic strength of the media in which they are immersed. An advantage of these particular systems when compared to conventional polyelectrolytes is that due to the presence of ionic instead of ionizable groups, they will not be sensitive to pH, allowing its application in all nearly all pH ranges. Finally, the prepared cationic and anionic hydrogels presented potential capacity to adsorb different charged molecules, namely a metal

ion, an anionic dye and an aminoacid with adsorption capacities higher than 80% for chromate, 95% bromocresol green and 70% for L-tryptophan, respectively.

The results presented in this work showed that it is possible to functionalize poly(HEMA) based hydrogels to prepare different types of polyelectrolytes depending on the used ratio of cationic and anionic monomers. Those ionic hydrogels may find different type of applications that can range from the adsorption of charged molecules for wastewater treatment or biomolecules separation, in the case of the cationic and anionic polyelectrolytes, or for the development of stimuli-responsive hydrogels with good mechanical stability in the case of the prepared polyampholytes.

Resumo

O desenvolvimento de novas áreas de pesquisa sobre líquidos iónicos deve-se às suas propriedades únicas e ao facto da pesquisa desenvolvida ao longo de vários anos apontar um trabalho bastante significativo no leque dos materiais que sejam capazes de atender às necessidades presentes, pensando já nas futuras. As áreas de potencial interesse são notavelmente amplas e as propriedades ímpares dos líquidos iónicos envolvem vastas áreas de aplicação, incluindo sistemas de extração/separação (fases estacionárias para cromatografia), meios de síntese e reação (electrólitos em electroquímica e polimerização também como uma nova geração de solventes). Contudo, ainda existe muito trabalho a ser desenvolvido, sobretudo devido aumento significativo da variedade de líquidos iónicos presentes atualmente no mercado, o que significa também que existe um vasto leque de oportunidades pronto para o desenvolvimento. O principal objectivo deste trabalho recai sobre o desenvolvimento e caracterização de hidrogéis super absorventes à base de 2-hydroxyethyl methacrylate (HEMA) que foram sintetizados por polimerização radicalar vinílica. Estes hidrogéis foram projetados de forma a conterem diferentes razões molares de catiões e aniões, fornecidos pelos monómeros vinílicos 1-butyl-3-vinylimidazolium chloride (BVI_mCl) and 3-sulphopropyl-acrylate potassium (SPAK), respectivamente. Os hidrogéis que resultaram deste processo são, por definição, polímeros anfóliticos, podendo ter inúmeras aplicações. Os materiais preparados foram posteriormente caracterizados através de várias técnicas. Análise elementar, FTIR de transmissão e SEM que permitiram assegurar a homogeneidade das amostras e ainda a modificação do poli(HEMA) com grupos funcionais catiónicos e aniónicos; propriedades termo-mecânicas avaliadas através de análise termogravimétrica, DSC e testes de tração, que demonstraram que os hidrogéis têm uma estabilidade térmica relativamente elevada e que os polímeros anfóliticos apresentam propriedades mecânicas bastante interessantes devido à reticulação iónica estabelecida devido à interação entre os grupos catiónicos e aniónicos existentes na matriz do hidrogel; os resultados sobre a capacidade de sorção de água que revelaram hidrogéis super absorventes à base de poli(HEMA) podem ser obtidos pela técnica aplicada neste trabalho. Os polielectrólitos catiónicos e aniónicos apresentaram um grau de sorção particularmente elevado, pois foram capazes de aumentar o seu tamanho cerca de 100 vezes relativamente à sua massa seca, quando imersos em água. Para além disso, estes hidrogéis destacaram-se como sendo bastante sensíveis à força iónica do meio em que foram mergulhados. Uma vantagem destes sistemas em particular, quando comparados com os

polieletrólitos convencionais, é que devido à presença de grupos iônicos em vez de grupos ionizáveis, estes não são sensíveis ao pH do meio, permitindo assim a sua aplicação em praticamente toda a gama de pH disponível. Finalmente, os hidrogéis catiónicos e aniônicos preparados neste trabalho apresentam-se com tendo capacidade para adsorver diferentes moléculas carregadas, nomeadamente metais, corantes aniônicos e aminoácidos, com capacidades de sorção superiores a 80% para o ião cromato, 95% para o verde de bromocresol e ainda 70% para o aminoácido, respectivamente.

Os resultados obtidos nesta tese demonstraram que é possível funcionalizar hidrogéis preparados a partir de poli(HEMA), de forma a obter diferentes polieletrólitos, dependendo da razão entre monómeros catiónicos e aniônicos utilizados. É possível encontrar inúmeras aplicações para os hidrogéis apresentados que podem ir desde adsorção de moléculas carregadas para tratamento de águas residuais ou separação de biomoléculas, para o caso dos polieletrólitos aniônicos e catiónicos, até ao desenvolvimento de hidrogéis sensíveis a estímulos externos, ou polímeros inteligentes, com uma boa estabilidade mecânica, para o caso dos polímeros anfóliticos preparados.

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List of Abbreviations

AA	Acrylic acid
AIBN	Azobis(isobutyronitrile)
AM	Acrylamide
APS	Ammonium persulphate
ATRP	Atom transfer radical polymerization
BSA	Bovine serum albumin
BVImCl	1-butyl-3-vinylimidazolium chloride
C	Carbon
CaCl ₂	Calcium chloride
DSC	Differential scanning calorimetry
E	Young's modulus
EGDMA	Ethylene glycol dimethacrylate
FTIR	Transmission Fourier transform infrared
GPE	Gel polymer electrolytes
H	Hydrogen
HEMA	Hydroxyethyl methacrylate
HPLC	High-performance liquid chromatography
IL	Ionic liquid
IPN	Interpenetrating Polymeric Network
K ₂ CrO ₄	Potassium chromate salt
KPS	Potassium persulphate
Li-Tf ₂ N	Lithium bis(trifluoromethanesulfonyl)imide
LCST	Lower critical solution temperature

MAA	Methacrylic acid
MBA	N.N'-methylenebis(acrylamide)
MgCl ₂	Magnesium chloride
MMA	Methyl methacrylate
N	Nitrogen
NaCl	Sodium Chloride
PBS	Phosphate-buffered saline
PDEAEMA	Poly(N.N'-diethyl aminoethyl methacrylate)
PDMAEMA	Poly(N.N'-dimethyl aminoethyl methacrylate)
PIL	Polymeric(ionic liquid)
PNIPAAM	Poly(<i>N</i> -isopropylacrylamide)
Poly(VdF-HFP)	Poly(vinylidene fluoride) hexafluoropropylene
RAFT	Reversible addition-fragmentation transfer
RTIL	Room temperature ionic liquids
S	Sulfur
SAP	Superabsorbent polymers
SDT	Simultaneous DSC-TGA
SEM	Scanning electron microscopy analysis
SPAK	3-sulphopropyl acrylate potassium salt
SPE	Solid polymer electrolytes
T _d	Degradation temperature
TETA	Triethylenetetramine
Tf ₂ N	bis(trifluoromethanesulfonyl)imide
UCST	Upper critical solution temperature
VOC	Volatile organic compounds

WS	Water swelling
WVS	Water Vapor Sorption
ϵ_t	Tensile strain
σ_t	Tensile stress

Goals and Motivations

The main goal of this work was to develop and to characterize 2-hydroxyethyl methacrylate (HEMA) based superabsorbent ionic hydrogels synthesized by addition polymerization in aqueous solution, namely by free radical vinyl polymerization using ammonium persulfate (APS) as a thermal initiator and N,N'-Methylenebis(acrylamide) (MBA) as a crosslinker. These ionic hydrogels were designed to contain different molar amounts of cationic and anionic charges, provided by the vinyl monomers 1-butyl-3-vinylimidazolium chloride (BVImCl) and 3-sulphopropyl-acrylate potassium (SPAK), respectively. The BVIm-based monomer was chosen due to its chemical stability and capacity to solubilize a broad range of molecules while the SPAK-based monomer was chosen due to its capacity to originate superabsorbent hydrogels. The prepared ionic hydrogels were characterized for their physico-chemical (Fourier transform infrared spectroscopy, elemental analysis and scanning electron microscopy with energy dispersive X-Ray); thermo-mechanical (thermogravimetric analysis, differential scanning calorimetry and tensile tests); fluid handling capacities (water vapor sorption and water swelling capacities at different ionic strength) and for their capacities to adsorb charged species from different chemical families, including metals, dyes and biomolecules using Chromate ions, bromocresol green and tryptophan, respectively as models. The results were discussed in terms of the influence of the amount/type of ionic charges, chemical crosslinking degree, electrostatic crosslinking and external media on the properties of the prepared hydrogels and possible applications in each case are suggested.

1. Introduction

1.1. Hydrogels

Hydrogels are polymer networks which, depending on the nature and properties of the co-monomers, can absorb large amounts of water or biological fluids, increasing thousands of times their dry mass in response to external stimuli, without dissolving (Ahmed, 2015; Hackl et al., 2015; Peppas et al., 2000; Scognamillo et al., 2011). Hydrogels can be classified depending on their source, composition, configuration, type of crosslinking and network electrical charge (Ahmed, 2015) as:

i) Depending on source: natural-based hydrogels, such as proteins and polysaccharides or synthetic-based hydrogels, prepared by chemical polymerization methods;

ii) Depending on the composition: homo-polymer hydrogels, when the polymeric network is composed by only one monomer specie; co-polymer hydrogels, when the polymeric network is composed by two or more different monomer species; or as multi-polymer interpenetrating network (IPN) hydrogels, when two independent crosslinked networks are connected by weak (not chemical) bonds;

iii) Depending on the configuration: amorphous or non-crystalline, semi-crystalline and crystalline hydrogels;

iv) Depending on the type of cross-linking: physically and chemically crosslinked hydrogels;

v) Depending on the network electrical charge: nonionic (or neutral) hydrogels; ionic hydrogels, if there are anionic or cationic ionizable groups on the polymer backbone; and amphoteric or zwitterionic hydrogels if there are both anionic and cationic ionizable groups on the polymer backbone (Ahmed, 2015). According to NIST, the main difference between amphoteric and zwitterionic hydrogels is that in the former the hydrogel monomeric units contain only one reactive site that is able to dissociate into anionic and cationic ionizable groups while in the later the same monomeric unit contains two distinct ionized or ionizable sites, one able to ionize into cationic and the other into anionic groups (Hackley & Ferraris, 2001). Amphoteric or zwitterionic materials will be discussed in more detail in section 1.3.

Hydrogels are insoluble in water due to physical or chemical crosslinking. Physical crosslinking results from weak bond interactions whereas chemical crosslinking is usually

associated to thermal, photo, redox, electrochemical or radiation initiated free radical polymerizations. Crosslinking enhances the mechanical properties of polymer hydrogels, which may be weak due to polymer chain and water thermodynamic compatibility (Ullah et al., 2015) and permits to control other hydrogel properties such as biodegradation and chemical or physical response to externally applied stimuli (Ahmed, 2015). The crosslinking degree depends on the application and should be optimized since low crosslinking may lead to hydrogels with loose mechanical properties but a high degree of crosslinking may also lead to brittle and less elastic hydrogels (Bandomir et al. 2014). The most commonly used crosslinkers, which are used in more than 80% of the reported works (Kryscio & Peppas, 2012), are methylene bis-acrylamide (MBA) and ethylene glycol dimethacrylate (EGDMA) (Ahmed, 2015; Peppas et al., 2000). Taking into account their solubility in water (20 mg/mL and 1.086 mg/mL at 25°C respectively), MBA is recommended for aqueous solution polymerization reactions while EGDMA is recommended for bulk polymerization reactions. Independent on the synthesized polymer an external stimulus is required in order to start the polymerization, and according to the synthesis route there are different types of initiator that can be used.

Free radical solution polymerization is defined by IUPAC as a chain polymerization in which the kinetic-chain carriers are radicals. It is one of the most used hydrogels synthesis route, especially because it is a simple technique. Furthermore, the presence of a solvent decreases solution viscosity, which allows an efficient heat reaction removal decreasing the chance to occur the gel effect. On the other hand, the presence of a solvent requires its removal before processing the final polymer and can cause chain transfer to the solvent, solvation of ionic chain ends and counter-ions and addition of impurities into the system. This route involves the use of vinyl monomers and an initiator which has to be first activated to produce radicals. Commonly used initiators include thermal initiators such as ammonium persulphate (APS), potassium persulphate (KPS), and photo initiators such as azobis(isobutyronitrile) (AIBN) which can be activated by both is a photo-initiator and a thermal-initiator used vinyl-based polymer synthesis. These radicals, which are highly reactive, are then transferred from the initiator molecules to the vinyl monomer units present in the system leading to chain growing polymerization.

Hydrogels are interesting materials due to their characteristic properties such as high water absorption capacity and biocompatibility which make them resemble living tissues and therefore excellent candidates to be used for the development of biomaterials such as contact lenses, membranes for biosensors, supports for artificial tissue and organs and drug delivery

devices. The hydrophilicity of hydrogels may result from the presence of hydrophilic amine, carboxyl or hydroxyl functional groups in the polymer chain but may also result from changes in the osmotic pressure between the polymer and the surrounding media where it is immersed (Peppas et al., 2000; Ullah et al., 2015). Water may flow inside a polymeric network when a driving force is generated between the bulk of the network and the medium inducing the swelling of the network. The amount of water that is absorbed is determined by a number of factors including the network free volume, the network/medium driving force and the hydrophilicity of the functional groups present in the polymer matrix.

Hydrogels have been proposed for many applications, including biomaterials for biomedical and pharmaceutical applications (Peppas et al., 2000), tissue engineering (Hackl et al., 2015), bio-sensing (Ma et al., 2016), separation technology (Ullah et al., 2015), agriculture and hygienic products (Ahmed, 2015) and wastewater treatment (Bekiari et al., 2016). Ideally, hydrogels must have a required number of features such as very high water swelling capacity in water and also in saline solutions (like biologic fluids), desired selective absorption, chemical stability (having the lowest possible amount of unreacted monomers), adequate thermo-mechanical performance and biodegradability without the formation of potential toxic species. Although it is not always easy to achieve all of these features simultaneously, it is nowadays possible to achieve almost all of them, according to the required final properties of the hydrogel. Nevertheless there are still many restrictions to the use of hydrogels which include their low solubility, high crystallinity, low biodegradability, inadequate mechanical and thermal properties and presence of unreacted monomers. Therefore it is always possible to further optimize each production steps in order to fulfill every need.

1.1.1. Superabsorbent hydrogels

Superabsorbent polymers (SAP) are a special class of lightly crosslinked hydrophilic hydrogels that have uniquely high swelling degree. They are able to absorb water or biological fluids more than 100 times their dry weight due to the thermodynamic compatibility between water molecules and chemical groups of the polymeric network of the hydrogel (Gawande & Mungray, 2015; Guilherme et al., 2015; Kabiri et al., 2011; Peppas et al., 2010). Furthermore, SAPs are able to maintain their network steady even in the swollen state as a result of elastic retraction forces of the network due to crosslinking (Buchholz & Graham, 1997; Guilherme et al., 2015). Although SAPs fit in the same classification of hydrogels, they have some different features which make them suitable for more specific application than hydrogels in general. They were industrially developed in Japan and USA in the 80s for hygienic products (Kabiri et al., 2011). Currently, SAPs still find important applications on the development of many hygienic products, in agriculture to reserve water and to deliver nutrients into the soil, in pharmaceuticals and more recently in forward osmosis as low energy consuming membranes (Gawande & Mungray, 2015; Kabiri et al., 2011). Compared to hydrogels, SAPs present faster swelling response, higher degradability and porosity but are stimuli-responsive as well. Moreover, and just like other hydrogels, SAPs have low-cost and are highly renewable. SAP properties can be tailored mostly through the type and hydrophilicity of the monomer, method of synthesis, degree of crosslinking, degree of neutralization and nature of the swelling medium. Although the first SAPs were prepared from hydrophilic polymers such as poly(vinyl alcohol), PVA, or poly(ethylene oxide), PEO, (Buchholz & Graham, 1997), currently, SAPs are prepared mostly from partially neutralized polymers. For hydrogels prepared with weak carbonic acids such as poly(acrylic acid) the main factor that influences the swelling degree is the degree of dissociation of the ionic groups, and a high dissociation leads to a larger swelling degree. Therefore, the degree of dissociation is the key to control the swelling degree, instead of hydrophilicity as formerly thought (Peppas, et al., 2010). The most commonly used monomers, method of synthesis and initiating system for the preparation of synthetic SAPs and some general features are presented in Table 1 (Ahmed, 2015; Omidian, et al. 2005):

Table 1. Monomers, method of synthesis and initiating system commonly used for the preparation of synthetic SAPs.

Commonly used monomers	acrylamide, acrylic acid and acrylate-based salts such as sodium and potassium acrylates
Method of synthesis	Bulk, solution, inverse-suspension
Initiating system	Thermal and redox
Water adsorption mechanisms	Diffusion (high) and capillary (low)
Swelling dependence on size	Size-dependent
Type of absorbed water	Mostly bond
Retained water under pressure	High

It should be noted that the features presented in Table 1, are based on SAPs synthesized with commonly used monomers presented in the same table. Recent reports on SAPs include a robust and highly stretchable superabsorbent hydrogel polymerized from nonionic N,N-dimethylacrylamide (DMMA) and ionic sodium acrylate by free radical polymerization and crosslinked with N,N-methylenebis acrylamide. This hydrogel presented an impressive swelling degree of 3000 mass of swollen gel per mass of dry gel, which is one of the highest reported so far. Apart from the remarkable swelling degree, this hydrogel exhibit better mechanical properties than most SAPs (Cipriano et al., 2014).

1.1.2. Poly(2-hydroxyethyl methacrylate) based hydrogels

Poly(2-hydroxyethyl methacrylate) (poly(HEMA)) is one of the most studied non charged hydrogel developed from the pioneer work of Wichterle and Lim in 1960 which first reported the synthesis of HEMA-based hydrogels for biological applications (Wichterle & Lim, 1960). Poly(HEMA) is largely used for the development of biomedical devices such as contact lenses and drug delivery systems due to its softness, water swelling capacity, elasticity, transparency, high environmental sensitivity, sorption capacity and mechanical properties(Ahmed, 2015; Peppas et al., 2006). Such properties can be improved through

surface modification or with copolymerization with other monomers depending on the desired final properties (Meyvis et al., 2000; Sefton et al., 2000). In its chemical structure HEMA contains both hydrophobic and hydrophilic functional groups, methyl and hydroxyl groups, respectively. Therefore, although HEMA is an hydrophilic monomer, poly(HEMA) is hydrophobic (Okano et al., 1981). For this reason, although poly(HEMA) is used in many applications as biomaterials in intraocular lenses or drug delivery systems, where a high water content is required, HEMA needs to be copolymerized with a more hydrophilic co-monomer in order to optimize the hydrophilic properties of the final material. Along with HEMA, hydroxyethyl acrylate (HEA), methacrylic acid (MAA), acrylic acid (AA) and acrylamide (AM) are some of the monomers commonly used to produce diverse HEMA based hydrogels (Hackl et al., 2015; Lord et al., 2006; Ahmed, 2015).

As highlighted before, poly(HEMA) based hydrogels have been widely studied for numerous applications specially in the biomedical field. However, these hydrogels are being also evaluated for a different promising application which is their use as stationary phase for the separation of charged species including biological macromolecules such as proteins (bovine serum albumin and lysozyme (Unsal et al., 2005)), antibodies (immunoglobulin G (Bayramoglu & Yakup Arica, 2009)); and metal ions (Tukenmez & Bicak, 2016). These materials may therefore also found important applications in many biotechnology separation and wastewater treatment processes (Unsal et al., 2005; Tukenmez & Bicak, 2016) among others. For this purpose poly(HEMA) has to be functionalized especially because it is a neutral polymer and therefore does not have the capacity to absorb charged molecules. In this context Unsal and co-workers studied copolymerized HEMA with ethylene dimethacrylate (EDM) and obtained poly(HEMA-co-EDM) which was further functionalized with Cibracron blue F3G-A, since it presents high affinity to many proteins and aminoacids (Unsal et al., 2005). Authors reported high protein recovery yields when this material was used as stationary phase for HPLC analysis. Wilson and co-workers synthesized a zwitterionic phosphorylcholine poly(HEMA)-based hydrogel in order to investigate the influence of electromigration on ion release from hydrogels with potential application for drug release applications (Wilson et al., 2014). Bayramoglu and Arica, investigated surface functionalized poly(HEMA/EGDMA) microspheres used as ion-exchange supports for adsorption and purification of human γ -globulin (IgG). Authors also suggested the possibility to graft the microspheres with other functional groups in order to obtain an extensive variety of chromatographic systems with different adsorption and selectivity capacities (Bayramoglu & Arica, 2009). More recently, Tukenmez and Binak, studied a new resin for metal ion recovery

in waste water, which was poly(HEMA) copolymerized with methyl methacrylate, MMA, and crosslinked with ethylene glycol dimethacrylate (EGDMA), which was further methane sulfonated using methane sulfonyl chloride-pyridine. Through complex functionalization procedures, authors obtained a high performance resin with good adsorption capacity and recyclability. Resins showed good metal recovery which exhibit high capacity and fast kinetics. The measured capacities for Cu(II), Ni(II) and Co(II) metal ions were between 1.2 and 1.7 mmol/g of resin. Authors also claimed that the resin structure is expected to recycle more than 100 or 200 times (Tukenmez & Bicak, 2016).

1.2. Stimuli responsive hydrogels

Stimuli responsive hydrogels have the ability to react under external stimuli and experience extremely intense changes in their swelling behavior, network structure, or mechanical strength. Its response will depend on the type of stimuli, which can be either physical or chemical. Physical stimuli include changes in temperature, light, pressure, mechanic stress and even magnetic or electric fields. On the other hand, chemical stimuli include changes in pH, chemical agents and ionic strength. More recently, biochemical stimuli, which includes the response to enzymes, antigen and biochemical agents are also been studied (Gil & Hudson, 2004; Ullah et al., 2015). Such materials are called as ‘smart materials’ because of their ability to respond under particular conditions (Ahmed, 2015; Peppas et al., 2000; Ullah et al., 2015) which may result from changes in one or on a combination of two or more stimuli-responsive mechanisms. It is essential to obtain hydrogels with reversible response, meaning that, in the absence of the stimuli, the material should have the capability to return to its original state. Therefore it is important to study the system in order to predict and control the hydrogel’s responsiveness (Tokarev et al., 2009).

Stimuli responsive hydrogels are suitable for many industries, such as pharmaceutical, biomedical, biotechnology and even agriculture and countless applications, such as in the separation of biomolecules, drug delivery devices, actuators, biosensors and tissue engineering (Ahmed, 2015; N. A. Peppas et al., 2000; Stuart et al., 2010; Ullah et al., 2015).

1.2.1. Temperature - responsive hydrogels

Temperature-responsive hydrogels have applications in several fields, particularly in pharmaceutical and biomedical fields, due to their ability to swell and shrink according to changes in temperature (Peppas et al., 2000; Ullah et al., 2015). These thermosensitive hydrogels exhibit a critical solution temperature, hence, small changes around that critical temperature make the chains to expand or to contract. Such response is not determined by common swelling behavior, but it is due to hydrophilic and hydrophobic interactions that are established or not when temperature changes. Therefore, the origin of the response is based on hydrophobic-hydrophilic balancing effects and consequent rearrangement of functional pendant groups (Kost & Langer, 2012). These hydrogels can be divided into positive or negative temperature-responsive systems, depending if they have an upper critical solution temperature, (UCST) or a lower critical solution temperature (LCST). In the first case, (UCST) hydrogels collapse if temperature decreases below the UCST because of the formation of a complex structure by hydrogen bonds. This structure is disrupted at temperatures above the UCST, increasing the free volume in the polymeric network and allowing hydrogel's swelling. In the second case (LCST), the hydrogel shrinks when the temperature goes above the critical temperature, but swells at lower temperatures (Bag & Rao, 2006; Gil & Hudson, 2004; Peppas et al., 2000; Ullah et al., 2015). One of the most studied thermosensitive polymer is poly(*N*-isopropylacrylamide) or PNIPAAm (Hirotzu et al.1987) This polymer presents a LCST of 34,3°C, but it is possible to increase its critical temperature by functionalizing the gels with ionic copolymers or changing solvent composition which makes PNIPAAm a very promising material for biomedical and pharmaceutical applications (Gil & Hudson, 2004; Peppas et al., 2000).

1.2.2. pH-responsive hydrogels

Hydrogels formed by ionizable pendant groups usually present a response to an external change in pH since those groups can either accept or donate protons. Therefore, pH responsive hydrogels can be classified into anionic or cationic hydrogels. Such hydrogels that contain ionizable pendant groups form polyelectrolytes when immersed in aqueous media (Bag & Rao, 2006; Peppas et al., 2000). Anionic hydrogels form polyacids and usually have carboxylic or sulphonic acid as pendant groups. In this case, the ionic species release protons when the pH of the environment is above the pK_a of these groups, generating electrostatic repulsive forces between the chains, and thus increasing the swelling of the hydrogel (Ullah et

al., 2015). The most commonly used polyacids are poly(acrylic acid) and poly(methacrylic acid) (Gil & Hudson, 2004). Cationic hydrogels form polybases and usually have amine groups as ionizable pendant groups, which are ionized at pH below pK_b thus increasing the swelling capacity of the hydrogels due to electrostatic repulsive forces that promote sudden volume changes (Ullah et al., 2015). Good examples of polybases are poly(N,N'-dimethyl aminoethyl methacrylate) (PDMAEMA) and poly(N,N'-diethyl aminoethyl methacrylate) (PDEAEMA) (Gil & Hudson, 2004). Several authors refer pH-sensitive hydrogels has very promising polyelectrolyte over neutral networks, especially for the development of controlled delivery devices (Peppas et al., 2000).

The response of the hydrogel to pH also depends on the ionic strength of the media, which is the direct measure of the ions concentration in the solution. Ionic strength will instigate dramatic changes in the hydrogels swelling behavior, network structure, permeability and mechanical strength. Therefore, the control over ionic strength will provide a full command on the main features of the hydrogel for desired applications (Peppas et al., 2000).

1.2.3. Electro - responsive hydrogels

Electro-responsive hydrogels present a response when stimulated by an electric pulse but are also usually sensitive to changes in pH since they have ionizable pendant groups in their structure. These materials are therefore considered as multifunctional smart materials (Murdan, 2003; Ullah et al., 2015). When an electric field is applied the electro-sensitive hydrogels they deswell or bend according to the position of the electrodes relatively to the hydrogel (Murdan, 2003). Such response is due to the hydrogel's capacity to convert electrical energy into mechanical energy (Roy et al., 2010). When the hydrogel is positioned parallel towards the electrode it will bend. Anionic hydrogels collapse towards the anode, since anions migrate to the anode whereas cationic hydrogel collapse towards the cathode, since protons migrate to the cathode (Murdan, 2003). On the other hand when the hydrogel is places perpendicularly towards the electrode deswelling occurs. This control of the hydrogel behavior is achieved not only by changing the position of the hydrogel relatively to the electrodes, but also through precise control on the magnitude and duration of the electric pulses applied, on the pH and salt concentration of the medium and on the thickness and shape of the hydrogel (Murdan, 2003; Roy et al., 2010).

Electro conductive hydrogels are being purposed are interesting materials to developed artificial muscles using for instance composites of acrylic acid and acrylamide functionalized

with a polypyrrole/carbon black as additive. Lira et al. studied other electro sensitive polymeric systems for drug release devices such polyaniline-polyacrylamide copolymer by electro polymerization of the conducting polymer. Hsu and Block studied hydrogels matrices such agarose, agarose-carbomer 934P copolymer and agarose-xanthan gum copolymer for electrically-modulated drug delivery and proved that drug migration was possible. This research gave room to new developments and applications of these hydrogels.

Electro-responsive hydrogels have drawn attention for many applications, but especially for controlled drug delivery. Controlled release happens when the biomolecule is attached with the polymeric network such this biomolecule is release to the surrounding fluid towards a pre-studied stimulus in a specific way (Guisseppi-Elie, 2010). Since the polymer has two redox states in response to an electric signal, the biomolecule will be attached to the hydrogel in one redox state and discharged to the surrounding fluid in the other (Kost & Langer, 2012). Therefore, it will be required that the polymer have delocalized charge center for electromigration in response to oxidation or reduction (Guisseppi-Elie, 2010).

1.3.Polyelectrolytes

Polyelectrolytes are a class of polymers, which contain ionizable or ionic groups, or both, through its network (Jenkins, et al. 1996). Depending on the type/concentration of ionizable groups, polyelectrolytes can be classified as polycations and polyanions, if they are constituted only by cationic and anionic ionizable functional groups, or as polyzwitterions and polyampholytes (Martínez et al. 2012; Lowe & McCormick, 2002; Scrantom et al. 2010). The main difference between polyzwitterions and polyampholytes is that in the former the same monomeric unit contains ionizable groups of opposite sign while in the later ionizable anionic and cationic groups are distributed through the polymer network (Wilkinson & McNaught, 1997). Examples of synthetic polyelectrolytes include poly(acrylic) and poly(methacrylic) acids, poly(styrene sulfonate), poly(vinyl amine) and poly(4-vinyl pyridine) and of naturally occurring polyelectrolytes include proteins, polysaccharides and DNA(Dobrynin & Rubinstein, 2005; Scrantom et al., 2010).

Due to its nature, when polyelectrolytes interact with water, the ionizable groups will dissociate meaning that the chains of the polymer will be charged. Therefore electrostatic interactions will occur, not only between the ionizable groups inside the polymeric chain but also with mobile charged species that may be present in the surrounding fluid (as explained in

section 1.2.2). For that reason, when developing this type of materials it is crucial to take into account not only the polyelectrolyte properties but also the properties of the solution (such as viscosity and ionic strength) in which the material is going to be in contact with. For example, when immersed in an aqueous solution without ions, polyelectrolytes will experience an increase in the network free volume due to the increase of electrostatic forces along the polymeric chain. However, in the presence of a solution with a considerable ionic strength, the polyelectrolyte will inevitably shrink due to screening effects or polyelectrolyte effect, which reduces the electrostatic field because of the mobile charges in solution, making the polyelectrolyte behave like a non-ionic polymer (Scrantom et al, 2010). Due to repulsive electrostatic interactions between ionizable groups with the same charge, polyelectrolytes demonstrate solution rheological properties impressively distinctive from neutral polymers (Mecerreyes, 2011).

Polyelectrolytes are extremely useful as delivery/capture vehicles (Kim et al., 2016) and are therefore suitable for several applications such as drug delivery, protein separation, chemical sensors and ion-exchange chromatography (Lázaro et al., 2012; Scrantom & Rangarajan, 1995). However, it is often necessary to introduce some structural variations, in order to provide a higher mobility of charged molecules within the polymer network and consequently, higher ionic conductivity. Moreover, it is possible to reduce ion-ion interactions inside the network and simultaneously increase the flexibility of the chains and decreasing the glass transition temperature through the copolymerization with non-charged monomers or mixture with non-charged polymers (Shaplov et al., 2011). Due to their chemical nature polyampholytes permit a fine tune of important properties such as swelling behavior (Baker et al., 1995) and responsiveness to pH, temperature and ionic strength (Singh et al., 2007). Since they carry both cationic and anionic groups, polyampholytes experience both electrostatic repulsion and attraction which determines their behavior in aqueous solutions (Berlinova et al. 2000). On one hand, electrostatic repulsions will increase the free volume between the polymer chains and on the other hand, electrostatic attraction will promote complexation between opposite charges, which is affected by both molecular weight and amount of the ionic pendant groups (Chen et al., 2000). Such electrostatic interactions are determined by internal factors, such as hydrophobicity, nature, structure, amount and space reorganization of ionizable anionic and cationic pendant groups and by external factors, such as the ionic strength, pH and temperature of the surrounding fluid (Xiao et al. 2013). Furthermore, synthetic polyampholytes experience two phenomenon: the isoelectric point, in which the number of opposite charges is the same, so the total charge of the polymeric network will be

equal to zero and the antipolyelectrolyte effect when low molecular charged species are added (NaCl, CaCl₂ or MgCl₂) and the polymer will experience a chain expansion at the isoelectric point and become water-soluble (Baker et al.1995; Dobrynin et al. 2004; Ibraeva et al., 2004).

Polyampholytes have enormous potential in a large number of applications such as in biotechnology (amino acid and protein separation), medicine (drug delivery), water treatment, adsorption/release of charged molecules, as anti-biofouling coatings and for the development of mechanically tough hydrogels (Gui et al. 2009; Ibraeva et al. 2004; Schlenoff, 2014; Wang et al. 2015; Xiao et al. 2013).

1.5. Poly(ionic liquids)

The first known report on ionic liquids (ILs) dates back to the beginning of the XX century (Walden, 1914), but at that time little attention was paid to this report. However, by the end of the same century, another work reported the synthesis of air- and water-stable imidazolium-based ILs (Wikes, 1992) and since then massive research has been done in this field with repercussion in several research areas including in polymer science as will be seen in this section.

Ionic liquids are molten salts (composed by both cationic and anionic ions) which melt below 100°C and some even at 25°C and are therefore also known as room temperature ionic liquids (RTIL) (Nishimura & Ohno, 2014; Yuan, Mecerreyes, & Antonietti, 2013). Although its structure is similar to any other salt, they don't share its tendency to crystalize, due to their bulky and asymmetrical cation structure (Mallakpour & Dinari, 2012). As shown in Figure 1, ILs are composed by an organic cation combined with either an inorganic or an organic anion (Portal, 2013). Typical IL cations include imidazolium, pyridinium, alkylammonium, alkylphosphonium and pyrrolidiniums (Yuan & Antonietti, 2011). The side chains of the cations play an important role in the IL's properties, mainly in their melting point and toxicity (Madria, 2011). On the other side, the choice of the anion has a strong impact on the chemical properties and functionality of the IL (Portal, 2013). Imidazolium-based ILs are the most common and have low viscosity and relatively high electrical conductivity of 10⁻³ S.cm⁻¹ at 25°C, however, they have limited electrochemical window (4V vs. Li/Li⁺) and poor electrochemical stability (Li et al., 2016).

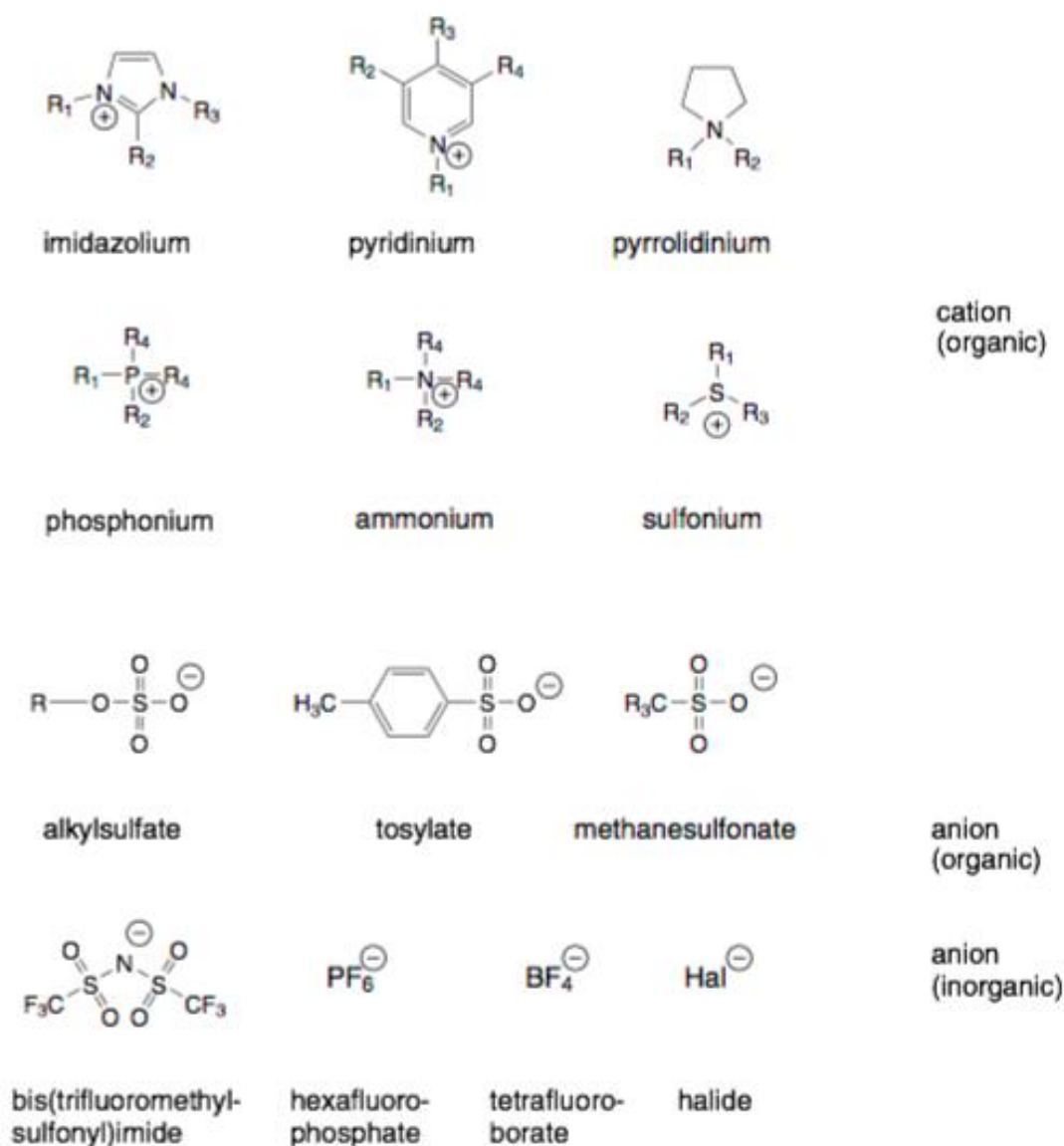


Figure 1. Examples of the most common cationic and anionic moieties of ionic liquids.

ILs have been widely studied due to their chemical, thermal and electrochemical stability, low vapor pressure and consequent negligible volatility, high ionic conductivity and non-flammability (Lu et al., 2009; Ohno et al., 2004; Zhang et al., 2006). Nature, structure and interaction of both cation and anion have an important role in each of these properties and therefore its choice is very important regarding the final desired properties of the IL (Marsh et al., 2004; Niedermeyer et al., 2012). A wide variety of ILs are currently available, all of them with unique properties and suitable for countless applications. Recent studies suggest the use of ILs as greener electrolytes for electrochemical applications (Yuan et al., 2013); as polymer additives, because they may perform as non-volatile plasticizers (Scott et al., 2003), as

surfactants in the development of novel nanocomposites (Ye & Elabd, 2011) or to improve the dispersion of nanotubes in polymeric matrices (Carrión, et al., 2007). Apart from such applications, novel studies were conducted for IL employment as solvent replacement, purification of gases, homogeneous and heterogeneous catalysis, biological reactions media and removal of metal ions (Keskin et al., 2007). Moreover they have been used as solvent systems in chemical reactions, medium to solubilize gases, separations extractions and chemical sensing. For example, the ability of IL to be used as solvents is very useful for many chemical reactions, particularly when distillation is not applicable for solvent recovery or when the components of a chemical reaction are thermally sensitive (Mallakpour & Dinari, 2012). Wei, et al used an imidazolium ionic liquid to functionalize the surface of multi-walled carbon nanotubes (MWNTs) to prevent MWNTs aggregation. Moreover, the incorporation of such IL, also contribute for the formation of a hydrophilic surface for ion accessibility, which was applied for electrochemical determination of dihydroxybenzene isomers (Wei et al., 2016). Jolanta Flieger and Anna Czajkowska-Żelazko gathered a number of applications of ILs in different areas of separation techniques, such as extraction, capillary electrophoresis and liquid chromatography. Those include the use of imidazolium-based ILs as surface modifiers in silica matrices for stationary phases in liquid chromatography (Qiu, et al., 2006).

Due to their good electrical conductivity, tunable viscosity and solubility, ILs can be used for modification of the capillary electrophoresis wall (Qin & Li, 2002), and also as background electrolytes in aqueous and non-aqueous electrophoresis. This approach allowed the separation of a wide variety of compounds, such as polyphenols in grape seed extracts, carboxylic acids and phenols, small organic anions or even basic proteins. These separation techniques provided higher separation selectivity and efficiency and therefore several studies are still being conducted in order to explore IL's properties as much as possible (Czajkowska-Żelazko, et al., 2011).

Despite all these advantages, the use of ILs is still limited because they are still very expensive for large use in industrial applications (Mecerreyes, 2015). Moreover, and despite ILs are considered as 'green solvents', and interesting alternatives to industrial volatile organic compounds (VOC), this assumption is mostly based on their low volatility; however, and since ILs are salts, they are soluble in water (at different extents depending on the hydrophobicity of the cation and anion) and they can be very harmful to the aquatic ecosystems when released into the environment (Yoo et al., 2016), considering their excellent thermal and chemical stability. That is why is so important to perform a fully life-cycle assessment, including toxicity and biodegradability, ideally, to each IL, which is extremely

difficult due to the large variety of ILs commercially available (Thuy Pham et al., 2010). Moreover this evaluation risk is influenced by many factors such as exposure time, concentration and biological system that is being considered, which further difficult comparison among different ILs. So, when a certain IL is considered toxic, it is necessary to specify in which conditions the experiment was conducted. It is currently accepted that IL's toxicity mainly depends on the length of the side chain, and in some cases, also the nature of the anion (Pendleton & Gilmore, 2015). In general terms, the lower the alkyl side chain of the IL cation, the lower the toxicity (Madria, 2011; Russina et al., 2014). Nevertheless, it has been shown that functionalization of the alkyl chains with polar groups may reduce the toxicity of the IL towards cell cultures of marine bacteria *Vibrio fischeri*, limnic green algae *Scenedesmus vacuolatus* and fresh water plant *Lemna minor*, although maintaining their antimicrobial activity (Stolte et al., 2007; Thuy Pham et al., 2010).

The interest in the new properties, structures and possible applications of ILs lead to the development of a new class of polymers, which incorporated some of the outstanding features of ILs into the stability and mechanical performance of polymers (Mecerreyes, 2015; Yuan & Antonietti, 2011; Yuan et al., 2013). Polymerization of ionic liquids has been extensively studied because they are easily synthesized and are suitable for many applications in various fields of chemistry and industry, due to the ILs unique properties mentioned above (Lu et al., 2009). These applications include the use of polymer electrolytes in secondary batteries, sensors and some ionic devices (Shaplov et al., 2015). Generally speaking, polymerized ionic liquids, usually known as PILs, refer to a singular type of polyelectrolytes whose monomer units are functionalized ILs. As referred before, polycations, polyanions and polyampholytes can be obtained depending if the functionalization is on the cation, on the anion or in both (Mecerreyes, 2011; Yuan & Antonietti, 2011). These polyelectrolytes can work as 'smart materials' what means that under particular conditions of pH, temperature, ionic strength and other internal or external stimuli they will have a certain response dependent on polyelectrolyte's properties (Holzapfel et al., 2013). By its turn, PILs final properties depend on the properties of the monomers, on the crosslinking ratio and on the amount of positive and negative charges that will be present in the polymer chain. Moreover, contrarily to polyelectrolytes, which have both ionizable and/or ionic groups depending on the pH of the media, PILs only have ionic groups, which make them ionized independently of the pH of the media; this constitutes an advantage because PILs will be charged in the entire pH range.

Polymer ionic liquids (PILs) can be synthesized by several methods, depending on the envisaged final properties of the polymer. Among the most commonly used methods are: free

radical polymerization, which is the most common method due to its simplicity, however it is completely random and extremely difficult to control (Lu et al., 2009); surface-initiated atom transfer radical polymerization (ATRP), which is easy to perform and it can be controlled (He et al., 2008); reversible addition-fragmentation transfer (RAFT), which can be applied in a wide range of monomers (Perrier et al., 2002) and ionic polymerization, which can refer to anionic or cationic polymerization and it is considered as an alternative to free radical polymerization (Vijayaraghavan & MacFarlane, 2004). Cationic and anionic polymerizations represent a different type of chain growth polymerization in which a cationic/anionic initiator creates reactive centers in the monomers by transferring positive/negative charge, respectively.

There are several factors that may be considered in order to tailor the properties of PILs according to the envisaged applications (Nobuoka et al., 2007). One of the most important is the nature of the IL because it will certainly condition the properties of the PILs formed with that IL (Mecerreyes, 2015). It is also important not to neglect the counter-ion nature as well, because it may affect some of the PILs properties such melting point, ionic conductivity, solubility and hydrophilicity (Portal, 2013; Mecerreyes, 2011). For instance it was previously demonstrated that the counterion's nature plays a substantial role in the protein absorption capacity of an imidazolium-based PIL due to specific counterion-protein interactions (Yang et al. 2015). The second step is to look at the polymer suitable for a backbone that matches with the desirable PIL's final properties. When we talk about both physical and chemical PIL's final properties we have to think about monomers composition, as was mentioned before, but also about polymerization itself. Thus, it is possible to form very mechanically stable structure composed by repeating monomer units covalently attached to a polymeric backbone, with the advantage of providing to the final structure the unique properties of ILs, as good electrochemical stability and high ionic conductivity and also the mechanic strength of polymer chains taking polymeric materials to a whole different level (Lu et al., 2009; Mecerreyes, 2011; Yuan et al., 2013).

Imidazolium-based polymers have been widely studied as are the cases of poly(1-vinyl-3-alkyl imidazolium) (Mecerreyes, 2011), poly(butyl-3-methylimidazolium hexafluorophosphate) (Lu et al., 2009), poly(1-methyl-3-alkyl imidazolium) (Texter, 2012) along with different counter-ions such Cl⁻, Br⁻, I⁻, BF₄⁻ or PF₆⁻ (Cordella et al., 2015; Green et al., 2009; Ito et al. 2000; Texter, 2012). Moreover, imidazolium cation have been incorporated into polymer back bones such as vinyl, styrenic, (meth)acrylic and (meth)acrylamide and ethylene glycol monomers, among others. Other types of cation, shown

in Figure 1, have also been used with similar polymer backbones, but less intensively (Mecerreyes, 2011).

The current interest in PILs research, as in polymers in general, is the development of multifunctional and versatile materials (Yuan et al., 2013). The use of PILs as polyelectrolytes has been reviewed (Green et al., 2009; Yuan et al., 2013) and a broad range of possible applications were highlighted such as the development of electrochemical devices (based on poly(1-vinyl-3-ethyl imidazolium) bistrifluoromethane sulfonamide); of polymeric surfactants in the synthesis of conductive polymer organic dispersions (based on poly(3,4-ethylenedioxythiophene copolymerized with poly(1-vinyl-3-ethylimidazolium bromide)), of anion sensitive smart materials; of cationic and anionic PIL brushes. There and also other emerging applications that include reversible sorption of CO₂ (based on poly[1-(4-vinylbenzyl)-3-butylimidazolium tetrafluoroborate), selective coatings, catalysts, stationary phases for chromatography and bio-sensing (Mecerreyes, 2011; Yuan et al., 2013).

2. Materials and methods

2.1. Chemicals

3-Sulfopropyl acrylate potassium salt ($M_w=232,3$ g/mol), hydroxyethyl methacrylate ($M_w=130,14$ g/mol; $\geq 99\%$), ammonium persulfate ($M_w=228,18$ g/mol; 98%), lithium bis(trifluoromethanesulfonyl)imide ($M_w=287,09$ g/mol), phosphate buffered saline (pH=7.4 at 25°C), L-tryptophan ($M_w=204,23$ g/mol; $\geq 98\%$), methylenebis(acrylamide) ($M_w=154,17$ g/mol; 99%) and Potassium Chromate salt ($M_w=194,19$; 99%) were purchased from Sigma-Aldrich Portugal and used as received. Bromocresol green sodium salt was obtained from Estabelecimentos Barral, Portugal and used as received. 1-butyl-3-vinylimidazolium chloride ($M_w=186,68$ g/mol; $\geq 99\%$) was purchased from Ionic Liquids Technologies GmbH, Germany. It is worth to mention that all the monomers used in this work are sold out with stabilizers in order to minimize polymerization reactions inside the package. These stabilizers should be removed in order to maximize the polymerization yields however in this work they were used as received.

2.2. Synthesis of polyelectrolytes and polyampholytes

Different types of charged hydrogels were synthesized by free radical polymerization in aqueous media using ammonium persulfate (APS) as a thermal initiator (at 0.5 % molar relatively to the total number of monomers in solution). The monomers used to produce the charged copolymers were 1-butyl-3-vinylimidazolium chloride (BVimCl) and 3-sulfopropyl-acrylate potassium salt (SPAK) at different BVimCl/SPAK molar ratios (0/100, 25/75, 50/50, 75/25 and 100/0) in order to control the type and density of ionic charges in the hydrogels. The monomer 2-hydroxyethyl methacrylate (HEMA) was also used at a fixed amount (7,16 mmol) in all cases as the non-charged polymer backbone. The total number of moles of monomers used to prepare each hydrogel was 15 mmol. This means that the amount of HEMA used in each synthesis represents almost 50% of the total molar number in each sample and the remaining 50% correspond to the above referred different molar ratios of BVimCl/SPAK. Crosslinked hydrogels were also prepared by using N,N'-

methylenebis(acrylamide)(MBA) as crosslinker agent at two different molar percentages (0.5 and 1%) relatively to the total number of monomers in solution. Non-charged crosslinked and non-crosslinked poly(HEMA) was also prepared for comparison purposes. The chemical structure of the monomers used in this work is given in Figure 2 and the chemical composition of each hydrogel is summarized in Table 2.

To prepare the ionic hydrogels the monomers were dissolved in 2ml of distilled water and stirred for 30 minutes. In the case of the chemically cross-linked samples, MBA was also added at this stage. The initiator APS was then added and the samples were further stirred for 15 minutes and then degassed for 3 minutes using ultrasounds at 40°C to remove dissolved oxygen. In order to control the size and thickness of the hydrogels, the degassed homogeneous solutions were inserted between two glass plates covered by acetate sheets and separated by a silicone spacer with 2 mm. Polymerization was carried out in an oven at 50°C for 24h and then at 70°C for 24h. All the hydrogels were synthesized in duplicates to ensure reproducibility.

After polymerization samples were washed to remove unreacted monomers by immersion in a large amount of distilled water (2 liters/sample), which was changed twice. To ensure maximum monomer removal the water was analyzed by UV-Vis until no peak was detected. On average each sample was completely washed after using 10 liters of distilled water. After washing the samples were dried at 50°C until complete dryness (approximately 3 days depending on the water content).

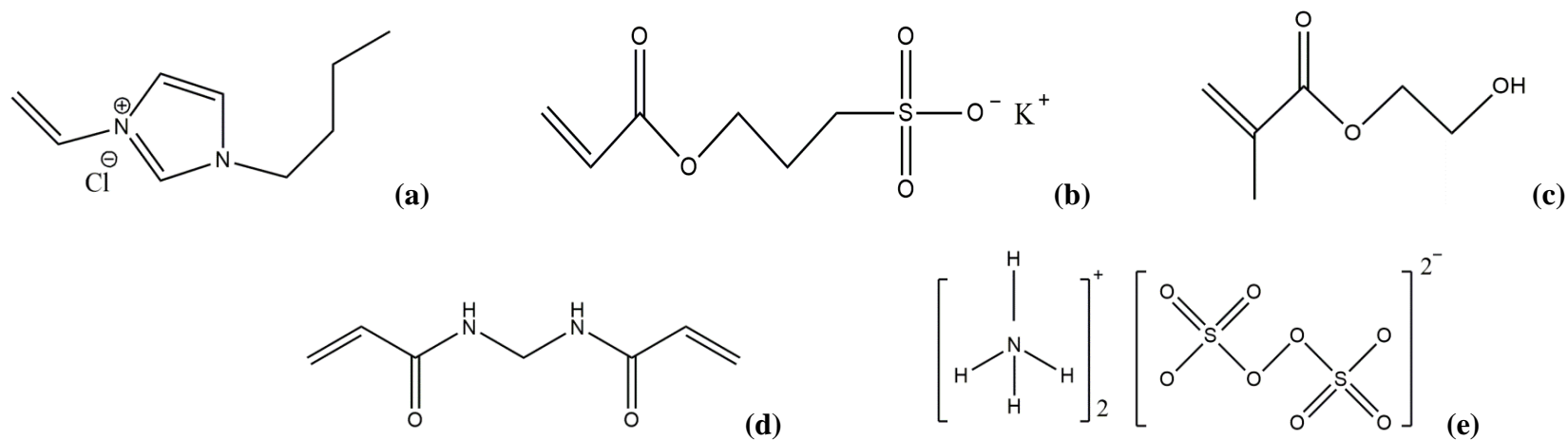


Figure 2. Chemical structures of the monomers BVImCl (a), SPAK (b) and HEMA (c); of the crosslinker MBA (d) and of the initiator APS (e).

Table 2. Summary table of synthesized PILs according to chemical composition.

Hydrogel samples															
	25/75 R0	25/75 R0.5	25/75 R1	50/50 R0	50/50 R0.5	50/50 R1	75/25 R0	75/25 R0.5	75/25 R1	100/0 R0	100/0 R1	0/100 R0	0/100 R1	P(HEMA) R0	P(HEMA) R1
BVimCl	25			50			75			100		0		0	
SPAK	75			50			25			0		100		0	
HEMA	~ 50			~ 50			~ 50			~50		~50		100	
MBA	0	0.5	1	0	0.5	1	0	0.5	1	0	1	0	1	0	1
APS	0.5														

The general reaction mechanism includes three main steps for chain growth: initiation, propagation and termination. Initiation is the first step of chain growth polymerization and starts when an energy source (temperature in this case) creates an active center in the initiator, leading to the formation of radicals, as is it shown in Figure 3.

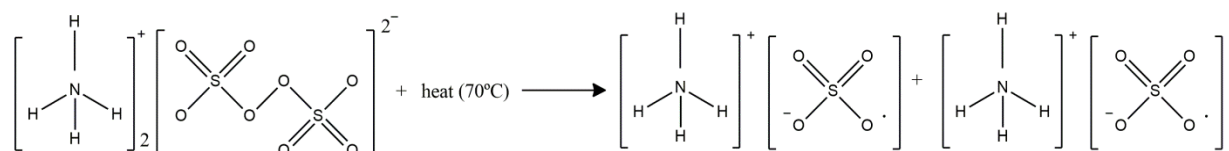


Figure 3. Initiation step: Thermal decomposition of APS.

Radicals grow and propagate really quickly and the second step starts: propagation. During this step, the radical initiator attacks the monomer(s) and free radical polymerization starts. There will be a chain growth or chain propagation, which is influenced by chain and monomer reactivity, monomer availability, solvent and temperature. A possible mechanism of chain propagation is schematized in Figure 4. It should be noted that this is a free radical polymerization, which occurs extremely quickly and randomly therefore Figure 4 only intends to illustrate what could happen in an ideal system, for an equal molar quantity of cationic and anionic monomers.

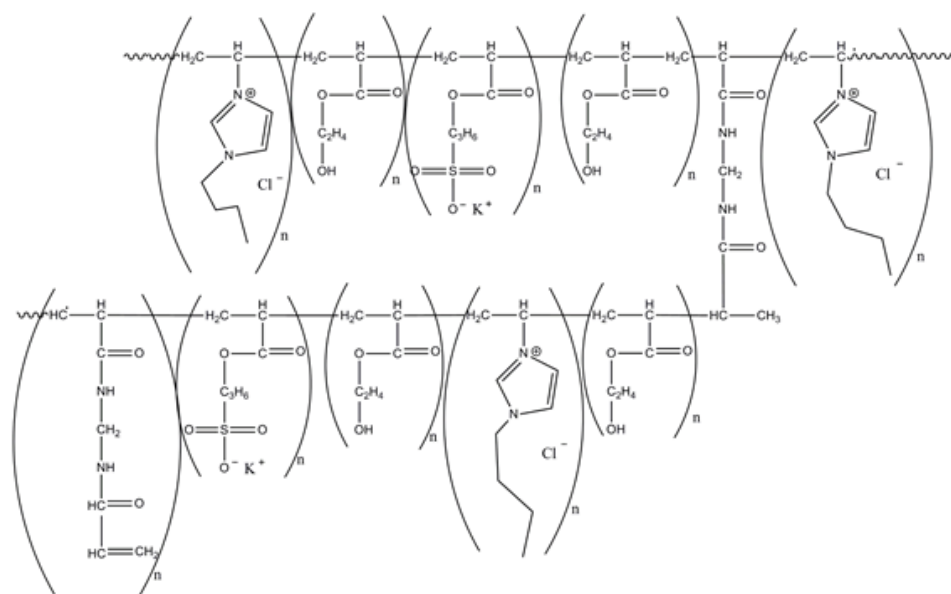


Figure 4. Schematic representation of the propagation mechanisms for crosslinked copolymer (HEMA- BVImCl- SPAK) (d).

2.2.1. Anion exchange (substitute $[Cl]^-$ by $[Tf_2N]^-$)

Poly(butyl 3-vinylimidazolium-(trifluoromethanesulfonyl)imide) was synthesized through anion exchange of the chlorine anion from the 75/25 sample with the bis(trifluoromethanesulfonyl)imide anion of lithium bis(trifluoromethanesulfonyl)imide (Li-Tf₂N), as described in literature with some adjustments (Mi et al, 2013): 100 mg of 75/25 (0.24 mmol of IL) was placed in an aqueous solution (80 mL) with an excess of Li-Tf₂N (0.468 mmol) and stirred for 24h at ambient temperature. The obtained polymer, 75/25-Tf₂N, was with filter paper and washed 4 times with distilled water. After being completely dried the hydrophobic 75/25-Tf₂N sample weighted 95.43 mg. The molecular weight of chlorine is 35,45 g/mol and that of bis(trifluoromethanesulfonyl)imide is 280,15 g/mol. Therefore, during experiments where 75/25-Cl is compared with 75/25-Tf₂N, it is essential to consider this difference in order to have the same molar number of charges to permit fair comparison.

2.3. Characterization tests

2.3.1 Elemental analysis

The real charge composition of each prepared hydrogel was determined by elemental analysis. This method consists in burning the dried samples in an excess of oxygen and further quantification of the combustion products to obtain the ration of the elements that compose the sample. The amounts of carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) in percent weight of the hydrogel were determined by the differential thermal conductivity method using a Fisons Instruments EA 1108 analyzer. Samples were analyzed in triplicate. The real molar fractions of BVimCl and SPAK in the hydrogels were calculated by considering that the molar fraction of BVimCl is half of that calculated for nitrogen while the molar fraction of SPAK is equal to that calculated for sulfur (according to their respective molecular structure given in Figure 2). The values were calculated considering average sulfur and nitrogen molar fractions.

2.3.2. Fourier transform infrared transmission spectroscopy (FTIR)-KBr

A Fourier transform infrared spectrometer (FT/IR Nicolet IR 300) was used in transmission mode at 4 cm^{-1} resolution using 128 scans between 500 and 4000 cm^{-1} , to identify the functional groups of BVimCl and SPAK, as well as their possible interactions. To prepare the FTIR-KBR pellets, $0,5-0,6$ mg of hand grinded dry sample was mixed with KBr, both previously stored at 50°C for 24h, in a 1:100 proportion. After mixing, the pellet was prepared using a hand press.

2.3.3. Scanning electron microscopy analysis (SEM)

The surface and cross section morphologies and spatial distribution and homogeneity of the monomers BVimCl and SPAK in the prepared hydrogels was analyzed using a scanning electron microscope (Jeol, model JSM 5310, Japan), coupled to energy dispersive X-rays (Phillips, EDX Genesis, model XL 30). SEM-EDX micrographs were obtained at 10 kV for gold-sputtered samples.

2.3.4. Water swelling (WS)

Dried samples of each hydrogel were maintained at 25°C in controlled humidity with silica-gel for 24 h before analyses. After initial weighing, each sample was immersed in 15 ml of distilled water or in 15 ml of PBS buffer ($\text{pH} = 7,4$), both at 25°C . The mass of the samples was measured at fixed time intervals of 30 minutes in the first 3 hours and then at each hour until equilibrium. Before weighting the excess surface water was removed using a filter paper. After weighting the samples were returned to the same media (water or PBS buffer). The amount of water absorbed by each hydrogel was calculated using the following equation:

$$SW (g_{\text{water}}/g_{\text{hydrogel}}) = \frac{m_t - m_i}{m_i}$$

where m_t is the mass of the swollen hydrogel at time t and m_i is the initial mass of the dry hydrogel. Measurements were performed in duplicate for each sample.

2.3.5. Water Vapor Sorption (WVS)

To perform the water vapor sorption experiments, hydrogel samples were previously stored in vacuum at 25°C for 24 h. The tests were carried out by keeping the samples in flasks inside a desiccator containing a potassium sulfate saturated solution, providing a relative humidity of ~99% at 25°C. The dried hydrogel and the system flask+sample were first weighted and then stored at controlled atmosphere. The system flask+sample was then weighted at regular time intervals of 1 h or 2 h. The water vapor sorption of each sample was calculated using the following equation:

$$WVS (\%) = \frac{m_t - m_{t0}}{m_i} \times 100$$

where m_t is the mass of the system flask+sample at time t and m_{t0} is the mass of the system flask+sample at time $t=0$ and m_i the initial mass of the dry hydrogel. All the samples were measured very carefully but fast enough in order to keep the equilibrium atmosphere inside the flasks. Measurements were performed in duplicate for each sample.

2.3.6. Thermal characterization – SDT and DSC

The thermal stability of the hydrogels was measured by thermogravimetric analysis using a Thermogravimetric Analyzer (TA Instruments, Q600, USA). Dried samples (4-7 mg) were placed in an alumina pan and analyzed from room temperature up to 600 °C, at a heating rate of 10 °C min⁻¹, under a dry nitrogen atmosphere (flow rate 100 ml min⁻¹). Fully water swelled hydrogels (equilibrated in distilled water for 24 h) were also analyzed up to 250 °C, at the same heating rate and nitrogen atmosphere, in order to quantify the total amount of water absorbed by the hydrogels and to compare with the results obtained from the water swelling experiments.

Differential scanning calorimetry (DSC) analysis was used to identify the existence of thermal events such as melting, freezing and glass transition temperatures and/or enthalpies in the hydrogels. Analyses were performed using a DSC-Q100 equipment (TA Instruments) and water vapor saturated samples sealed in aluminum pans with a pinhole. Before measurements samples were stored for 1 week at 90 % RH to guarantee that water vapor sorption equilibrium is attained. Measurements were carried out by consecutive cooling, heating and re-cooling runs at an inert

nitrogen atmosphere (50 ml min^{-1}) according to the following sequence: samples were equilibrated at $40 \text{ }^\circ\text{C}$, cooled down to $-80 \text{ }^\circ\text{C}$, heated up to $100 \text{ }^\circ\text{C}$, equilibrated for 10 minutes and then re-cooled again to -80°C . This cycle was repeated 3 times until any traces of water are detected during the cooling/heating runs. By using this procedure it was possible to simultaneously identify and quantify the thermal events promoted by the water absorbed by the hydrogels and those present in the dried samples. Notice that attempts were made to measure the thermal events of the fully water swelled samples but it was not possible due to the large amount of water absorbed by the prepared hydrogels (including those that were cross-linked with MBA).

2.3.7. Mechanical properties – Tensile tests

Tensile mechanical properties were measured at room temperature using a Mechanical tests were carried out in tensile mode using a texture profile analyzer (TA-XT Express, Stable Micro Systems Ltd., U.K.) at room temperature for 50/50 samples. The initial gauge length and testing speed were approximately 20 mm and 2 mm/s, respectively (for a test distance of 40 mm and 5 g trigger force). The thickness of each film was measured at three different points using a digital micrometer (Mitutoya, model MDC-25S, Japan).

Tensile strength and maximum elongation are properties directly measured with tensile tests. However, others that can be determined through these previous properties such as Young's modulus or yield strength. Thus, through the maximum force applied to the sample before disruption measured by the equipment allows to determine tensile stress (σ_t), tensile strain (ε_t) and Young's modulus (E) of the samples through stress-strain curves. First, tensile stress was obtained in MPa by the following equation:

$$\sigma_t(\text{MPa}) = \frac{F}{A_0}$$

where F is the maximum force applied to the sample before disruption in grams and A_0 is the initial cross-section area in mm^2 . During the tests, the elongation of the sample is registered under the effect of applied force. This elongation measurements or total deformation from the initial dimension, L_0 , allows to determine the strain, ε , through the following equation:

$$\varepsilon_t = \frac{\Delta L}{L_0}$$

where $\Delta L = L - L_0$, representing the change in gauge length. Through both of these two estimated properties it is possible to determine the Young's modulus or elastic modulus, which is a measure of a material's resistance to being deformed elastically when a force is applied (for the linear part of the curve):

$$E \text{ (MPa)} = \frac{\sigma}{\varepsilon}$$

Furthermore, during the tensile tests it was also studied the hydrogel's linear elasticity, which is the ability of the hydrogel to undergo reversible deformation.

The tests were performed using 50/50 samples fully hydrated in PBS, previously cut in rectangular shape. Tests were also performed for the samples swelled in water but the results were not conclusive because the samples have low mechanical stability due to their relative high swelling degree. The other prepared hydrogels did not present enough mechanical strength that permits them to be analyzed by this technique

2.3.8. Adsorption experiments

The adsorption kinetic studies were measured for different charged molecules, namely chromate (Cr VI), L-tryptophan and bromocresol green sodium salt. Measurements were performed using a spectrophotometer (Jasco, model V650, Japan) by monitoring the maximum absorbance at a fixed wavelength depending on the adsorbate. Each sample/solvent/adsorbate concentration ratio was previously optimized in preliminary tests. Pre-swollen samples were immersed in each solution and at regular time intervals an aliquot was removed and analyzed in the spectrophotometer. Samples were previously swollen in order to avoid volume changes in the solution were they are immersed considering their high water swelling capacity. After measurement the aliquot was returned to the original solution. In all cases the samples were stored at 25°C with stirring (100 rpm) and the measurements were performed at the same temperature. The measurements were performed in duplicate for all samples and until a constant adsorption profile was reached. Details for each absorbent are the following:

- Adsorption of Cr (VI): samples of pre-swelled hydrogels (~50 mg) were immersed into 50 ml of a potassium chromate (K_2CrO_4) aqueous solution (20 mg/l) and placed in a thermo-shaker at 25°C and 100 rpm. The absorbance was measured at 370 nm and the mass of Cr (VI) adsorbed was quantified using the calibration curve given in appendix B. The samples analyzed in this case were those with a higher amount of BVImCl (75/25) without crosslink, because the solute to be absorbed is negatively charged. Moreover, the influence of the surface area of the samples and also the influence of IL's anion on the mass of solute absorbed was also studied by testing the samples dried in a conventional oven and freeze dried, and also samples after anion exchange (75/25-Tf₂N).

- Adsorption of L-tryptophan: samples of pre-swelled hydrogels (10 or 120 mg) were immersed into 10 and 50 mL, respectively of an L-tryptophan aqueous solution (~50 mg/l) and placed in a thermo-shaker at 25°C and 100 ppm. The absorbance was measured at 278 nm and the mass of L-tryptophan absorbed was quantified using the calibration curve given in appendix B. The samples analyzed in this case were those with higher amount of SPAK (25/75) and with higher amount of BVImCl (75/25), because L-tryptophan was on its isoelectric point, therefore it has an equal amount of positive and negatively charges. The influence of the surface area of the samples on the amount of solute adsorbed was also studied by testing samples dried in a conventional oven and freeze dried.

- Adsorption of bromocresol green sodium salt: samples of pre-swelled hydrogels (~ 10 mg) were immersed into 10 ml of a bromocresol green sodium salt aqueous solution (20 mg/l) and placed in a thermo-shaker at 25°C and 100 rpm. The absorbance was measured at 616 nm and the mass of Cr (VI) absorbed was quantified using the calibration curve given in appendix B. The samples analyzed in this case were those with a higher amount of BVimCl (75/25, 75/25-R1, A100/0 and A100/0-R1) because the solute to be absorbed is negatively charged. The influence of the porosity of the samples on the amount of solute absorbed was also studied by testing samples dried in a conventional oven and freeze dried.

3. Experimental results and discussion

3.1. Elemental analysis

Elemental analysis was performed in order to quantify the real composition of the materials obtained after the polymerization and washing procedures.

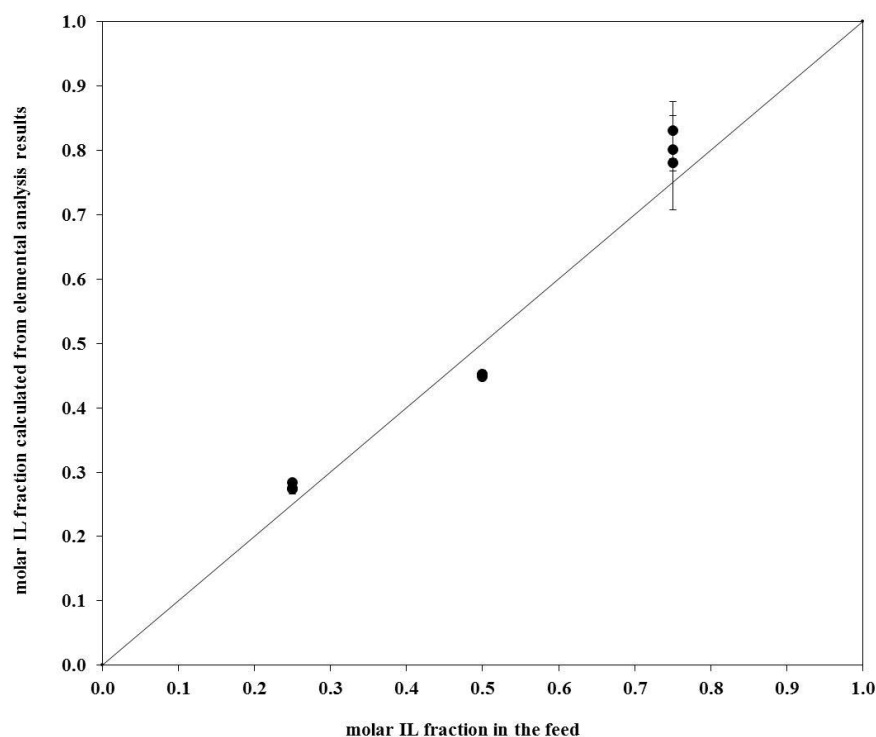


Figure 5. Molar compositions of monomers obtained from elemental analysis as a function of compositions of monomer in feed mixture.

Figure 5 presents the molar compositions of the monomers used to prepare samples 25/75, 50/50 and 75/25, with and without crosslinker (monomers in the feed) versus the molar compositions for the corresponding samples obtained from elemental analysis. The results demonstrate that the cation/anion molar ratio of the synthesized samples is similar to that expected theoretically (diagonal line). Although some deviations were observed: samples 25/75 and 75/25 have more IL than expected (~11 and 7%, respectively) while samples 50/50 have less IL than expected (~10%). This result indicates that samples 50/50 are not neutral as originally planned but may present an excess of anionic groups, since its real composition is 45/55. Nevertheless a clear gradual increase in the amount of cationic groups is still verified for the prepared samples 25/75 < 50/50 < 75/25. The samples that present higher deviations

on the expected chemical composition are the ones that contain higher IL amounts. The influence of the crosslinker on these samples is also more visible than for samples 25/75 and 50/50. The differences observed may be due to several factors such as differences in the reactivity of the monomers, un-complete polymerization or loss of low molecular polymer chains while washing, among others. In future works it would be interesting to study the feed compositions that should be used in order to obtain a neutral polyampholytes as previously reported in the literature (Ihsan et al., 2013).

3.2. Fourier transform infrared transmission spectroscopy

FTIR transmission spectroscopic measurements (using KBr pellet) were performed in order to identify the monomers present in each sample and also the existence of possible interactions among them. Poly(HEMA) has a O-H stretching region between 3200 and 3666 cm^{-1} , which is also visible in almost all polymers due to the presence of water, even when it is present at small quantities. In this case this region appears in the spectrum not only due to water content but also due to the stretching of the hydroxyl groups. This broad band masks a first overtone of the C=O stretching at 3434 cm^{-1} . Another characteristic range to detect the C=O band is between 1660 - 1772 cm^{-1} . with maximum at 1724 cm^{-1} (Morita, 2014).

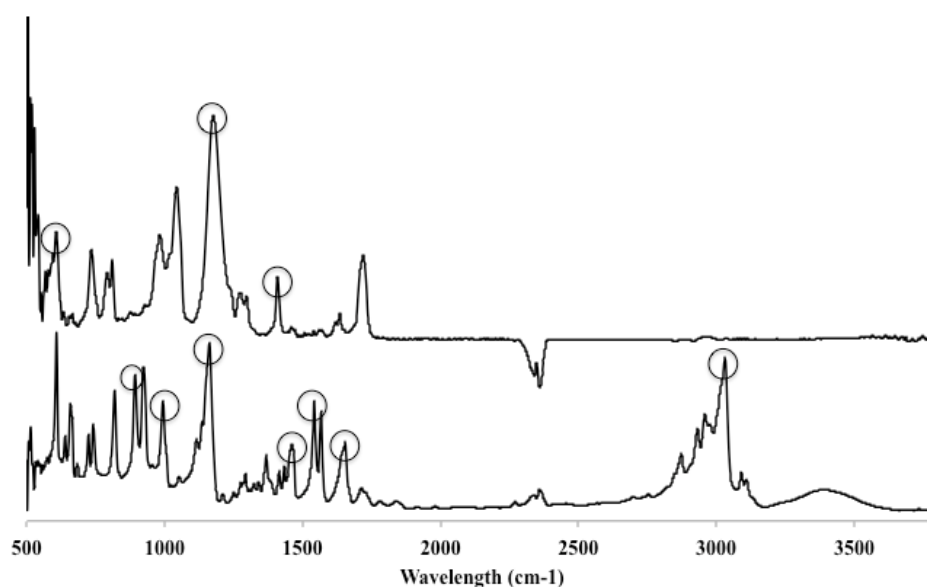


Figure 6. FTIR-KBr spectrum of SPAK (top) and BVImCl (bottom) monomers.

Typical SPAK and BVImCl monomer bands are identified in Figure 6. Those for SPAK corresponds to C-S stretching at 607 cm^{-1} , SO_3 symmetrical stretching at 1141 cm^{-1} and SO_3 unsymmetrical stretching at 1392 cm^{-1} (Narimani et al, 2012). Typical BVImCl bands can be found in the range $890\text{-}1540\text{ cm}^{-1}$ for the imidazolium ring. more specifically at 890 cm^{-1} for the imidazole ring in plane bending (Rajkumar & Rao, 2008)), at 1160 cm^{-1} for the imidazolium H-C-N vibration, at 1460 cm^{-1} for the imidazolium ring vibration (Minamimoto et al, 2015) and at 1540 cm^{-1} for the imidazolium ring stretching (Epishina et al, 1967). It is also possible to find bands for vinyl bonds at 990 cm^{-1} and 1648 cm^{-1} (Dharaskar et al. 2013) and for N-H stretching at 3030 cm^{-1} (Minamimoto et al, 2015).

Figure 7 illustrates the FTIR-KBr spectrum of non-crosslinked co-polymer samples 25/75, 50/50 and 75/25 samples when compared with poly(HEMA). The dark circles highlighted in the spectra of poly(HEMA) and modified poly(HEMA) hydrogels identify the new peaks that appear the co-polymer matrices and those that disappear when compared to the original poly(HEMA) matrix. Such differences demonstrate that the poly(HEMA) matrix was modified with both BVImCl and SPAK. In the dashed lines spectra, which correspond to the co-polymer samples, the peaks situated between 600 and 700 cm^{-1} show an evidence of the presence of SPAK, while peaks between 1000 and 1120 cm^{-1} can indicate the presence of BVImCl or SPAK. Furthermore, the peak between 1550 and 1650 cm^{-1} that appears in all spectra confirms the presence of BVImCl. In Figure 7 it is also possible to see that samples 25/75, 50/50 and 75/25 show almost the same peaks for the same wavelength, indicating that all the monomers are present, as expected, although at different molar ratios which cannot be concluded from the spectra because this technique is not quantitative.

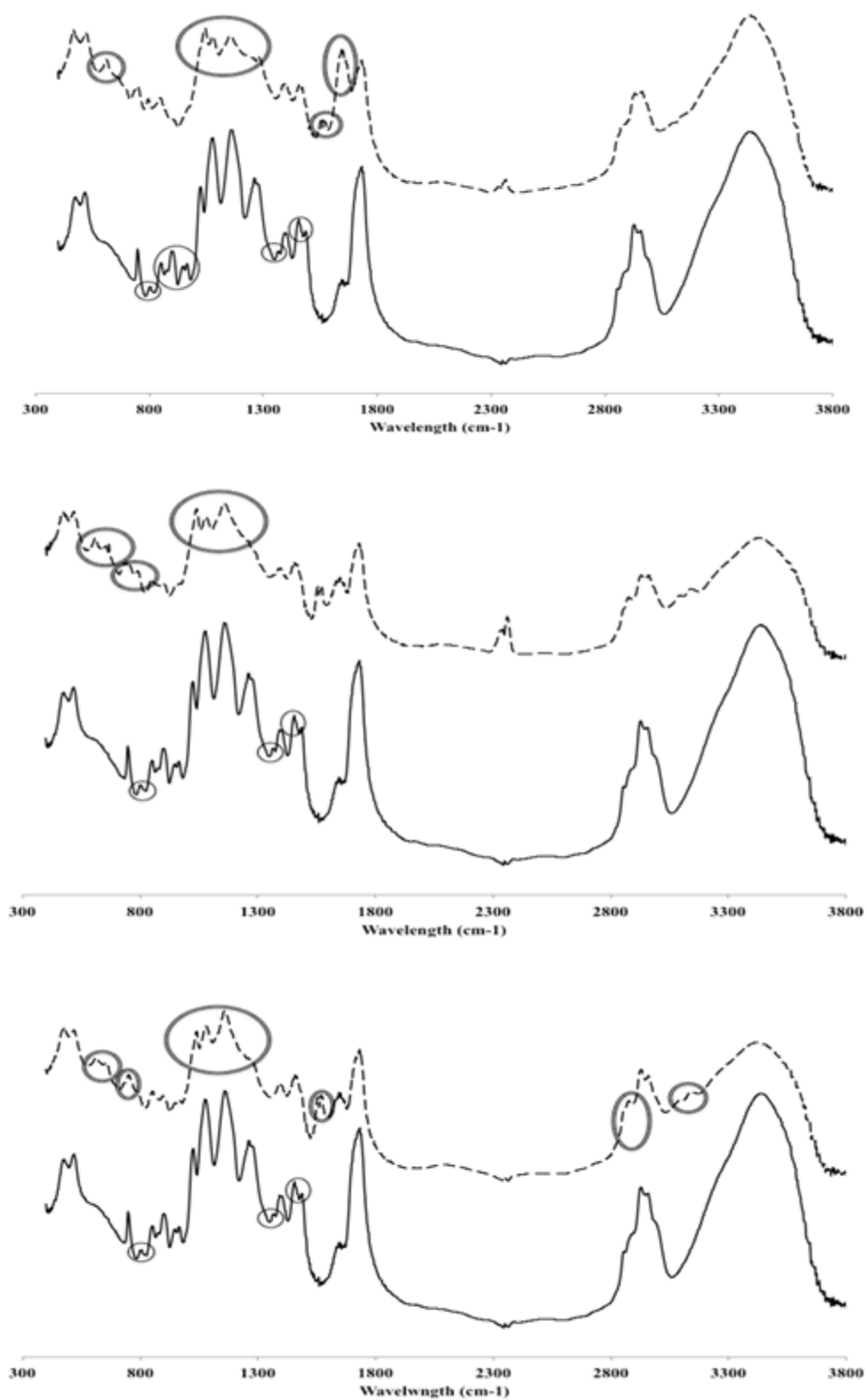


Figure 7. FTIR-KBr spectrum of poly(HEMA) (full line) compared with the copolymers (dashed lines) 25/75 (top), 50/50 (middle) and 75/25 (bottom) .

3.3. Scanning electron microscopy with energy dispersive X-ray analysis

SEM-EDX was performed for samples 25/75, 50/50 and 75/25 in order to understand if the monomers were homogeneously distributed in the polymeric matrix.

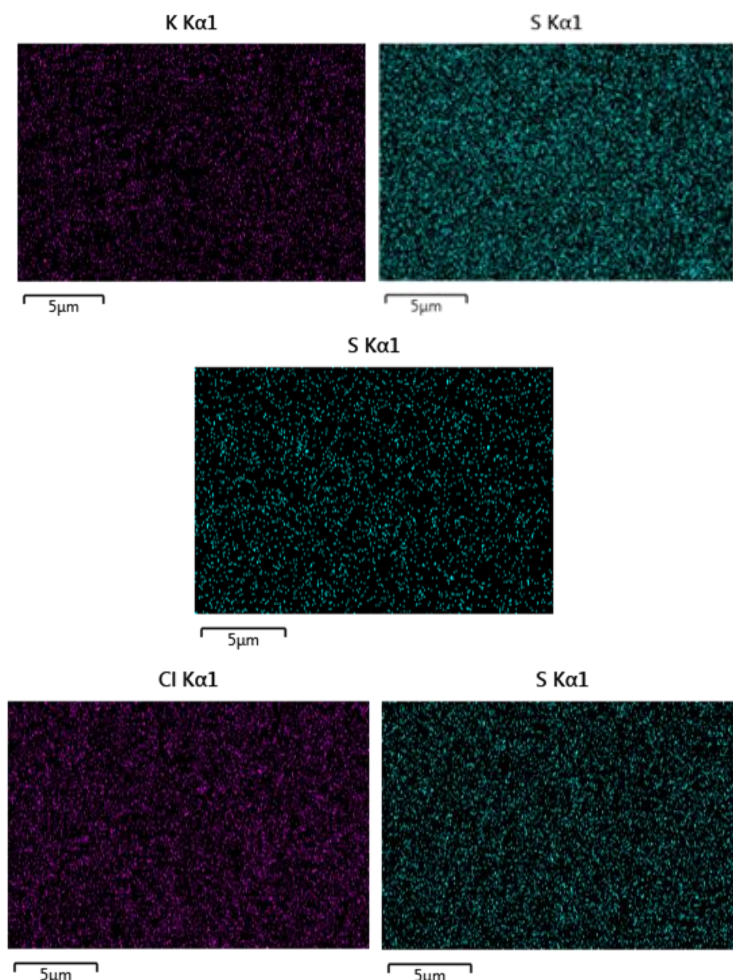


Figure 8. Surface SEM-EDX micrographs for samples 25/75 (top), 50/50 (middle) and 75/25 (bottom).

From Figure 8 it is possible to confirm for all three samples that the monomers are homogeneously distributed in the polymeric matrix. It should be noted that for the samples with more SPAK (25/75) sulfur was detected but it wasn't possible to detect chlorine or nitrogen atoms from the IL. However for samples with more IL both chlorine and sulfur atoms were identified (Figure 8 bottom). Finally, for samples 50/50 the only element detected by this technique was sulfur. Such results mean that is easier to identify the key elements when they are presented in the matrix in higher molar quantity, although sulfur was an exception as is possible to see in figure 8 (top).

3.4. Water swelling capacity

The water swelling capacity of hydrogels may be triggered by internal or external stimulus like changes in ion strength, pH or temperature (Shah. et al. 2015). Those stimuli create a driving force between the inside and the outside of the polymeric network, inducing a solvent flow that causes volumetric changes in the hydrogel network, as illustrated in Figure 9.

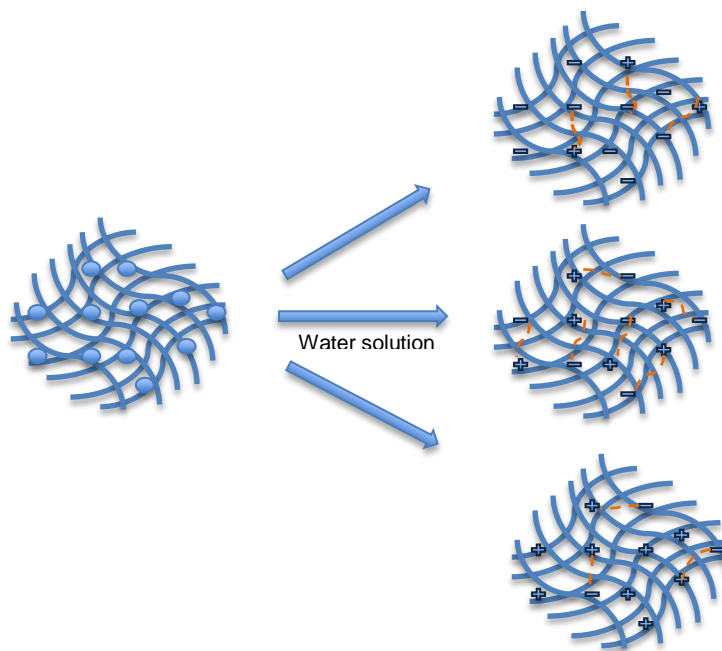


Figure 9. Illustration of hydrogels behavior in the presence of water: 25/75 (top), 50/50 (middle), 75/25 (bottom).

However the network of the hydrogel must contain hydrophilic groups and/or groups that are sensitive to the applied stimuli. By controlling the amount/type of those sensitive groups as well as by increasing/decreasing the crosslinking degree of the hydrogel it is possible to control its water swelling behavior (Bag & Rao. 2006; Gerlach & Arndt. 2009). In this work, the water swelling capacities of the prepared polyelectrolytes were studied at 25°C in order to understand the effect of the amount/type of ionic groups present in the hydrogel; hydrogel's crosslinking degree; and ionic strength of the media on the water swelling capacity of the prepared polyelectrolytes.

3.4.1. Effect of the amount/type of ionic groups present in the hydrogel

To understand the effect of the presence of positive and negative charges on the water swelling capacity of the hydrogels, three monomer ratios were used and the results are shown in Figure 10. It can be observed that, in fact, the amount of charges in the polymeric network affects drastically the swelling degree as predicted in the literature (Gerlach & Arndt. 2009).

When the charged samples are immersed in water, an osmotic driving force is created, forcing the water to go inside the polymeric network in order to “dilute” the charges. Therefore, the copolymers containing a large amount of ionic groups (samples 25/75 and 75/25) have an enormous swelling degree. Up to 100g of water/g of dry sample, which is significantly higher than that measured for the non-charged poly(HEMA), as desired. Such results indicate that both hydrogels fit in SAP classification, once according to their definition are able to absorb more than 100 times their dry weight (Gawande & Mungray, 2015; Guilherme et al., 2015). According to what was expected, poly(HEMA) has a negligible water sorption capacity and that is why there are numerous studies on poly(HEMA) functionalization in order to develop a more hydrophilic polymer for biomedical applications (Hackl et al, 2015; Lord et al, 2006).

It is interesting to refer that the sample 50/50 has a swelling degree higher than poly(HEMA) but significantly lower (~400%) than samples 25/75 and 75/25. This may happen because in sample 50/50 there is almost equilibrium between positive and negative charges, which may cancel each other, leading to an almost neutral network, which consequently will absorb a lower amount of water. For sample 50/50 the amount of charges inside the network is lower leading to a lower osmotic pressure between the inside and the outside of the network which results in a decrease on the water swelling capacity of this sample.

Sample 50/50 is not completely neutral because it has an excess of negative charges as previously discussed based on elemental analysis results and that is why the swelling capacity of samples 50/50 is higher than that of poly(HEMA). A hypothesis for the complexation mechanism, due to electrostatic forces, that may be occurring is represented in orange lines in Figure 9. This mechanism may in fact happen also for samples 25/75 and 75/25. For example, in the case of sample 25/75

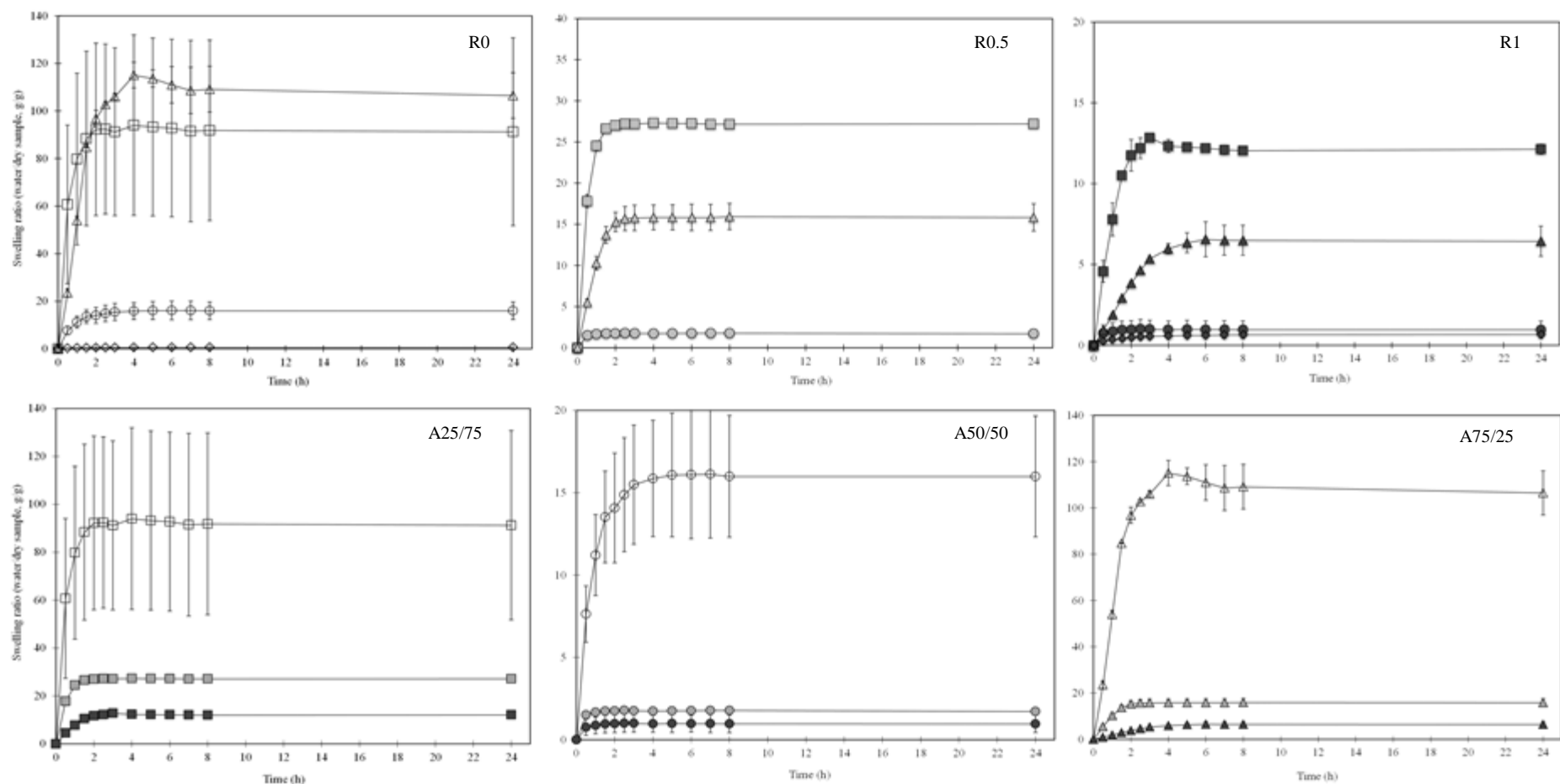


Figure 10. Effect of ionic groups and crosslinking degree on the water swelling behavior of hydrogels in water: 25/75 (\square), 50/50 (\circ), 75/25 (Δ) and poly(HEMA) (\diamond) for a monitoring period of 24h. Results for non-crosslinked hydrogels are presented as empty symbols; those crosslinked at 0.5% as grey symbols and those crosslinked at 1% as dark symbols.

(copolymer with 25% of positive and 75% of negative charges), it may happen that approximately all the positive charges are complexed with the same percentage of negative charges, leaving only 50% of free negative charges that are in fact responsible for the observed swelling. The opposite occurs for sample 75/25. These charges induce electrostatic repulsion between the polymer chains, leading to an increase in the free volume within the polymer network, which allows water to go inside the mesh (Chen et al, 2000). Furthermore, samples prepared with a higher amount of SPAK may be more hydrophilic due to the higher hydrophilicity of this monomer, that, along with electrostatic repulsions, cause an even higher increase of free volume and consequently, more water will be absorbed.

Finally and as can be observed in Figure 10 (middle and bottom) the same trend is observed for the other crosslinking ratios studied and which will be further discussed in section 3.4.2.

3.4.2. Effect of the crosslinking degree

The presence or absence of crosslinking is another variable that has a significant effect on the swelling behavior hydrogels. Its presence is required to avoid hydrogel's dissolution in water, to enhance its mechanical properties and to control/tune the stimulus response. As the molar percentage of crosslink increases, the lower will be the mobility of the hydrogel chains and the lower is the free volume within those chains that water molecules can occupy (Gerlach & Arndt, 2009; Khalid et al, 2009).

To study the effect of the crosslinking degree on the water swelling capacity, three different molar percentages of the crosslinker MBA were considered and the results are presented in Figure 10. As expected, the swelling capacity decrease as the degree of crosslinking increases. Based on the results given on Table 3 it is possible to conclude that the degree of crosslinking did not affect all the hydrogels in the same way.

Table 3. Effect of the crosslinking degree on the equilibrium water swelling capacity of the prepared hydrogels.

Sample	Equilibrium Water Swelling	Ratio without/with crosslinking
25/75	91,3	--
25/75-R0,5	27,2	3,4
25/75-R1	12,1	7,5
50/50	25,1	--
50/50-R0,5	1,7	14,6
50/50-R1	1	26,1
75/25	106,5	--
75/25-R0,5	15,8	6,7
75/25-R1	6,4	16,5

Based on the results from Table 3 is possible to confirm that the degree of crosslink didn't affect all the polymers the same way. The samples more affected by the crosslinking degree are those that have similar amount of positive and negative charges and therefore are almost neutral, where the samples with 1% of crosslink had a swelling degree 26 times lower than the analogous without crosslink. This may occur mostly because they are affected not only by the chemical crosslinking with MBA but also by the formation ionic complexes between positive and negative charges. On the other hand, the copolymers with more negative charges were less affected by the crosslinking degree, which may be due to the higher hydrophilicity of SPAK that overcomes the effect of the chemical crosslinker.

3.4.3. Effect of the ionic strength of the media

In order to understand the influence of the ionic strength of the media on the kinetics and on the water sorption capacity of hydrogels 25/75, 50/50 and 75/25 were immersed in phosphate buffered saline solution (pH=7.4) with an ionic strength of 0,14M. According to Figure 13 the water swelling capacity at these conditions is significantly lower than that measured in pure water. In the case of PBS buffer the difference between the amount of charged species inside and outside of the polymer network is much lower, what means that less water will flow into the network (Scrantom. et al. 1995) as illustrated in Figure 11.

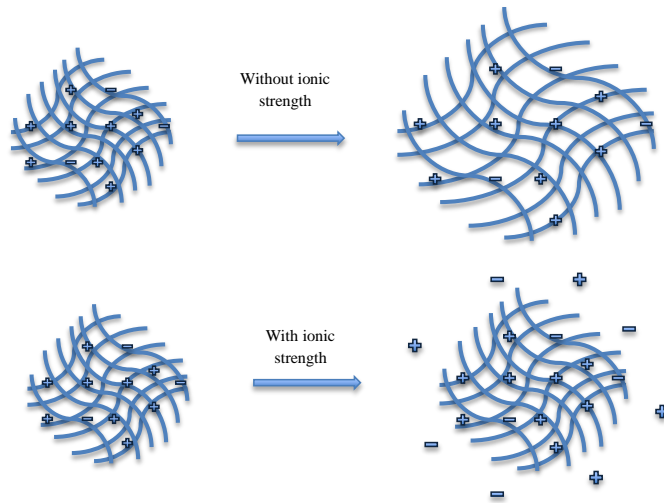


Figure 11. Illustration of hydrogels response in water with (bottom) and without (top) ionic strength.

Figure 12 directly compares the equilibrium water swelling capacity obtained in both media in order to facilitate understanding.

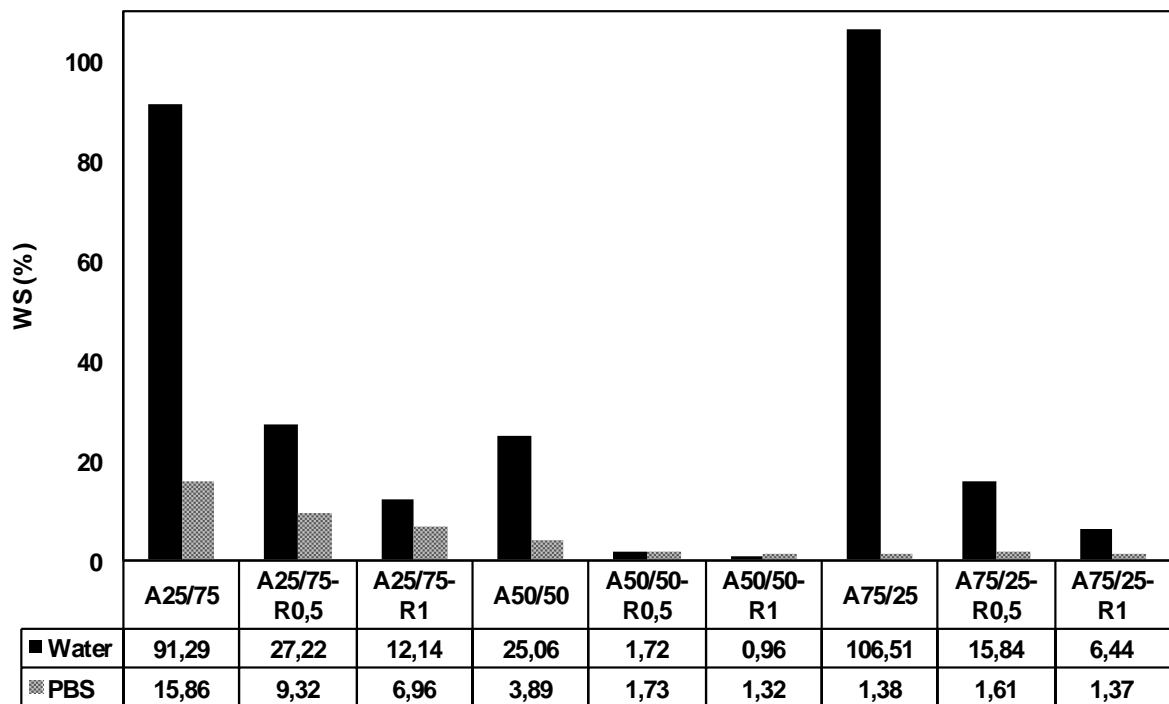


Figure 12. Equilibrium water swelling capacity (after 24h) of crosslinked and non-crosslinked hydrogels 25/75, 50/50 and 75/25 when immersed in water (dark bars) and in PBS (grey bars).

An interesting result is that samples 75/25 (samples with more IL) are much more affected by the ionic strength of the media than samples 25/75. When immersed in water the hydrogel with higher amount of IL (75/25) absorbs more than that with a higher amount of SPAK (25/75) while in PBS it absorbs $\sim 16\times$ less. Notice that the swelling capacity of the non-crosslinked 75/25 sample is only slightly higher than that measure for non-charged poly(HEMA). For crosslinked samples the swelling behavior of samples 75/25 is similar to that measured for samples 50/50. Furthermore, and as expected the swelling degree in PBS also decreases as the crosslinking degree increases (Gerlach et al, 2009; Scrantom et al, 1995). As can be seen in Figure 13 samples 25/75 and 50/50 are more sensitive to the crosslinking degree than samples 75/25. Nevertheless and for all samples the effect of the crosslinking degree is less significant in PBS than in water since in the PBS swelling depends on a combined effect of osmotic gradient and network free volume due to chemical crosslinking while in water it only depends on the later. From Table 4 it is possible to conclude that crosslinking affected all the samples in approximately the same way, except for sample 75/25, that only absorbed 1g of water/g of dry sample.

Table 4. Effect of the crosslinking degree on the equilibrium water swelling capacity in PBS-buffer of the prepared hydrogels.

Sample	Equilibrium Water Swelling (PBS-buffer)	Ratio without/with crosslinking
25/75	15,9	--
25/75-R0,5	9,3	1,7
25/75-R1	7,0	2,3
50/50	3,9	--
50/50-R0,5	1,7	2,2
50/50-R1	1,3	2,9
75/25	1,4	--
75/25-R0,5	1,6	0,9
75/25-R1	1,4	1,0

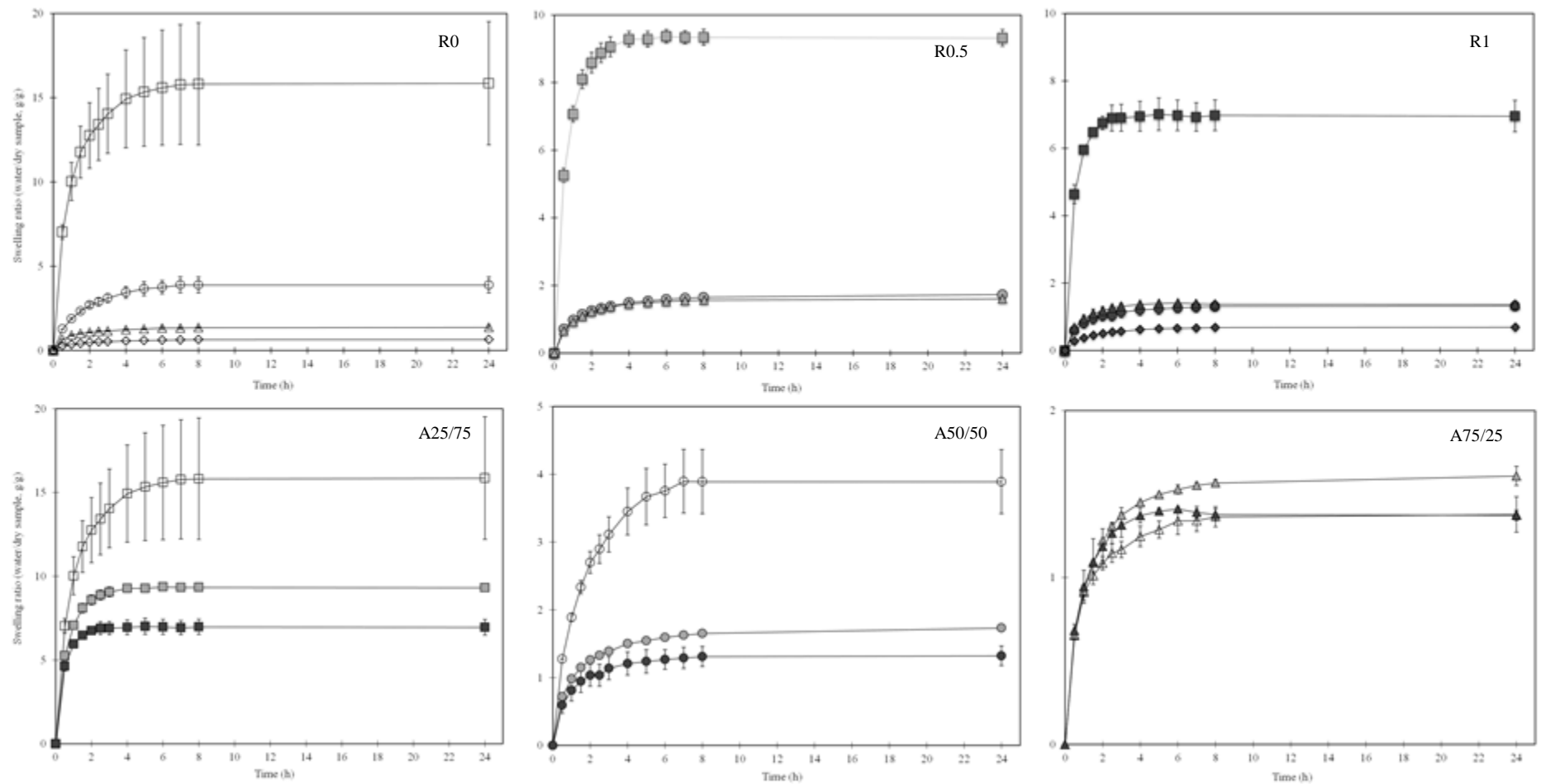


Figure 13. Charges effect on Water Swelling behavior with ionic strength of 25/75 (squares). 50/50 (spheres), 75/25 (triangles) and poly(HEMA) (diamonds) for a monitoring time of 24h. Results for polymers without crosslink are presented in empty symbols (upper figure), 0.5% of crosslink in grey symbols (middle figure) and 1% of crosslink in dark symbols (bottom figure).

3.5. Water vapor sorption capacity

The water vapor sorption capacity of the hydrogels was measured at a high relative-humidity environment (99%) and a constant temperature of 25°C. The measurement of this property is relatively complicated, because there are many variables that can affect it considerably, including the properties of water by itself. Such properties include water's affinity to absorb to high energy surface (as glass), low saturation temperature and slightly high heat of vaporization, which can cause thermal effects on a polymer that does not have a high surface area (Schult & Paul, 1996). However, since all the samples were studied at the same conditions, these effects may be neglected. The phenomena involved in the water vapor sorption capacity of hydrogels is different to that verified for the hydrogels immersed in aqueous media since the osmotic gradient effect is not present. However this property does depend on the chemical composition of the hydrogel and it is an indirect measure of the hydrogel's hydrophilicity. The higher the hydrophilicity the higher the affinity of the water vapor molecules to the network of the hydrogel which will be retained in-between the polymer chains and consequently affect the mechanical properties of the hydrogel by plasticizing it. During the experiments it was indeed observed that the samples became rubber like after attaining water vapor sorption equilibrium.

3.5.1. *Effect of the amount/type of ionic groups present in the hydrogel*

Figure 14 illustrates the water vapor absorption kinetic curves of non-crosslinked hydrogels. The results clearly shows that samples 25/75 and 75/25 present higher WVS than poly(HEMA) meaning that the presence of anionic and cationic groups in samples 25/75 and 75/25 increase the hydrophilicity of the HEMA based hydrogels, as expected. When comparing to non-charged poly(HEMA), equilibrium water vapor sorption increases by 3%, 74% and 20% for samples 50/50, 25/75 and 75/25, respectively. The higher hydrophilicity of SPAK may again explain the higher hydrophilicity of the copolymers containing this monomer. The lower water vapor sorption capacity of the sample 50/50 may be due the complexation of the hydrophilic ionic groups that have therefore lower tendency to interact with water and also due to

a decrease in the free volume within the network that decrease the amount of water vapor molecules that the hydrogel can absorb. Despite osmotic gradients are not present, the observed trends are similar to those measured for the samples immersed in water meaning that the chemical composition of the hydrogels mainly affect their affinities for water molecules.

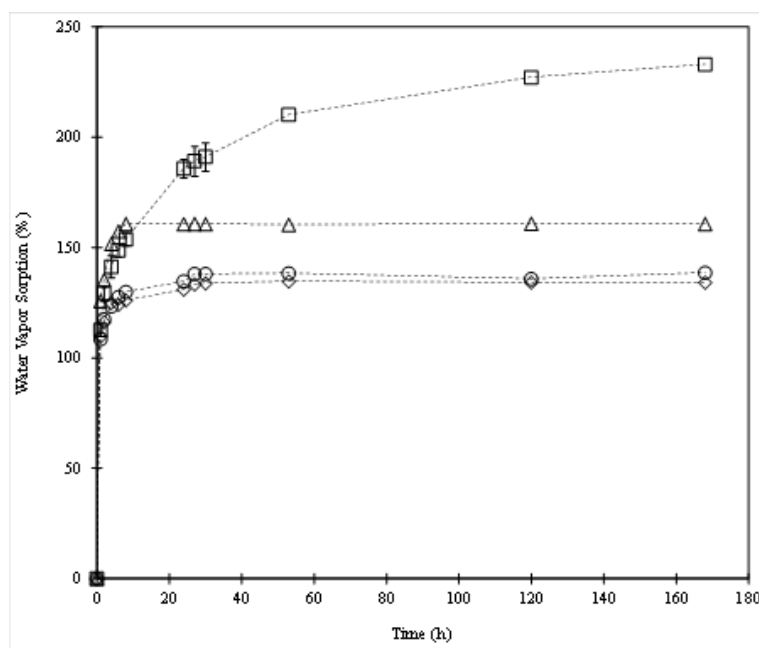


Figure 14. Effect of ionic groups on the water vapor sorption capacity of non-crosslinked hydrogels: 25/75 (□), 50/50 (○), 75/25 (Δ) and poly(HEMA) (◇) for a monitoring period of 7 days.

3.5.2. Effect of the crosslinking degree

Figure 15 suggests that crosslinking does not have a significant effect on the water vapor sorption capacity of the hydrogels, except in the case of the sample 25/75, for which a decrease of 17% was observed when comparing non-crosslinked samples and those crosslinked at 1% of MBA. For the remaining samples, the charge's effect overlapped the influence of the crosslinking degree and almost any change was detected. These results indicate that the crosslinking effect is more important when hydrogel samples are immersed in water because of the flux of water that enters into the network due to osmotic gradients.

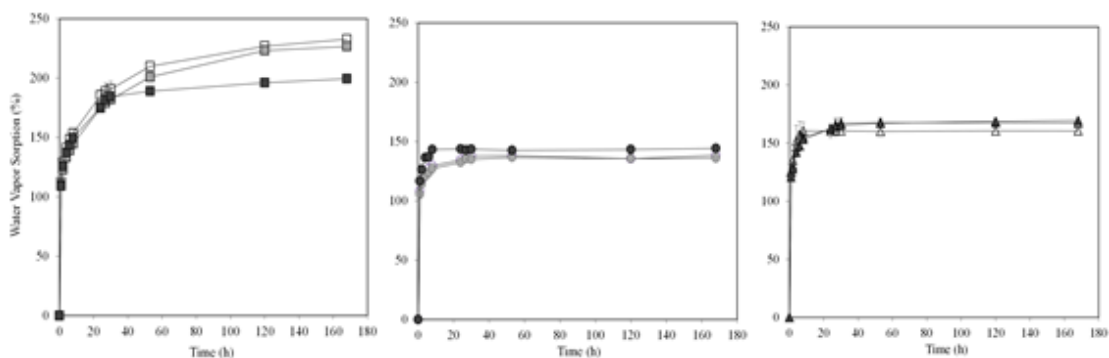


Figure 15. Effect of the crosslinking degree on the water vapor sorption capacity of non-crosslinked and crosslinked hydrogels: 25/75 (squares), 50/50 (circles), 75/25 (triangles) for a monitoring period of 7 days. Results for non-crosslinked hydrogels are presented as empty symbols; those crosslinked at 0.5% as grey symbols and those crosslinked at 1% as dark symbols.

3.4.6. Thermal properties

Polymeric materials may undergo both physical and/or chemical changes when heat is applied depending on their characteristics and also on the intrinsic properties of the monomers. In this work the thermal stability of the produced hydrogels was studied by thermogravimetric analysis. Ionic liquids are usually identified as compounds that present high thermal stability and consequently it may be expected that they originate polymers or copolymers also presenting high thermal stability. Yet, the thermal stability of ILs depends on the cation but also on the anion that constitutes de IL (Mecerreyes. 2011; Yuan. et al. 2011).

Water in hydrogels

Water may flow inside a polymeric network when a driving force is generated between the bulk of the network and the medium inducing the swelling of the network. The amount of water that is absorbed is determined by a number of factors including the network free volume, the network/medium driving force and the hydrophilicity of the functional groups present in the polymer matrix. When the water flows into the hydrogel matrix it preferentially interacts with the hydrophilic groups that exist in the matrix because those interactions are the most thermodynamically

favorable. These water molecules are strongly bounded to the network(hydrogen bonded water) and are usually identified as ‘primary bound water’ or ‘non-freezable water’. Although the interaction of water with exposed hydrophobic groups is not favorable, they are forced to interact due to the osmotic pressure, creating the ‘second bound water’ also known as ‘freezing bound water’, which have weak interactions with the polymer network (Carvalho et al. 2013).Until the swelling equilibrium is not reached, the hydrogel continues to absorb water, even when the hydrophilic and the hydrophobic sites are saturated. This is called ‘free water’ and occupies the free space between the hydrogel chains (Hoffman, 2002). Unlike bonded water and since it is not bonded to the network neither to any functional group, these water molecules may undergo phase transition and even flow out of the hydrogel (deswelling).It is important to notice that this is a dynamic system, what means that water molecules can constantly shift between the bond and the free state.

The influence of IL and SPAK on the thermal stability of poly(HEMA) based copolymers was studied and the results are presented in Figure 16.

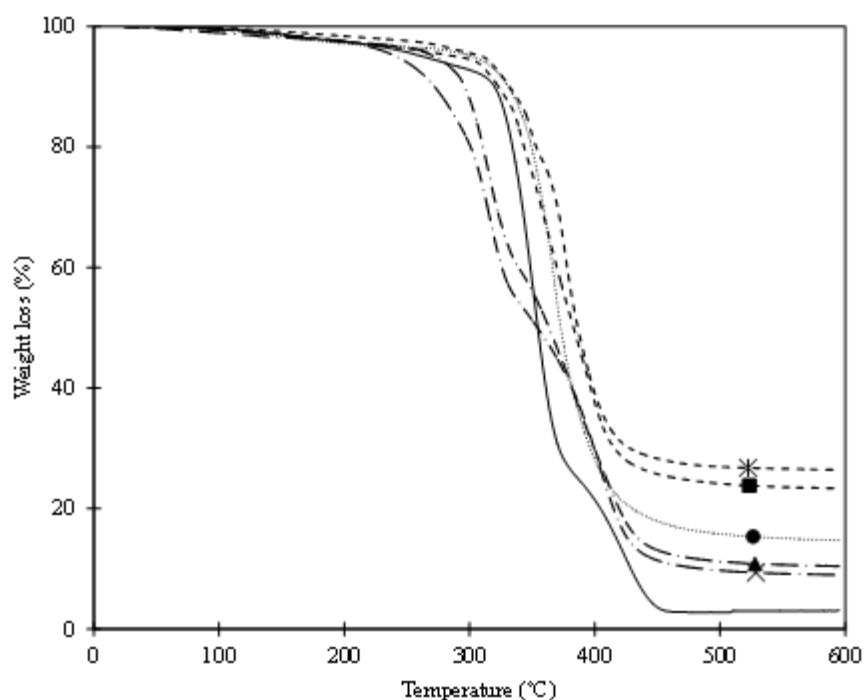


Figure 16. Thermogravimetric profiles of poly(HEMA) (full line) and copolymers of HEMA and SPAK or BVIImCl: 100% SPAK (*); 100% BVIImCl (x); 25/75 (■). 50/50 (●) and 75/25 (▲).

The results given in Figure 16 and Table 5 clearly indicate that the incorporation of BVImCl monomers into the poly(HEMA) backbone leads to a decrease in the thermal stability of the poly(HEMA-BVImCl) copolymer while the incorporation of SPAK monomers leads to an increase in the thermal stability of the poly(HEMA-SPAK) copolymer. The degradation temperatures given in the Table 5 correspond to the maximum of the peak of the first derivative of the thermogravimetric profiles. Therefore, and although ILs are known for their thermal stability, these results indicate that SPAK is the monomer that provides more thermal stability to the polyelectrolytes. Sample 50/50 presents higher thermal stability than poly(HEMA) which may be because it has a higher amount of SPAK, as confirmed by elemental analysis, and this monomer has higher thermal stability, but also because ionic complexation may originate materials with higher thermal stability. As can be also seen in Table 5 and Figure A.2 the crosslinking degree does not significantly affect the thermal stability of the hydrogels except for sample 25/75 for which the degradation temperature increases by 19 °C when the crosslinking degree increases to 1%.

Table 5. Influence of monomer composition and crosslinking degree on the thermal stability of the prepared hydrogels.

	Dried samples		Hydrated samples
	Degradation temperature (°C)	Weight loss at 200°C (%)	Total weight loss 25°C-600°C (%)
Poly(HEMA)	328.32	2.6	39.41
Poly(HEMA)-R1	371.03	1.5	39.84
A0/100	351.79	1.8	99.08
A0/100-R1	349.02	1.8	93.22
A100/0	289.01	3.1	98.75
A100/0-R1	288.49	3.0	89.56
25/75	326.87	2.4	98.76
25/75-R0.5	336.66	2.9	95.04
25/75-R1	345.77	2.6	96.01
50/50	343.64	2.8	95.86
50/50-R0.5	344.97	3.1	49.95
50/50-R1	345.02	3.0	39.60
75/25	293.22	2.5	98.19
75/25-R0.5	292.08	3.5	93.72
75/25-R1	291.96	3.6	86.08

The technique was also used to quantify the total amount of water retained in fully water swollen hydrogels and the results are presented also in Table 5. As can be seen in Figure 17 there is a linear correlation between these results and those previously discussed in section 3.4.1 proving the reproducibility of the results.

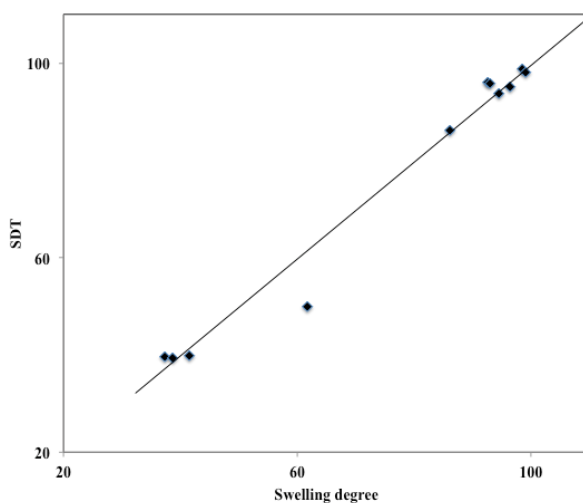


Figure 17. Correlation between the amount of water absorbed by the hydrogels measured by water swelling measurements and from weight loss measurements of fully hydrated samples obtained by SDT. (Correlation curve: $y = 1.0019x$; $R^2 = 0.99328$).

The thermal properties of the hydrogels were also studied by differential scanning calorimetry (DSC). The study was planned for hydrogel samples fully hydrated after being immersed in water for 24h and for samples plasticized with water after equilibrium at a relative humidity of 99% and at 25°C. However it was observed that for samples fully hydrated in water it was impossible to perform the measurements due to the large amount of water that the samples contain. A typical example of the DSC profile obtained is shown in Figure 18.

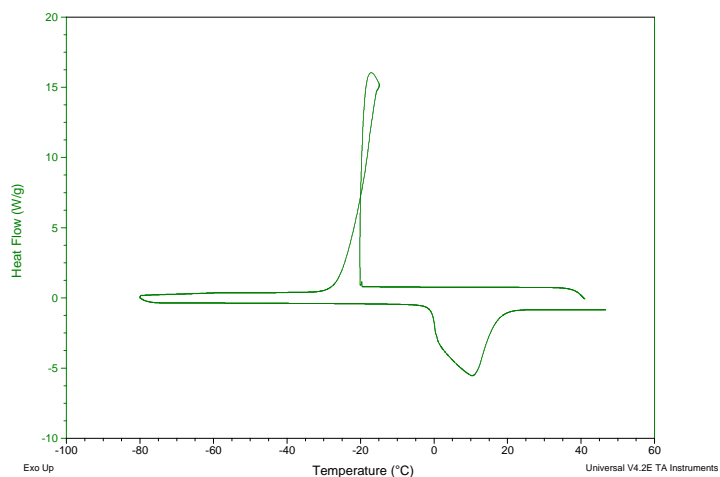


Figure 18. Typical example of the DSC profile obtained for fully swollen samples.

Therefore, this study was only performed for the samples plasticized with water vapor molecules. By using this technique it was possible to infer about the amount of free and bonded water that exist in the hydrogels after they were equilibrated with water vapor. Typical DSC profiles of the different hydrogels synthesized in this work are given in Figure 19.

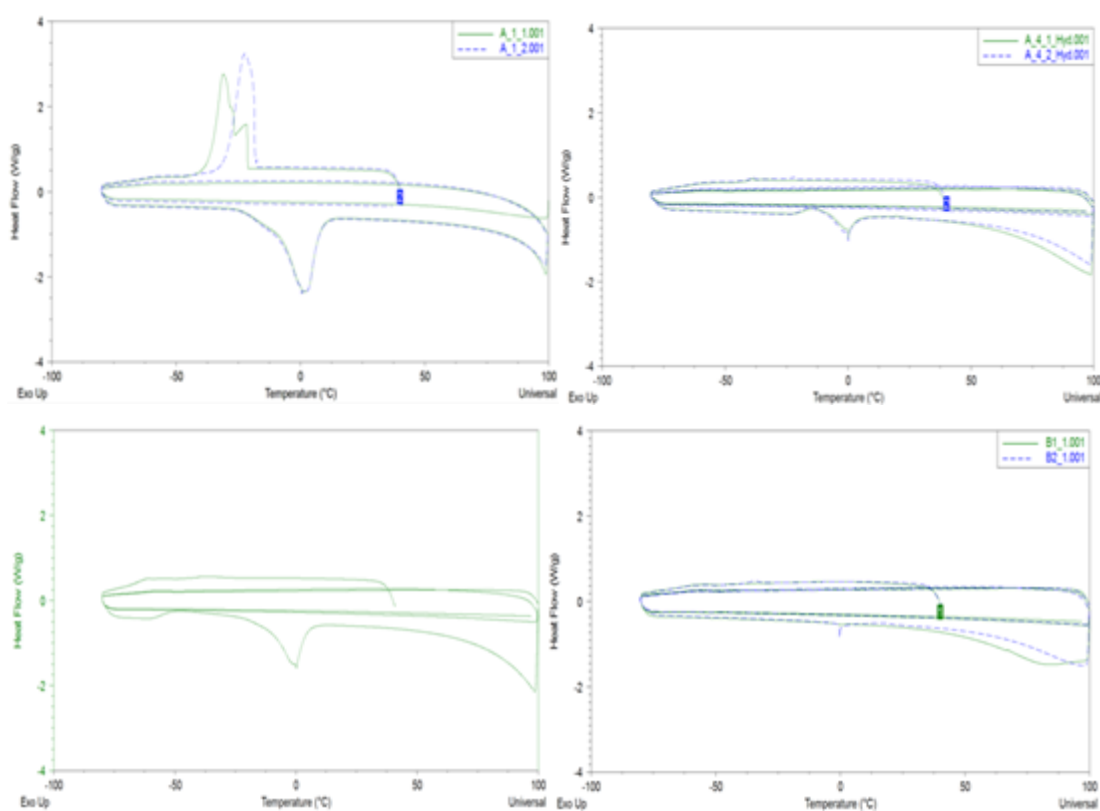


Figure 19. DSC profiles of 25/75 (top left), 50/50 (top right), 75/25 (bottom left) and poly(HEMA) (bottom right).

The enthalpic events observed for each sample are presented in Table 6 and Figure 19. From the first two columns of Table 6 it is possible to observe that only the samples with more SPAK (25/75) present a freezing temperature and enthalpy. Such phenomenon is also visible in Figure 19, where only 25/75 (top left) show an event when the sample is frozen. This means that the amount of water vapor molecules absorbed by this hydrogel is higher than for the other due to its higher hydrophilicity and as previously discussed. These water molecules are bounded to the network (freezable bond water) because the freezing temperature is lower than that for pure water. If the water molecules were not-interacting with the hydrogel network and only dispersed within the free volume of the network (free water) they would freeze at 0°C. For these samples the freezing temperature decreases and the freezing enthalpy increases with the crosslinking degree. The amount of water vapor molecules absorbed by the other hydrogel samples is not enough to be detected while decreasing the temperature of the samples. However it can be identified by the detected melting temperature and enthalpy given in the last two columns of Table 6, as also shown in Figure 19, where all the samples exhibit a phenomenon in the melting moment. These results confirm the water vapor sorption results previously discussed by showing that samples with more SPAK have higher melting enthalpies and those with more BVImCl or near neutral. These results again confirm that the copolymers synthesized in this work are more hydrophilic than poly(HEMA) which absorbs only a residual amount of water vapor molecules which are not detected by the used technique since any melting or freezing events were detected for these samples (Figure 19 bottom right).

Table 6. Thermal events identified by differential scanning calorimetry (DSC) analysis for all the studied hydrogels.

Sample	Freezing Temperature (°C)	Freezing Enthalpy (J/g)	Melting Temperature (°C)	Melting Enthalpy (J/g)
Poly(HEMA)	--	--	--	--
Poly(HEMA)-R1	--	--	--	--
A0/100	--	--	2.1 ± 0.9	165.4 ± 15.3
A0/100-R1	--	--	1.1 ± 0.9	167.9 ± 15.3
A100/0	--	--	0.4 ± 0.9	141.5 ± 15.3
A100/0-R1	--	--	-0.4 ± 0.9	79.9 ± 15.3
25/75	-26.7 ± 6.2	132.1 ± 4.1	0.7 ± 0.3	148.6 ± 3.0
25/75-R0.5	-31.6 ± 0.5	124.3 ± 0.1	1.1 ± 0.8	142.5 ± 2.0
25/75-R1	-48.1 ± 7.3	77.9 ± 6.1	0.6 ± 0.3	115.5 ± 6.2
50/50	--	--	0.1 ± 0.0	24.0 ± 2.6
50/50-R0.5	--	--	-1.5 ± 0.1	15.3 ± 7.3
50/50-R1	--	--	-0.1 ± 0.2	22.4 ± 9.4
75/25	--	--	0.0 ± 0.2	52.1 ± 15.3
75/25-R0.5	--	--	-2.1 ± 0.9	43.6 ± 14.9
75/25-R1	--	--	0.1 ± 0.3	45.5 ± 5.8

3.4.7. Mechanical properties – Tensile tests

The tensile strength (σ) and percentage of elongation (ϵ) of non crosslinked 50/50 samples fully swollen in PBS (pH=7,4) were calculated to evaluate its mechanical performance. The Young's modulus (E) was calculated from the linear region of the stress-strain graphic given in Figure 20 (top) with an average value of 3.0 ± 0.59 GPa. On the other hand, the average fracture strain was ~1600% of elongation relatively to the initial sample's length with a maximum elongation of 84 mm. Samples were also subjected to sequential elongation cycles as shown in Figure 20 (bottom). For the 3 testes cycles the samples showed almost negligible hysteresis, showing its potential to undergo reversible deformation. Due to the potential showed by 50/50 samples, particularly to reversible deformation, other experiments should be performed, because the tests here presented are only preliminary. Figure 21 shows a visual observation of a tensile test performed in a 50/50 sample.

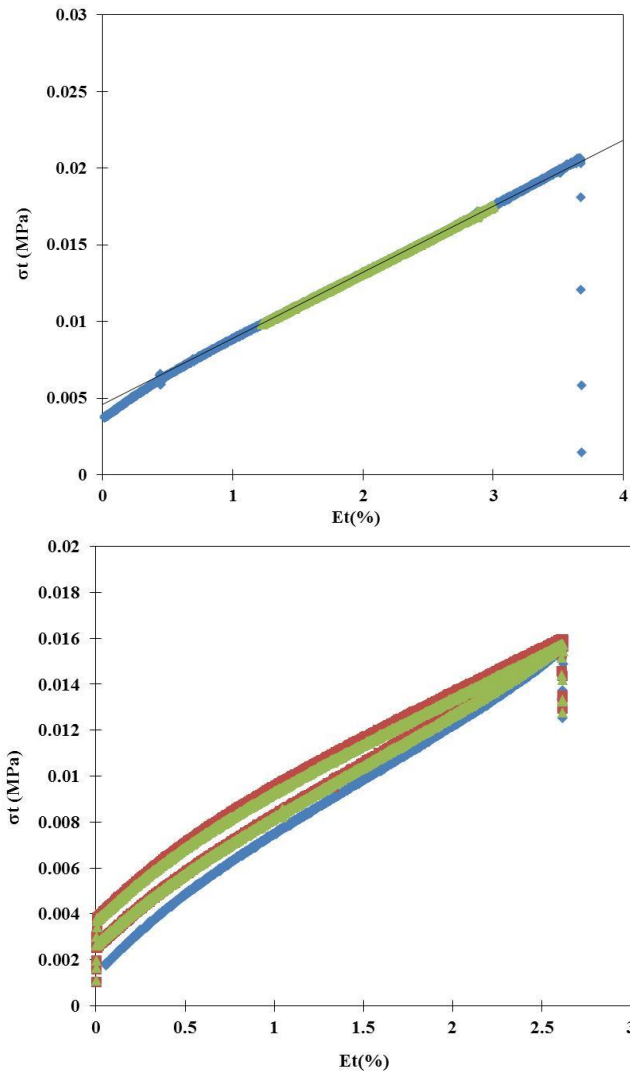


Figure 20. Example of a stress-strain curve measured for the 50/50 sample on top and of the sequential elongation cycles on the bottom (The blue, red and green lines represent the 1st, 2nd and 3rd cycles respectively).



Figure 21. Visual observation of a tensile test performed in a 50/50 sample, near to the fracture strain.

3.4.8. Sorption experiments

Sorption experiments were performed for different families of charged molecules in order to open a wide range of possible applications of the prepared hydrogels and which may include wastewater treatment and separation and purification methods in biotechnology or other related industries. Therefore the synthesized hydrogels were tested for their capacity to absorb a metal ion (Chromate ions), a pH sensitive dye (sodium salt of bromocresol green) and an amino acid (L-tryptophan).

3.4.8.1. Preliminary tests for the adsorption of Chromate ions

In this system the aim is to remove the dichromate anion (CrO_4^{2-}) from the solution and therefore it would be expected that the cationic hydrogels would be more suitable hydrogels to work as ion exchange materials. Nevertheless a first experiment was performed using non-crosslinked samples 25/75, 50/50 and 75/25. For sample 25/75 it was also evaluated the effect of ion exchange (chlorine anion vs bis trifluoromethanesulfonyl imide) on the adsorption of the dichromate anion. All the samples were dried in an oven and milled. The experiments were performed in duplicates. The adsorption profiles obtained are presented in Figure 22.

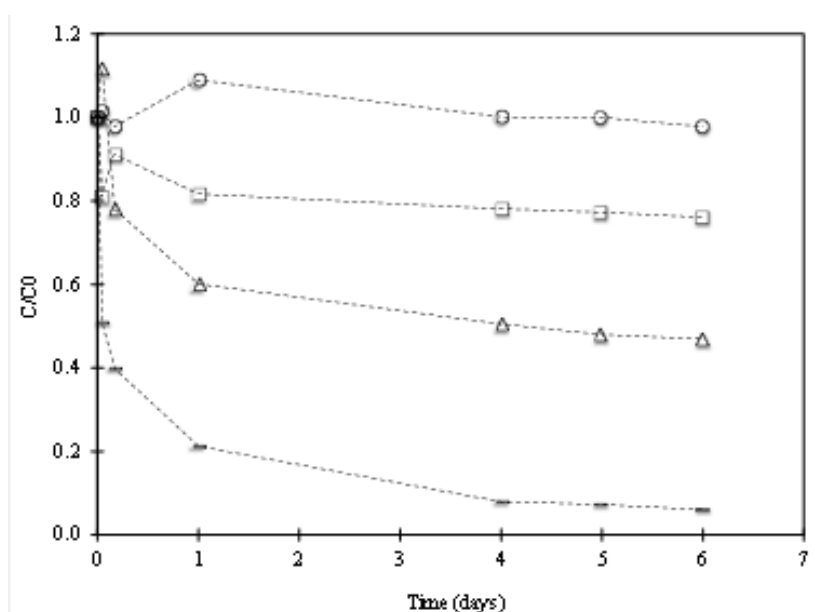


Figure 22. Adsorption profiles of K_2CrO_4 on non-crosslinked dried samples 25/75 (□), 50/50 (○), 75/25-Cl (Δ) and 75/25- Tf₂N (-).

According to Figure 22 it is possible to confirm that, as expected, only the cationic hydrogels are able to significantly adsorb the negatively charged chromate anions due to electrostatic attraction (Berlinova et al, 2000; Chen et al, 2000). Moreover, sample 75/25-Tf₂N showed a highly effective and faster adsorption capacity for chromate ions, ~ 67 % after 24h and 91 % after 6 days when compared with sample 75/25-Cl ~ 18 % after 24h and 24 % after 6 days. This happens due to the interaction between cationic and anionic moiety of the IL. Since there is a stronger interaction between chlorine and the cationic moiety of the IL compared to Tf₂N, it will be easier the ion exchange between Tf₂N and Chromate ions than the ion exchange between chlorine and Chromate ions (Fraser et al., 2007).

Based on the theoretical neutral charge of the 50/50 hydrogel, it was expected to observe a low or inexistent adsorption capacity for chromate ions. According to Figure 22, is observed a small but negligible sorption, which may be due to the slight unbalance of negative charges over positive charges as concluded from elemental analysis results. Moreover, 25/75 samples were also expected to have a negligible adsorption capacity due to the predominant presence of negative charges however a low, yet significant, sorption was detected. This result can be probably justified by diffusion phenomenon, instead of sorption, due to the extremely high swelling capacity of the 25/75 hydrogel that drags chromate ions into the hydrogel network that would subsequently be trapped in the polymeric network.

Based on the results obtained from the preliminary tests the experiment was repeated for sample 75/25-Cl and 75/25-Tf₂N dried and 75/25-Cl freeze dried in order to evaluate the effect of superficial area on the adsorption kinetic profiles. In the preliminary tests, the molar IL/K₂CrO₄ ratio was near 4, and as showed in Figure 22, none of the hydrogels was able to adsorb all chromate ions. Therefore, it was decided to increase this IL/K₂CrO₄ ratio to 19 in order to promote a complete adsorption.

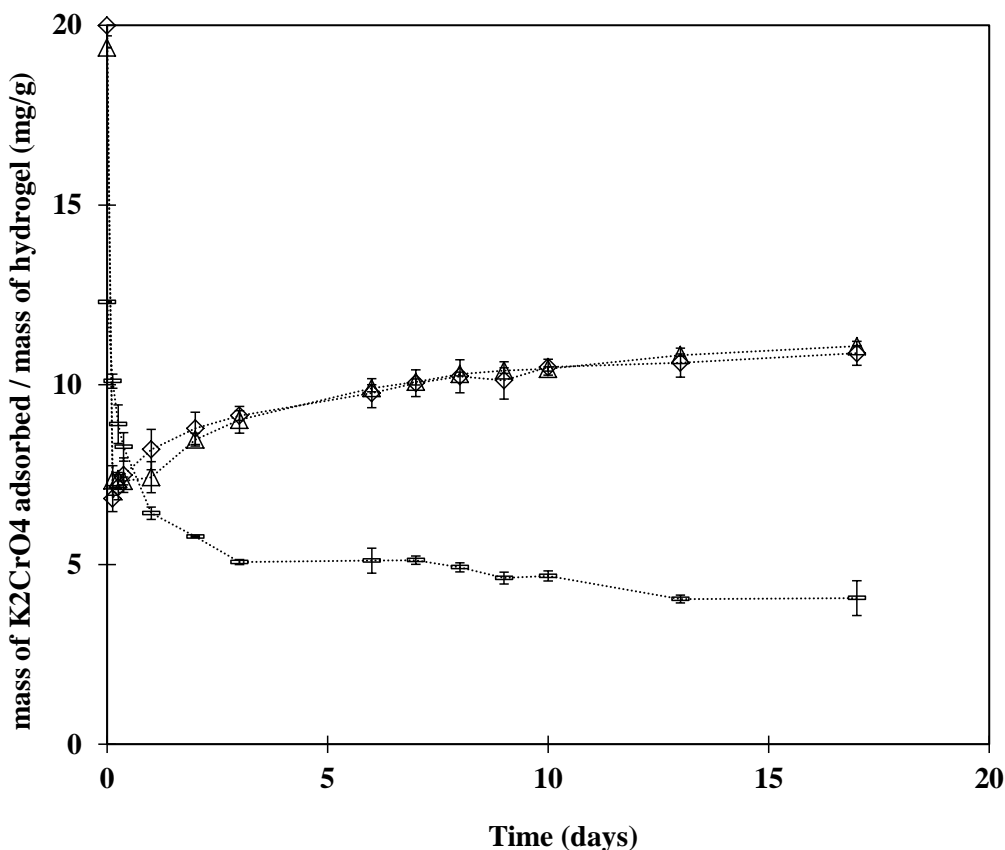


Figure 23. Adsorption profiles of a K_2CrO_4 on non-crosslinked dried samples 75/25 (Δ) and 75/25-Tf₂N (-) and on non-crosslinked and freeze dried 75/25-Cl (\diamond).

Figure 23 illustrates the sorption profiles of cationic hydrogels where it is noticeable that the drying process does not have any difference on the sorption capacity of samples 75/25 since both oven dried and freeze dried samples present a very similar kinetic profile. This result may indicate that the process is more controlled by the number of available positive charges on the network that may capture the chromate anions being less dependent on the surface area. This may be because the cationic hydrogel presents a high swelling degree and therefore there is enough free volume for the solute enters the network and interact with the charged groups that exist there. Here again, the sample 75/25-Tf₂N presents higher adsorption capacity of ~ 80 % when compared the ~ 45 % observed for the 75/25-Cl samples. The profiles obtained for samples 75/25-Cl first decrease but then seem to increase. This phenomenon may be due to the fast water exchanges that may occur after the hydrogel is immersed in water due to its high hydrophilicity. Only after equilibrium is achieved it is possible to quantify the real amount of chromate anions that were indeed adsorbed by the cationic groups from the network. This does not happen for the 75/25-Tf₂N sample because it is more hydrophobic due to the hydrophobic nature

of the bis trifluoromethanesulfonyl imide anion. It should be noted that due to ion exchange, the molar mass of 75/25-Tf₂N samples was considerably changed. While atomic mass of chloride is approximately 35.45 mol/g, the atomic mass of bis trifluoromethanesulfonyl imide is around 280.15 mol/g. Therefore some adjustments were made in the mass of 75/25-Tf₂N in order to reach the same positive charges than 75/25-Cl for the right comparison between the samples. The study of the influence of the anion present in the ionic liquid was studied according to Hao Mi and co-workers, which investigated the influence of an hydrophobic anion (bis(trifluoromethanesulfonyl) imide, Tf₂N) for a highly effective separation of methyl blue and chromium ions from water (Mi et al. 2013). According to that study, poly(3-ethyl-1-vinylimidazolium bis(trifluoromethanesulfonyl) imide) reached a maximum adsorbed percentage for Chromate ions of 98 % and was able to adsorb more than 72 % of Chromate ions within 6h, while 75/25-Tf₂N synthesized in the present work, was able to absorb ~56 % in the same period, reaching the adsorption equilibrium around 80 %. Such difference because Hao Mi and co-workers used a different molar IL/K₂CrO₄ ratio, which was more than 23. This means that they used more IL mass to absorb the same molar weight of K₂CrO₄. The difference in both results can also be due to the presence of anionic groups in the 75/25 network that decreases the number of available cations for adsorption as was already discussed. From Figure 24 it is possible to observe that the K₂CrO₄ solution was yellow colored at the beginning and becomes nearly colorless after 17 days, indicating that most of the chromate anions in solution were adsorbed by the 75/25-Cl and 75/25-Tf₂N samples as confirmed by their yellow color after the experiment.



Figure 24. Visual observation of the K₂CrO₄ solutions and of the samples 75/25 dried (left), 75/25-Tf₂N dried (middle) and 75/25 freeze dried (right) after the experiment.

3.4.8.2. Preliminary tests for the adsorption of sodium salt of bromocresol green

The second tested adsorbate was bromocresol green sodium salt, which is a pH indicator that will ionize in water to the monoanionic form, indicated by yellow color and will further deprotonate at higher pH (pKa 4.6) to the dianionic form, indicated by the blue color as showed in Figure 25.

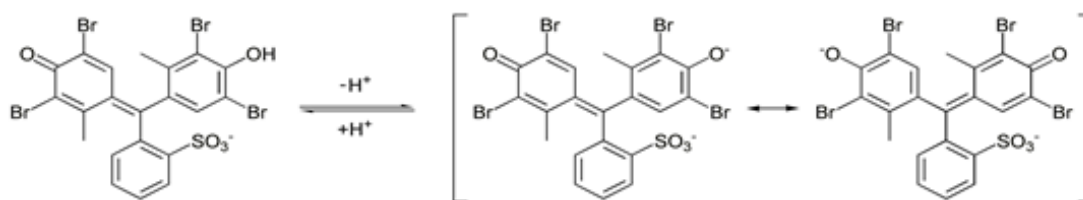


Figure 25. Bromocresol green sodium salt ionic equilibrium at pH=4.6.

In water (pH ~6.5) bromocresol green will originate a blue solution and will absorb in visible range at 618 nm. The first experiments were performed using samples 25/75, 25/75-R1, 75/25 and 75/25-R1 all freeze dried. Similar to the preliminary experiments for the adsorption of chromate ions, the aim of those first experiments was to demonstrate that the cationic hydrogels would be more suitable for the adsorption of bromocresol anion. Figure 26 corroborates what was expected, since only the cationic hydrogels were able to significantly absorb the anionic form of bromocresol green due to electrostatic attraction (Berlinova et al, 2000; Chen et al, 2000). From Figure 26 it is possible to observe that the bromocresol green solution with blue color becomes nearly colorless after 16 days, indicating that most of the bromocresol anion in the solution is adsorbed by 75/25 and 75/25-R1, regardless of the presence of crosslinker. It is also visible that 25/75 and 25/75-R1 samples did not adsorb any bromocresol green ions from the solution, due to electrostatic repulsion. Therefore, based on the results obtain from the preliminary tests, the experiment was reproduced in the exact same conditions for samples 75/25, 75/25-R1 and A100/0-R1 dried and also freeze dried in order to evaluate the effect of superficial area on the adsorption kinetic profiles.

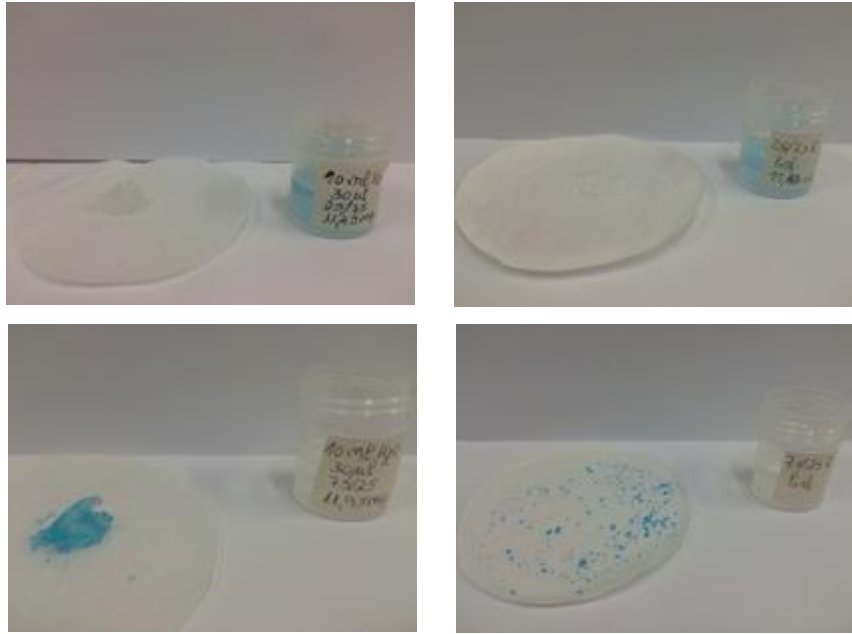
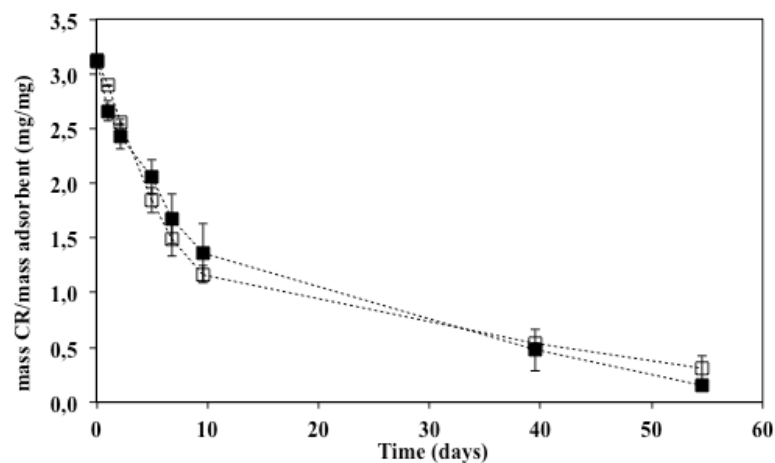
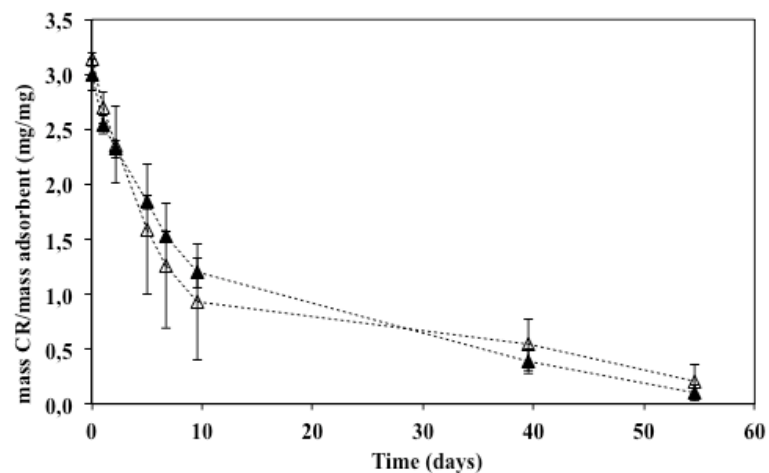


Figure 26. Visual observation of the bromocresol green solutions and of the samples 25/75 (top) and 75/25 (bottom) after 55 days. The pictures on the left represent non-crosslinked samples and those on the right represent samples crosslinked at 1%.

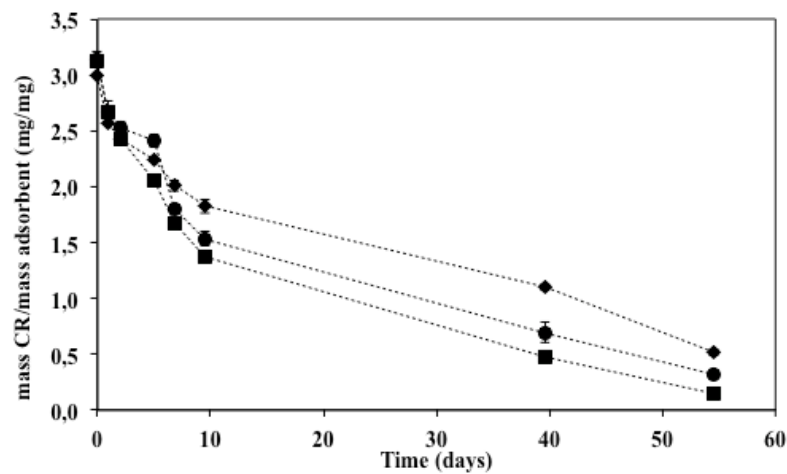
Figure 27 illustrates the sorption profiles of all the studied samples where it is possible to see that there is only a slightly difference between crosslinked and non-crosslinked samples. On the other hand, Figure 27 also demonstrates that there is no significant difference between samples with different superficial area, suggesting that, similar to the sorption of chromate ions, the process is mainly controlled by the number of accessible positive charges on the network that are able to electrostatically attract bromocresol anions. The main differences were observed between A100/0-R1 and 75/25-R1 samples. Although A100/0-R1 samples have more positive charges, 75/25-R1 has a more efficient sorption capacity for the bromocresol anions. It should be noted that the experiments were only conducted using crosslinked A100/0 samples because non crosslinked A100/0 samples almost dissolve in water. This does not happen with 75/25 samples, because of the ionic crosslinking that induces the formation of electrostatic complexes between positive and negative charges, providing mechanical stability. The same happens with the 25/75 hydrogels, which also present higher mechanical stability than A0/100 samples. It should be noted that the experiment is currently taking place, as is possible to see from Figure 27, because the samples didn't reach equilibrium sorption yet.



(a)



(b)



(c)

Figure 27. Adsorption profiles of bromocresol green. (a) Effect of crosslinking on 75/25-R1 dried samples; (b) Effect of crosslinking on 75/25-R1 freeze dried samples; (c) effect of processing on crosslinked A100/0-R1 samples: dried (●) and freeze dried (◆). Empty and full symbols represent non crosslinked and crosslinked samples, respectively.

3.4.8.3. Preliminary tests for the adsorption of L-tryptophan

The third adsorbate studied was L-tryptophan, which is an aminoacid that has both positive and negative charges at the studied pH (~6.5 for water) and according to Xie and co-workers (Xie et al., 2011). This system was not fully studied due to time constrains but some conclusions can already be made. Nevertheless these results should be regarded as preliminary tests.

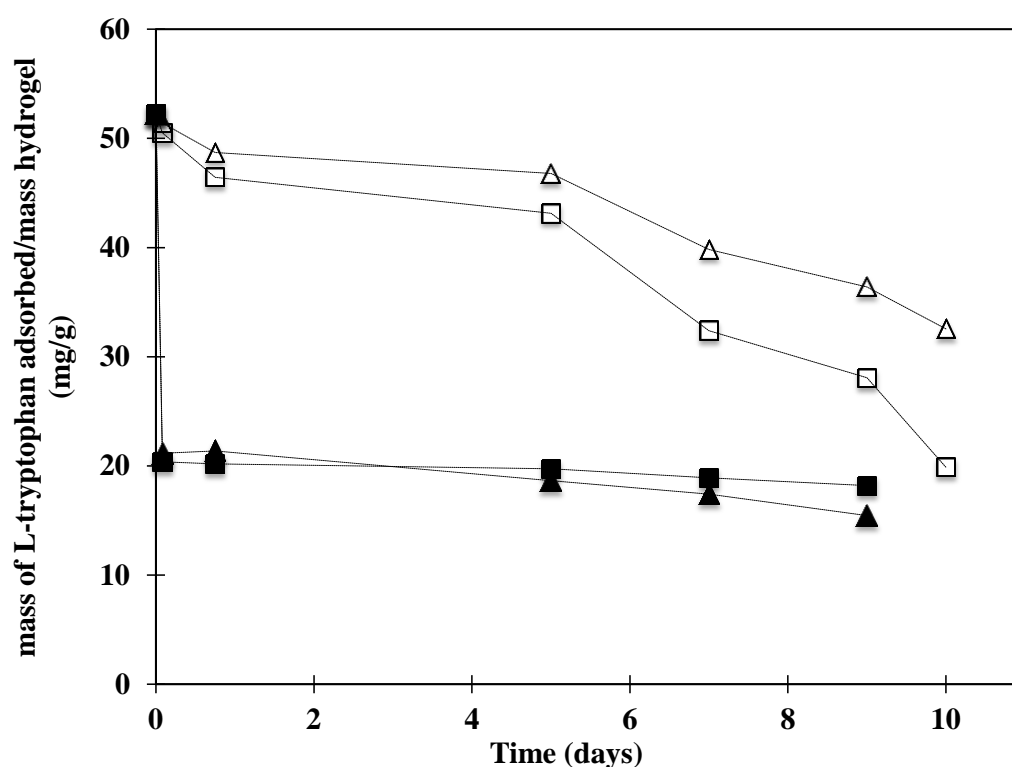


Figure 28. Adsorption profiles of L-tryptophan in samples 25/75 (squares) and 75/25 (triangles). Empty symbols represent dried samples and full symbols represent freeze dried samples.

Figure 28 illustrates the adsorption profiles of L-tryptophan in samples 25/75 and 75/25 dried and freeze dried, where is possible to observe that, contrary to what happened for chromate and bromocresol ions, there is a very significant effect of processing (dried vs freeze drying) on the amount of L-tryptophan adsorbed. However purport that there is a significant difference between dried and freeze dried samples, it can be explain through the IL/L-tryptophan molar ratio, which was 8 for dried and 20 for freeze dried samples. This means that for freeze dried samples the molar mass of

the sample was higher for the same molar mass of L-tryptophan. In Figure 28 it is also noticeable that there is only a minor difference between 25/75 and 75/25 samples with a slightly higher L-tryptophan adsorption capacity for 25/75. Therefore these results show that both cationic and anionic polyelectrolytes are able to adsorb the aminoacid at the studies conditions because it is on its isoelectric point, thus being able to interact with both positively and negatively charged hydrogels. It must also be taken into account that previous experiments were performed with the aminoacid dissolved in PBS but in this case the adsorption capacity of the hydrogels was limited because they present a very low swelling capacity in buffer as discussed before. Therefore future work should account for the influence of the ionic strength of the media on the sorption capacity of these hydrogels.

Finally, the percentage of removal of chromate anion, bromocresol green, and L-tryptophan, ions on different ionic hydrogels are presented in Figure 29.

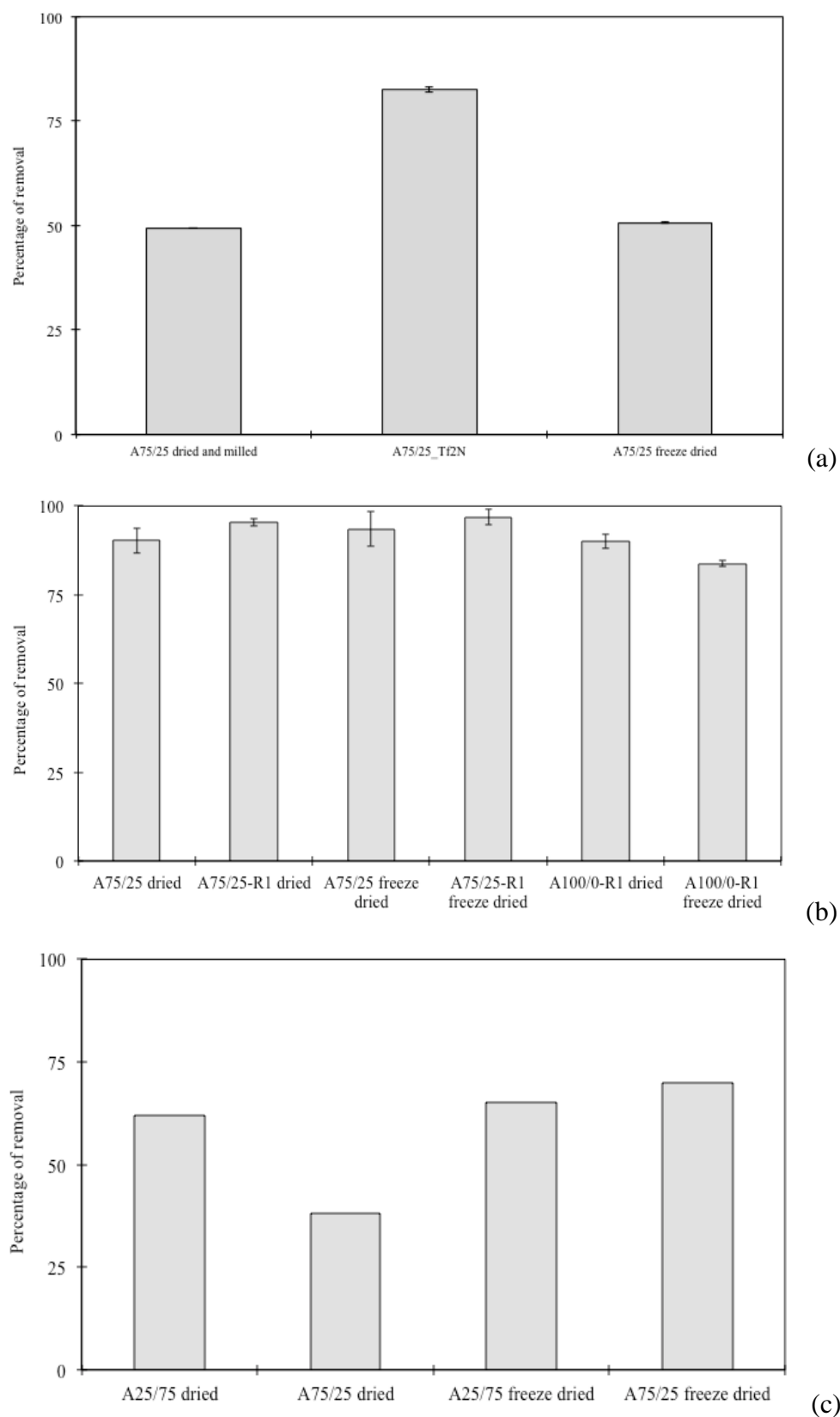


Figure 29. Percentage of removal of chromate anion (a), bromocresol green (b) and L-tryptophan (c) ions on different ionic hydrogels.

Conclusion

The present work showed the potential of poly(HEMA) based superabsorbent hydrogels after being modified with cationic and anionic groups provided by the copolymerization with 1-butyl-3-vinylimidazolium chloride (BVI_mCl) and 3-sulphopropyl acrylate potassium salt (SPAK), respectively. The influence of cationic and anionic monomers proportion as well as chemical crosslinking degree on several properties of the hydrogels was also studied and discussed. These hydrogels combine the unique properties of the ionic liquid BVI_mCl with the hydrophilicity of SPAK and the good mechanical properties and biocompatibility of HEMA. The main interesting findings and major conclusions that were taken from the study of the synthesized polyelectrolytes or polyampholytes include:

- From elemental analysis it was possible to conclude that cationic, anionic and almost neutral hydrogels can be obtained depending on the ratio of monomers used for the polymerization; To prepare the neutral hydrogel, and although the feed mixture had the same molar amount of positive and negative charges, the final hydrogel had slightly more negative charges, which had consequences in its final properties. Transmission FTIR also confirmed that the co-polymerization was successful;

- It was confirmed by SEM-EDX that the monomers were homogeneously distributed through the hydrogel matrices;

- Anionic and cationic samples, 25/75 and 75/25 respectively were the hydrogels that presented the higher water swelling degree, due to the presence of free charges within the polymeric network, which created a high driving force between the bulk of the hydrogel and the medium. The results also showed that such hydrogels fit in the SAP classification because they swell about 100 times their own dry weight;

- The neutral 50/50 sample did not absorb a large amount of water since there is equilibrium between opposite charges, which cancel each other out, and most likely form complexes among them, thus decreasing the osmotic pressure between the medium and the polymeric network;

- As expected an increase in the chemical crosslinking ratio with MBA led to a decrease on the water swelling degree due to the reduction of free volume available between hydrogel chains;

- All the samples absorbed more water in pure water than in PBS because the ionic strength of the former is negligible and therefore there is a high driving force between the inside and the outside of the polymeric network, and consequently, a large amount of water enters in the network until equilibrium is reached;

- Water vapor swelling demonstrated that all samples are hydrophilic and able to absorb water vapor molecules when exposed to a high humidity environment. However, unlikely in the case of water swelling, the crosslinking degree did not exhibit any influence on water vapor swelling;

- The thermal stability of poly(HEMA-SPAK) co-polymers was higher than that of poly(HEMA) while that of poly(HEMA-BVImCl) was lower than poly(HEMA). Neutral 50/50 samples also present good thermal stability (degradation temperature similar to that of SPAK-100%), which suggests that positive and negative charges do form complexes, increasing hydrogels stability. DSC curves show that only the sample 25/75 exhibited a freezing temperature and enthalpy, suggesting that those samples were the most hydrophilic and able to accommodate free water between the polymer chains. DSC results confirmed that the synthesized polyelectrolytes/polyampholytes were more hydrophilic than poly(HEMA) which did not present any enthalpic peak because these samples did not absorb a significant amount of water;

- The capacity of the ionic hydrogels to adsorb charged molecules was also studied. Adsorption experiments showed that the prepared polyelectrolytes were able to adsorb various types of charged molecules. In one hand, sample 25/75 was only suitable to adsorb L-tryptophan in aqueous media (pH~6.5), because this aminoacid was close to its isoelectric point at this experimental condition. On the other hand, sample 75/25 was effective to remove metals (chromate anion), dyes (bromocresol green) and also L-tryptophan;

- The influence of anion exchange for sample 75/25, by changing the $[\text{Cl}]^-$ by the $[\text{Tf}_2\text{N}]^-$ showed improved performance on the removal of chromate anions from a K_2CrO_4 solution. This was justified by the higher interaction energies between $[\text{Cl}]^-$ and the imidazolium cation when compared to $[\text{Tf}_2\text{N}]^-$, being therefore easier to substitute $[\text{Tf}_2\text{N}]^-$ by the anion that is intended to be adsorbed.

During the development of this thesis, there were some obstacles that started after synthesis, and were specifically due to the low mechanical strength of most hydrogels. Consequently, the water swelling experiments became more difficult to perform, however, the standard deviation was found to be within very acceptable values considering the superabsorbent capacity of these materials.

Future Work

During the development of the present thesis, specific studies, tests and future research pathways were discussed as interesting/necessary to be implemented in order to improve the potential of the synthesized polyelectrolytes. Some of those studies are detailed in what follows:

- To optimize the monomer ratio of the feed solution in order to obtain a neutral polyampholyte that will have a tougher network due to their multiple strong ionic bonds, which will work as soft crosslinkers bringing elasticity to the hydrogel chains;
- To complete the mechanical studies with other mechanical tests, which may include compression, deformation, adhesion, fatigue or rheological;
- To improve the mechanical properties of the hydrogels through two ways: i) study other crosslinker/monomer ratios aiming to find the optimum equilibrium between crosslinking ratio and suitable mechanical strength; ii) development of double network (DN) structures, which have proved to present high mechanical strength and toughness (Gong. 2010; Gong. et al. 2003; Haque. Kurokawa. & Gong. 2012; Na. et al. 2004);
- To perform electrochemical impedance spectroscopy measurements of fully swollen polyelectrolytes in order to explore their potential as electro-conductive hydrogels for biosensors and controlled drug delivery as exemplified;
- To perform further sorption experiments to explore the sensitivity of the hydrogels to temperature, pH or presence of ionic species, at different concentration, in solution. Furthermore, investigate the hydrogels capacity to absorb macromolecules using an absorbent column and study its performance, recyclability and regeneration for industrial purpose;
- Deeply study the influence of the Tf₂N anion, of the hydrogels superficial area and of material-absorbent interactions on the capacity of the hydrogels to absorb charged molecules and macromolecules;
- To perform antimicrobial activity tests due to the properties of IL.

References

- Ahmed, E. M. (2015). Hydrogel: Preparation, characterization, and applications: A review. *Journal of Advanced Research*, 6(2), 105–121. <http://doi.org/10.1016/j.jare.2013.07.006>
- Bag, D. S., & Rao, K. U. B. (2006). Smart polymers and their applications. *Journal of Polymer Materials*, 23(3), 225–248. <http://doi.org/10.1533/9780857097026.1.45>
- Baker, J. P., Blanch, H. W., & Prausnitz, J. M. (1995). Swelling properties of acrylamide-based ampholytic hydrogels: comparison of experiment with theory. *Polymer*, 36(5), 1061–1069. [http://doi.org/10.1016/0032-3861\(95\)93608-O](http://doi.org/10.1016/0032-3861(95)93608-O)
- Bandomir, J., Schulz, A., Taguchi, S., Schmitt, L., Ohno, H., Sternberg, K., Kragl, U. (2014). Synthesis and characterization of polymerized ionic liquids: Mechanical and thermal properties of a novel type of hydrogels. *Macromolecular Chemistry and Physics*, 215(8), 716–724. <http://doi.org/10.1002/macp.201400009>
- Bayramoglu, G., & Yakup Arica, M. (2009). Preparation and characterization of comb type polymer coated poly(HEMA/EGDMA) microspheres containing surface-anchored sulfonic acid: Application in γ -globulin separation. *Reactive and Functional Polymers*, 69(3), 189–196. <http://doi.org/10.1016/j.reactfunctpolym.2008.12.017>
- Berlinova, I. V., Dimitrov, I. V., Kalinova, R. G., & Vladimirov, N. G. (2000). Synthesis and aqueous solution behaviour of copolymers containing sulfobetaine moieties in side chains. *Polymer*, 41(3), 831–837. [http://doi.org/10.1016/S0032-3861\(99\)00264-5](http://doi.org/10.1016/S0032-3861(99)00264-5)
- Buchholz, FL & Graham, A. (1997). Superabsorbent polymers. *Modern Superabsorbent Polymer Technology*. Retrieved from http://chimianet.zefat.ac.il/download/Superabsorbant_polymers.pdf
- Carrión, F. J., Sanes, J., & Bermúdez, M. D. (2007). Effect of ionic liquid on the structure and tribological properties of polycarbonate-zinc oxide nanodispersion. *Materials Letters*, 61(23–24), 4531–4535. <http://doi.org/10.1016/j.matlet.2007.02.044>
- Carvalho, R. N. L., Lourenço, N. M. T., Gomes, P. M. V., & Fonseca, L. J. P. (2013). Swelling behavior of gelatin-ionic liquid functional polymers. *Journal of Polymer Science, Part B: Polymer Physics*, 51(10), 817–825. <http://doi.org/10.1002/polb.23252>
- Chang-Shan, H., & H. Block, L. (1996). Anionic Gels as Vehicles for Electrically-Modulated Drug Delivery. I. Solvent and Drug Transport Phenomena. <http://doi.org/10.1023/A:1016045427545>
- Chen, L., Honma, Y., Mizutani, T., Liaw, D. J., Gong, J. P., & Osada, Y. (2000). Effects of polyelectrolyte complexation on the UCST of zwitterionic polymer. *Polymer*, 41(1), 141–147. [http://doi.org/10.1016/S0032-3861\(99\)00161-5](http://doi.org/10.1016/S0032-3861(99)00161-5)
- Cipriano, B. H., Banik, S. J., Sharma, R., Rumore, D., Hwang, W., Briber, R. M., & Raghavan, S. R. (2014). Superabsorbent hydrogels that are robust and highly stretchable. *Macromolecules*, 47(13), 4445–4452. <http://doi.org/10.1021/ma500882n>

- Cordella, D., Kermagoret, A., Debuigne, A., Jérôme, C., Mecerreyes, D., Isik, M., ... Detrembleur, C. (2015). All Poly(ionic liquid)-Based Block Copolymers by Sequential Controlled Radical Copolymerization of Vinylimidazolium Monomers. *Macromolecules*, 48(15), 5230–5243. <http://doi.org/10.1021/acs.macromol.5b01013>
- Czajkowska-Żelazko, J. F. A. (2011). Ionic liquids in separation techniques. *Journal of Chromatography. A*. <http://doi.org/10.1016/j.chroma.2007.11.109>
- Dharaskar, S. A., Wasewar, K. L., Varma, M. N., Shende, D. Z., & Yoo, C. (2013). Synthesis, characterization and application of 1-butyl-3-methylimidazolium tetrafluoroborate for extractive desulfurization of liquid fuel. *Arabian Journal of Chemistry*, 1–10. <http://doi.org/10.1016/j.arabjc.2013.09.034>
- Dobrynin, A. V., Colby, R. H., & Rubinstein, M. (2004). Polyampholytes. *Journal of Polymer Science, Part B: Polymer Physics*, 42(19), 3513–3538. <http://doi.org/10.1002/polb.20207>
- Dobrynin, A. V., & Rubinstein, M. (2005). Theory of polyelectrolytes in solutions and at surfaces. *Progress in Polymer Science (Oxford)*, 30(11), 1049–1118. <http://doi.org/10.1016/j.progpolymsci.2005.07.006>
- Fraser, K. J., Izgorodina, E. I., Forsyth, M., Scott, J. L., & MacFarlane, D. R. (2007). Liquids intermediate between “molecular” and “ionic” liquids: Liquid Ion Pairs? *Chem. Commun.*, (37), 3817–3819. <http://doi.org/10.1039/B710014K>
- Gawande, N., & Mungray, A. A. (2015). Superabsorbent polymer (SAP) hydrogels for protein enrichment. *Separation and Purification Technology*, 150, 86–94. <http://doi.org/10.1016/j.seppur.2015.04.024>
- Gerlach, G., & Arndt, K.-F. (2009). Hydrogel Sensors and Actuators. *Springer Series on Chemical Sensors and Biosensors*, 6, 1–15. <http://doi.org/10.1007/b100321>
- Gil, E. S., & Hudson, S. M. (2004). Stimuli-responsive polymers and their bioconjugates. *Progress in Polymer Science (Oxford)*, 29(12), 1173–1222. <http://doi.org/10.1016/j.progpolymsci.2004.08.003>
- Gong, J. P. (2010). Why are double network hydrogels so tough? *Soft Matter*, 6(12), 2583. <http://doi.org/10.1039/b924290b>
- Gong, J. P., Katsuyama, Y., Kurokawa, T., & Osada, Y. (2003). Double-network hydrogels with extremely high mechanical strength. *Advanced Materials*, 15(14), 1155–1158. <http://doi.org/10.1002/adma.200304907>
- Green, O., Grubjesic, S., Lee, S., & Firestone, M. A. (2009). The Design of Polymeric Ionic Liquids for the Preparation of Functional Materials. *Journal of Macromolecular Science R*, Part C: *Polymer Reviews*, 49(May 2013), 339–360. <http://doi.org/10.1080/15583720903291116>
- Guilherme, M. R., Aouada, F. A., Fajardo, A. R., Martins, A. F., Paulino, A. T., Davi, M. F. T., Muniz, E. C. (2015). Superabsorbent hydrogels based on polysaccharides for application in agriculture as soil conditioner and nutrient carrier: A review. *European Polymer Journal*, 72, 365–385. <http://doi.org/10.1016/j.eurpolymj.2015.04.017>

- Guisseppi-Elie, A. (2010). Electroconductive hydrogels: Synthesis, characterization and biomedical applications. *Biomaterials*, 31(10), 2701–2716. <http://doi.org/10.1016/j.biomaterials.2009.12.052>
- Hackl, E. V., Khutoryanskiy, V. V., Tiguman, G. M. B., & Ermolina, I. (2015). Evaluation of water properties in HEA–HEMA hydrogels swollen in aqueous-PEG solutions using thermoanalytical techniques. *Journal of Thermal Analysis and Calorimetry*, 121(1), 335–345. <http://doi.org/10.1007/s10973-015-4446-y>
- Hackley, V. a., & Ferraris, C. F. (2001). The use of nomenclature in dispersion science and technology. *NIST Special Publication*, 960(3), 76.
- Haque, M. A., Kurokawa, T., & Gong, J. P. (2012). Super tough double network hydrogels and their application as biomaterials. *Polymer*, 53(9), 1805–1822. <http://doi.org/10.1016/j.polymer.2012.03.013>
- He, X., Yang, W., & Pei, X. (2008). Preparation , Characterization , and Tunable Wettability of Poly (ionic liquid) Brushes via Surface-Initiated Atom Transfer Radical Polymerization. *Society*, 4615–4621. <http://doi.org/10.1021/ma702389y>
- Hirotsu, S., Hirokawa, Y., & Tanaka, T. (1987). Volume-phase transitions of ionized N-isopropylacrylamide gels. *The Journal of Chemical Physics*, 87(2), 1392–1395. <http://doi.org/http://dx.doi.org/10.1063/1.453267>
- Hoffman, A. S. (2002). Hydrogels for biomedical applications. *Advanced Drug Delivery Reviews*, 54(1), 3–12. [http://doi.org/10.1016/S0169-409X\(01\)00239-3](http://doi.org/10.1016/S0169-409X(01)00239-3)
- Holzapfel, B. M., Reichert, J. C., Schantz, J. T., Gbureck, U., Rackwitz, L., Nöth, U., Hutmacher, D. W. (2013). How smart do biomaterials need to be? A translational science and clinical point of view. *Advanced Drug Delivery Reviews*, 65(4), 581–603. <http://doi.org/10.1016/j.addr.2012.07.009>
- Ibraeva, Z. E., Hahn, M., Jaeger, W., Bimendina, L. A., & Kudaibergenov, S. E. (2004). Solution properties and complexation of polyampholytes based on N,N-dimethyldiallylammonium chloride and maleic acid or alkyl (aryl) derivatives of maleamic acids. *Macromolecular Chemistry and Physics*, 205(18), 2464–2472. <http://doi.org/10.1002/macp.200400242>
- Ihsan, A. Bin, Sun, T. L., Kuroda, S., Haque, M. A., Kurokawa, T., Nakajima, T., & Gong, J. P. (2013). A phase diagram of neutral polyampholyte - from solution to tough hydrogel. *Journal of Materials Chemistry B*, 1(36), 4555–4562. <http://doi.org/10.1039/C3TB20790K>
- Ito, K., Nishina, N., & Ohno, H. (2000). Enhanced ion conduction in imidazolium-type molten salts. *Electrochimica Acta*, 45(8), 1295–1298. [http://doi.org/10.1016/S0013-4686\(99\)00335-7](http://doi.org/10.1016/S0013-4686(99)00335-7)
- Jenkins, A. D.; Kratochvíl, P.; Stepto, R. F. T.; Suter, U. W. (1996). International , Union of Pure Glossary of Basic Terms in Polymer. *Pure and Applied Chemistry*, 68(12), 2287–2311. <http://doi.org/10.1351/pac199668122287>

- K. Kabiri, H. Omidian, M. J. Zohuriaan-Mehr, S. D. (2011). Superabsorbent Hydrogel Composites and Nanocomposites: A Review. *Polymers and Polymer Composites*, 32, 277–289. <http://doi.org/10.1002/pc>
- Keskin, S., Kayrak-Talay, D., Akman, U., & Hortaçsu, Oner. (2007). A review of ionic liquids towards supercritical fluid applications. *Journal of Supercritical Fluids*, 43(1), 150–180. <http://doi.org/10.1016/j.supflu.2007.05.013>
- Khalid, S. H., Qadir, M. I., Massud, A., Ali, M., & Rasool, M. H. (2009). Effect of degree of cross-linking on swelling and drug release behaviour of poly(methyl methacrylate-co-itaconic acid) [P(MMA/IA)] hydrogels for site specific drug delivery. *Journal of Drug Delivery Science and Technology*, 19(6), 413–418. [http://doi.org/10.1016/S1773-2247\(09\)50085-8](http://doi.org/10.1016/S1773-2247(09)50085-8)
- Kim, K., Chen, W. C. W., Heo, Y., & Wang, Y. (2016). Polycations and Their Biomedical Applications. *Progress in Polymer Science*. <http://doi.org/http://dx.doi.org/10.1016/j.progpolymsci.2016.05.004>
- Kost, J., & Langer, R. (2012). Responsive polymeric delivery systems. *Advanced Drug Delivery Reviews*, 64(SUPPL.), 327–341. <http://doi.org/10.1016/j.addr.2012.09.014>
- Kryscio, D. R., & Peppas, N. A. (2012). Critical review and perspective of macromolecularly imprinted polymers. *Acta Biomaterialia*, 8(2), 461–473. <http://doi.org/10.1016/j.actbio.2011.11.005>
- L. V. Epishina; V. I. Slovetskii; V. G. Osipov; O. V. Lebedev; L. I. Khmel'nitskii; V. V. Sevost'yanova; T. S. Novikova. (1967). Infrared spectra and the structure of salts of imidazoles. *Chemistry of Heterocyclic Compounds*, 3, 570–575.
- Lázaro Martínez, J. M., Chattah, A. K., Sánchez, R. M. T., Buldain, G. Y., & Campo Dall'Orto, V. (2012). Synthesis and characterization of novel polyampholyte and polyelectrolyte polymers containing imidazole, triazole or pyrazole. *Polymer*, 53(6), 1288–1297. <http://doi.org/10.1016/j.polymer.2012.01.031>
- Li, Q., Chen, J., Fan, L., Kong, X., & Lu, Y. (2016). Progress in Electrolytes for Rechargeable Li-based Batteries and beyond. *Green Energy & Environment*. <http://doi.org/10.1016/j.gee.2016.04.006>
- Lira, L. M., & Córdoba De Torresi, S. I. (2005). Conducting polymer-hydrogel composites for electrochemical release devices: Synthesis and characterization of semi-interpenetrating polyaniline- polyacrylamide networks. *Electrochemistry Communications*, 7(7), 717–723. <http://doi.org/10.1016/j.elecom.2005.04.027>
- Lord, M. S., Stenzel, M. H., Simmons, A., & Milthorpe, B. K. (2006). The effect of charged groups on protein interactions with poly(HEMA) hydrogels. *Biomaterials*, 27(4), 567–575. <http://doi.org/10.1016/j.biomaterials.2005.06.010>
- Lowe, A. B., & McCormick, C. L. (2002). Synthesis and solution properties of zwitterionic polymers. *Chemical Reviews*, 102(11), 4177–4189. <http://doi.org/10.1021/cr020371t>

- Lu, J., Yan, F., & Texter, J. (2009). Advanced applications of ionic liquids in polymer science. *Progress in Polymer Science*, 34(5), 431–448. <http://doi.org/10.1016/j.progpolymsci.2008.12.001>
- Ma, S., Yu, B., Pei, X., & Zhou, F. (2016). Structural hydrogels. *Polymer*, 98, 516–535. <http://doi.org/10.1016/j.polymer.2016.06.053>
- Madria, N. (2011). Synthesis and toxicity studies of imidazolium-based ionic liquids. Master Thesis, Missouri University of Science and Technology.
- Mallakpour, S., & Dinari, M. (2012). *Green Solvents II*. <http://doi.org/10.1007/978-94-007-2891-2>
- Marsh, K. N., Boxall, J. A., & Lichtenthaler, R. (2004). Room temperature ionic liquids and their mixtures - A review. *Fluid Phase Equilibria*, 219(1), 93–98. <http://doi.org/10.1016/j.fluid.2004.02.003>
- Mecerreyes, D. (2011). Polymeric ionic liquids: Broadening the properties and applications of polyelectrolytes. *Progress in Polymer Science (Oxford)*, 36(12), 1629–1648. <http://doi.org/10.1016/j.progpolymsci.2011.05.007>
- Mecerreyes, D. (2015). *Applications of Ionic Liquids in Polymer Science and Technology*. <http://doi.org/10.1007/978-3-662-44903-5>
- Meyvis, T. K. L., De Smedt, S. C., Demeester, J., & Hennink, W. E. (2000). Influence of the degradation mechanism of hydrogels on their elastic and swelling properties during degradation. *Macromolecules*, 33(13), 4717–4725. <http://doi.org/10.1021/ma992131u>
- Mi, H., Jiang, Z., & Kong, J. (2013). Hydrophobic poly(ionic liquid) for highly effective separation of methyl blue and chromium ions from water. *Polymers*, 5(4), 1203–1214. <http://doi.org/10.3390/polym5041203>
- Minamimoto, H., Irie, H., Uematsu, T., Tsuda, T., Imanishi, A., Seki, S., & Kuwabata, S. (2015). Polymerization of room-temperature ionic liquid monomers by electron beam irradiation with the aim of fabricating three-dimensional micropolymer/nanopolymer structures. *Langmuir*, 31(14), 4281–4289. <http://doi.org/10.1021/la503252p>
- Morita, S. (2014). Hydrogen-bonds structure in poly(2-hydroxyethyl methacrylate) studied by temperature-dependent infrared spectroscopy. *Frontiers in Chemistry*, 2(March), 10. <http://doi.org/10.3389/fchem.2014.00010>
- Murdan, S. (2003). Electro-responsive drug delivery from hydrogels. *Journal of Controlled Release*, 92(1–2), 1–17. [http://doi.org/10.1016/S0168-3659\(03\)00303-1](http://doi.org/10.1016/S0168-3659(03)00303-1)
- Na, Y. H.; Kurokawa, T.; Katsuyama, Y.; Tsukeshiba, H.; Gong, J. P.; Osada, Y.; Okabe, S.; Karino, T. . M. S. (2004). Structural Characteristics of Double Network Gels with Extremely High Mechanical Strength. *Macromolecules*, 37(12), 5370–5374.

- Narimani, F., Zohuriaan-Mehr, M. J., Kabiri, K., Bouhendi, H., Omidian, H., & Najafi, V. (2012). Overentrant swelling behaviour of poly(potassium, 3-sulfopropyl acrylate-acrylic acid) gels. *Journal of Polymer Research*, *19*(12), 1–8. <http://doi.org/10.1007/s10965-012-0007-2>
- Nicholas A. Peppas, Allan Hoffman, Emo Chiellini, Fu-Zhai Cui, Karel Dusek, Jindrich Kopecek, Claudio Migliaresi, Yoshihito Osada, Buddy D. Ratner, Nathan Ravi, Etienne Schacht, T. T. (2010). *Biomedical Applications of Hydrogels Handbook*. <http://doi.org/10.1017/CBO9781107415324.004>
- Niedermeyer, H., Hallett, J. P., Villar-Garcia, I. J., Hunt, P. A., & Welton, T. (2012). Mixtures of ionic liquids. *Chemical Society Reviews*, *41*(23), 7780–7802. <http://doi.org/10.1039/c2cs35177c>
- Nishimura, N., & Ohno, H. (2014). 15Th Anniversary of Polymerised Ionic Liquids. *Polymer (United Kingdom)*, *55*(16), 3289–3297. <http://doi.org/10.1016/j.polymer.2014.02.042>
- Nobuoka, K., Kitaoka, S., Iio, M., Harran, T., & Ishikawa, Y. (2007). Solute-solvent interactions in imidazolium camphorsulfonate ionic liquids. *Physical Chemistry Chemical Physics : PCCP*, *9*(44), 5891–6. <http://doi.org/10.1039/b709407h>
- Ohno, H., Yoshizawa, M., & Ogihara, W. (2004). Development of new class of ion conductive polymers based on ionic liquids. *Electrochimica Acta*, *50*(2–3 SPEC. ISS.), 255–261. <http://doi.org/10.1016/j.electacta.2004.01.091>
- Okano, T., Nishiyama, S., Shinohara, I., Akaike, T., Sakurai, Y., Kataoka, K., & Tsuruta, T. (1981). Effect of hydrophilic and hydrophobic microdomains on mode of interaction between block polymer and blood platelets. *Journal of Biomedical Materials Research*, *15*(3), 393–402. <http://doi.org/10.1002/jbm.820150310>
- Omidian, H., Rocca, J. G., & Park, K. (2005). Advances in superporous hydrogels. *Journal of Controlled Release*, *102*(1), 3–12. <http://doi.org/10.1016/j.jconrel.2004.09.028>
- Pendleton, J. N., & Gilmore, B. F. (2015). The antimicrobial potential of ionic liquids: A source of chemical diversity for infection and biofilm control. *International Journal of Antimicrobial Agents*, *46*(2), 131–139. <http://doi.org/10.1016/j.ijantimicag.2015.02.016>
- Peppas, N. A., Bures, P., Leobandung, W., & Ichikawa, H. (2000). Hydrogels in pharmaceutical formulations. *European Journal of Pharmaceutics and Biopharmaceutics*, *50*(1), 27–46. [http://doi.org/10.1016/S0939-6411\(00\)00090-4](http://doi.org/10.1016/S0939-6411(00)00090-4)
- Peppas, N. A., Hilt, J. Z., Khademhosseini, A., & Langer, R. (2006). Hydrogels in biology and medicine: From molecular principles to bionanotechnology. *Advanced Materials*, *18*(11), 1345–1360. <http://doi.org/10.1002/adma.200501612>
- Perrier, S., Davis, T. P., Carmichael, A. J., Haddleton, D. M., Chemistry, I., Mediated, T. M., & Addition-fragmentation, R. (2002). First report of reversible addition – fragmentation chain transfer (RAFT) polymerisation in room temperature ionic liquids The Reversible Addition – Fragmentation chain Transfer (RAFT) polymerisation of acrylates , methacrylates and ionic liquids ; th, 2226–2227.

- Portal, O. C. (2013). Ionic liquids, 5(6). <http://doi.org/10.1038/nmat907> T4 - A taste of the future M4 - Citavi
- Qin, W., & Li, S. F. Y. (2002). An ionic liquid coating for determination of sildenafil and UK-103, 320 in human serum by capillary zone electrophoresis-ion trap mass spectrometry. *Electrophoresis*, 4110–4116. <http://doi.org/10.1002/elps.200290028>
- Qiu, H., Jiang, S., & Liu, X. (2006). N-Methylimidazolium anion-exchange stationary phase for high-performance liquid chromatography. *Journal of Chromatography A*, 1103(2), 265–270. <http://doi.org/10.1016/j.chroma.2005.11.035>
- Rajkumar, T., & Rao, G. R. (2008). Investigation of hybrid molecular material prepared by ionic liquid and polyoxometalate anion. *Journal of Chemical Sciences*, 120(6), 587–594. <http://doi.org/10.1007/s12039-008-0089-x>
- Roy, D., Cambre, J. N., & Sumerlin, B. S. (2010). Future perspectives and recent advances in stimuli-responsive materials. *Progress in Polymer Science (Oxford)*, 35(1–2), 278–301. <http://doi.org/10.1016/j.progpolymsci.2009.10.008>
- Russina, O., Fazio, B., Marco, G. Di, & Caminiti, R. (2014). *The Structure of Ionic Liquids*. <http://doi.org/10.1007/978-3-319-01698-6>
- Schlenoff, J. B. (2014). Zwitteration: Coating surfaces with zwitterionic functionality to reduce nonspecific adsorption. *Langmuir*, 30(32), 9625–9636. <http://doi.org/10.1021/la500057j>
- Schult, K. a, & Paul, D. R. (1996). Techniques for measurement of water vapor sorption and permeation in polymer films. *Journal of Applied Polymer Science*, 61(11), 1865–1876. [http://doi.org/10.1002/\(SICI\)1097-4628\(19960912\)61:11<1865::AID-APP2>3.0.CO;2-H](http://doi.org/10.1002/(SICI)1097-4628(19960912)61:11<1865::AID-APP2>3.0.CO;2-H)
- Scognamillo, S., Alzari, V., Nuvoli, D., Illescas, J., Marceddu, S., & Mariani, A. (2011). Thermoresponsive super water absorbent hydrogels prepared by frontal polymerization of N-isopropyl acrylamide and 3-sulfopropyl acrylate potassium salt. *Journal of Polymer Science, Part A: Polymer Chemistry*, 49(5), 1228–1234. <http://doi.org/10.1002/pola.24542>
- Scott, M. P., Rahman, M., & Brazel, C. S. (2003). Application of ionic liquids as low-volatility plasticizers for PMMA. *European Polymer Journal*, 39(10), 1947–1953. [http://doi.org/10.1016/S0014-3057\(03\)00129-0](http://doi.org/10.1016/S0014-3057(03)00129-0)
- Scrantom A. B., Rangarajan B., K. J. (1995). Biomedical Applications of Polyelectrolytes, 122, 217–230. <http://doi.org/10.4028/www.scientific.net/AST.57.50>
- Sefton, M. V., May, M. H., Lahooti, S., & Babensee, J. E. (2000). Making microencapsulation work: Conformal coating, immobilization gels and in vivo performance. *Journal of Controlled Release*, 65(1–2), 173–186. [http://doi.org/10.1016/S0168-3659\(99\)00234-5](http://doi.org/10.1016/S0168-3659(99)00234-5)

- Shah, R., Saha, N., & Saha, P. (2015). Influence of temperature, pH and simulated biological solutions on swelling and structural properties of biomineralized (CaCO₃) PVP–CMC hydrogel. *Progress in Biomaterials*, 4(2–4), 123–136. <http://doi.org/10.1007/s40204-015-0043-1>
- Shaplov, A. S., Marcilla, R., & Mecerreyes, D. (2015). Recent Advances in Innovative Polymer Electrolytes based on Poly(ionic liquid)s. *Electrochimica Acta*, 175, 18–34. <http://doi.org/10.1016/j.electacta.2015.03.038>
- Shaplov, A. S., Vlasov, P. S., Lozinskaya, E. I., Ponkratov, D. O., Malyskina, I. A., Vidal, F., Vygodskii, Y. S. (2011). Polymeric ionic liquids: Comparison of polycations and polyanions. *Macromolecules*, 44(24), 9792–9803. <http://doi.org/10.1021/ma2014518>
- Singh, P. K., Singh, V. K., & Singh, M. (2007). Zwitterionic polyelectrolytes: a review. *Polymer*, (30), 1–34.
- Stolte, S., Arning, J., Bottin-Weber, U., Müller, A., Pitner, W.-R., Welz-Biermann, U., Ranke, J. (2007). Effects of different head groups and functionalised side chains on the cytotoxicity of ionic liquids. *Green Chemistry*, 9(7), 760. <http://doi.org/10.1039/b615326g>
- Stuart, M. a C., Huck, W. T. S., Genzer, J., Müller, M., Ober, C., Stamm, M., Minko, S. (2010). Emerging applications of stimuli-responsive polymer materials. *Nature Materials*, 9(2), 101–113. <http://doi.org/10.1038/nmat2614>
- Texter, J. (2012). Anion responsive imidazolium-based polymers. *Macromolecular Rapid Communications*, 33(23), 1996–2014. <http://doi.org/10.1002/marc.201200525>
- Thuy Pham, T. P., Cho, C. W., & Yun, Y. S. (2010). Environmental fate and toxicity of ionic liquids: A review. *Water Research*, 44(2), 352–372. <http://doi.org/10.1016/j.watres.2009.09.030>
- Tokarev, I., Motornov, M., & Minko, S. (2009). Molecular-engineered stimuli-responsive thin polymer film: a platform for the development of integrated multifunctional intelligent materials. *Journal of Materials Chemistry*, 19(38), 6932. <http://doi.org/10.1039/b906765e>
- Tukenmez, E., & Bicak, N. (2016). Poly(HEMA) Microbeads with Multi Amine Surface Functions for Reversible Metal Complex Formation. *Macromolecular Symposia*, 364(1), 32–37. <http://doi.org/10.1002/masy.201500126>
- Ullah, F., Othman, M. B. H., Javed, F., Ahmad, Z., & Akil, H. M. (2015). Classification, processing and application of hydrogels: A review. *Materials Science and Engineering C*, 57, 414–433. <http://doi.org/10.1016/j.msec.2015.07.053>
- Unsal, E., Durdu, A., Elmas, B., Tuncel, M., & Tuncel, A. (2005). A new affinity-HPLC packing for protein separation: Cibacron blue attached uniform porous poly(HEMA-co-EDM) beads. *Analytical and Bioanalytical Chemistry*, 383(6), 930–937. <http://doi.org/10.1007/s00216-005-0121-7>

- V., Bekiari, Zamparas M., L. G. and B. G. (2016). Ionic hydrogels as potential sorbent materials for charged organic dyes, (May 2015).
- Vijayaraghavan, R., & MacFarlane, D. R. (2004). Living cationic polymerisation of styrene in an ionic liquid. *Chemical Communications (Cambridge, England)*, (6), 700–701. <http://doi.org/10.1039/b315100j>
- Walden, P. (1914). Molecular weights and Electrical Conductivity of Several Fused Salts. *Bull. Acad. Imp. Sci. St-Petersbourg*, (8), 405–422.
- Wang, F., Yang, J., & Zhao, J. (2015). Understanding anti-polyelectrolyte behavior of a well-defined polyzwitterion at the single-chain level. *Polymer International*, 64(8), 999–1005. <http://doi.org/10.1002/pi.4907>
- Wei, H., Wu, X.-S., Wen, G.-Y., & Qiao, Y. (2016). Imidazolium Ionic Liquid Functionalized Carbon Nanotubes for Improved Interfacial Charge Transfer and Simultaneous Determination of Dihydroxybenzene Isomers. *Molecules*, 21(5), 617. <http://doi.org/10.3390/molecules21050617>
- Wichterle, O., & Lím, D. (1960). Hydrophilic Gels for Biological Use. *Nature*, 185(4706), 117–118. <http://doi.org/10.1038/185117a0>
- Wikes, J. S. (1992). Air and Water Stable I-Ethyl-3-methylimidazolium Based Ionic Liquids. *Chemical Communications*, 4, 965–967.
- Wilkinson, A. D. McNaught, A. (1997). International Union of Pure and Applied Chemistry Compendium of Chemical Terminology. *Blackwell Scientific Publications, Oxford*. <http://doi.org/http://dx.doi.org/10.1351/goldbook.I03352>
- Wilson, A. N., Blenner, M., & Guiseppi-Elie, A. (2014). Polyplex formation influences release mechanism of mono- and di-valent ions from phosphorylcholine group bearing hydrogels. *Polymers*, 6(9), 2451–2472. <http://doi.org/10.3390/polym6092451>
- Xiao, H., Hu, J., Jin, S., & Li, R. H. (2013). Synthesis and Solution Properties of Zwitterionic Copolymer of Acrylamide with 3-[(2-Acrylamido)dimethylammonio]propanesulfonate. *Bull. Korean Chem. Soc.* 34(9), 2616–2622. <http://dx.doi.org/10.5012/bkcs.2013.34.9.2616>
- Xie, Y., Jing, K.-J., & Lu, Y. (2011). Kinetics, equilibrium and thermodynamic studies of l-tryptophan adsorption using a cation exchange resin. *Chemical Engineering Journal*, 171(3), 1227–1233. <http://doi.org/10.1016/j.cej.2011.05.031>
- Yang, J., Hua, Z., Wang, T., Wu, B., Liu, G., & Zhang, G. (2015). Counterion-Specific Protein Adsorption on Polyelectrolyte Brushes. *Langmuir*, 31(22), 6078–6084. <http://doi.org/10.1021/acs.langmuir.5b01145>
- Ye, Y., & Elabd, Y. A. (2011). Anion exchanged polymerized ionic liquids: High free volume single ion conductors. *Polymer*, 52(5), 1309–1317. <http://doi.org/10.1016/j.polymer.2011.01.031>

- Yoo, B., Jing, B., Jones, S. E., Lamberti, G. A., Zhu, Y., Shah, J. K., & Maginn, E. J. (2016). Molecular mechanisms of ionic liquid cytotoxicity probed by an integrated experimental and computational approach. *Scientific Reports*, 6(February), 19889. <http://doi.org/10.1038/srep19889>
- Yuan, J., & Antonietti, M. (2011). Poly(ionic liquid)s: Polymers expanding classical property profiles. *Polymer*, 52(7), 1469–1482. <http://doi.org/10.1016/j.polymer.2011.01.043>
- Yuan, J., Mecerreyes, D., & Antonietti, M. (2013). Poly(ionic liquid)s: An update. *Progress in Polymer Science*, 38(7), 1009–1036. <http://doi.org/10.1016/j.progpolymsci.2013.04.002>
- Zhang, S., Sun, N., He, X., Lu, X., & Zhang, X. (2006). Physical properties of ionic liquids: Database and evaluation. *Journal of Physical and Chemical Reference Data*, 35(4), 1475–1517. <http://doi.org/10.1063/1.2204959>

Appendix

Appendix A: SDT profiles

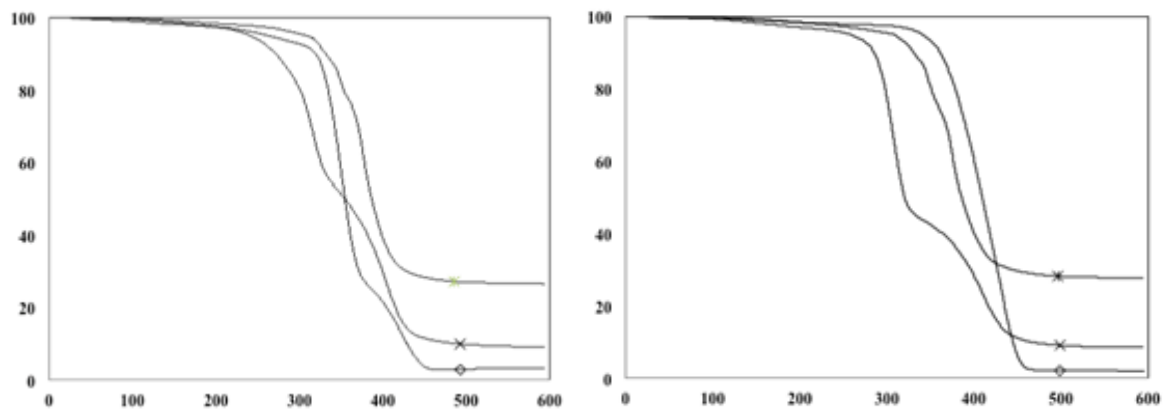


Figure A. 1. SDT profiles of poly(HEMA) (\diamond), A0/100 ($*$) and A100/0 (\times) without (left) and with chemical crosslinking, 1% (right).

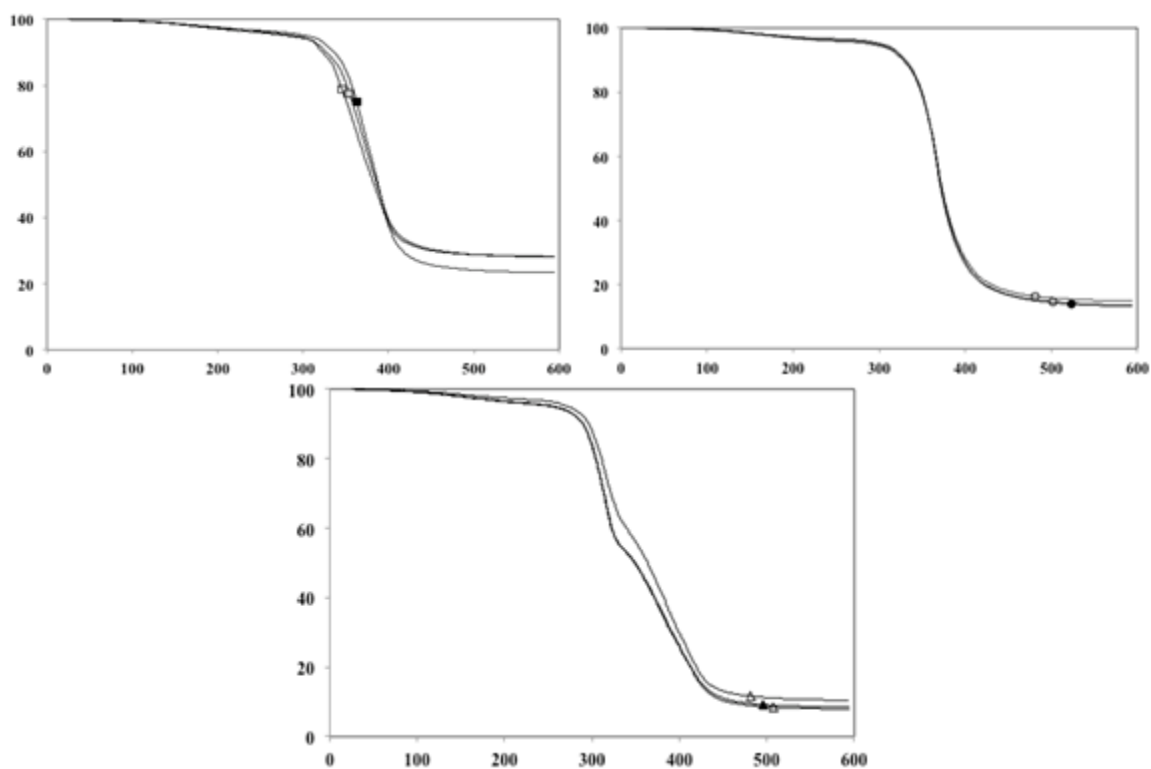


Figure A. 2. SDT profiles of samples A25/75 (squares), A50/50 (circles) and A75/25 (triangles) for non-crosslinked samples (empty symbols); 0.5% cross linked samples (grey symbols) and 1% cross linked samples (black symbols).

Appendix B: Calibration curves

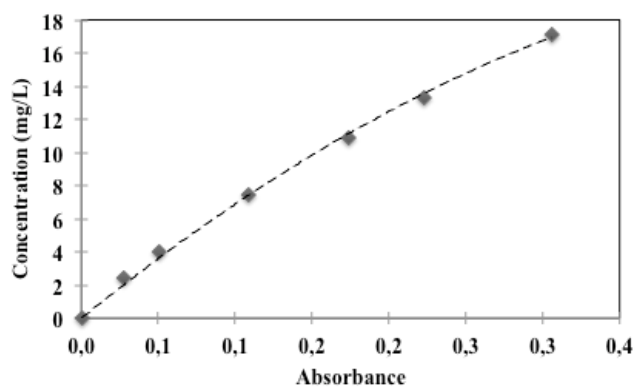


Figure B. 1 Calibration curve of K₂CrO₄; $y = -65,381x^2 + 75,462x$ $R^2=0,9983$

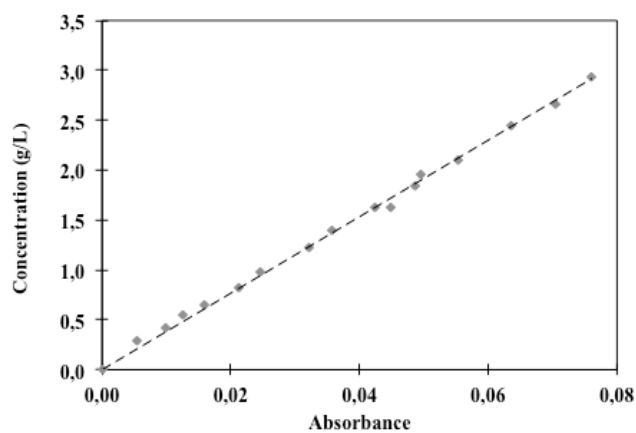


Figure B. 2 Calibration curve of Bromocresol green sodium salt; $y = 38,35x$ $R^2=0,9983$

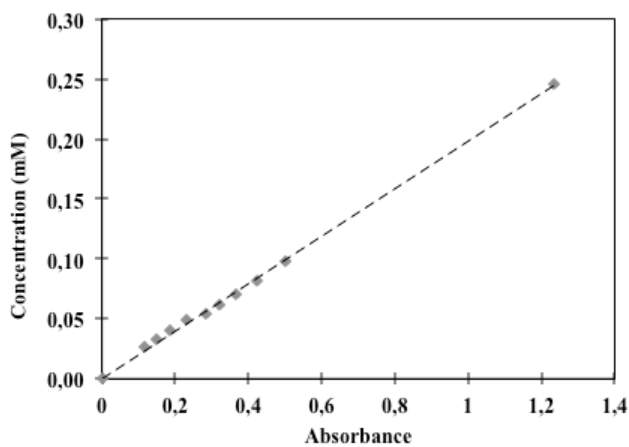


Figure B. 3 Calibration curve of L-tryptophan; $y = 0,1981x$ $R^2=0,9983$