



Noncollapsing polyelectrolyte conetwork gels in physiologically relevant salt solutions



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ABSTRACT

In consequence of some unique properties, such as nanophase separation, biocompatibility and mechanical stability, amphiphilic polymer conetworks (APCNs) have received significant attention in recent years. APCNs are composed of hydrophilic and hydrophobic polymer chains connected with covalent bonds. The unique properties of APCNs make them suitable for many specialized applications. Although APCNs were widely investigated and described in the literature, this is the first study on the swelling behavior of these materials in the solutions of physiologically relevant salts. Homopolymer polyelectrolyte hydrogels are known to suffer phase transition like rapid gel collapse at a certain salt concentration in the solutions of bi- or multivalent metal salts. Systematic swelling investigation of poly(methacrylic acid)-*l*-polyisobutylene (PMAA-*l*-PIB) conetwork series in CaCl₂ salt solutions led to unexpected findings. Our results indicate that these polyelectrolyte APCNs do not behave the same way in salt solutions as the homopolymer hydrogels, i.e. APCNs do not suffer gel collapse, the change of the swelling degree remains continuous with increasing salt concentration. The gel contraction was reversible by changing the solute to NaOH solution, i.e. the gels returned to their original volume by reswelling. This non-collapsing swelling means that the presence of hydrophobic polymer segments as cross-linkers in amphiphilic polyelectrolyte gels radically change the swelling behavior of such materials, which become substantially different from that of homopolymer polyelectrolyte gels.

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1. Introduction

Homopolymers and homopolymeric hydrogels [1–4] have gained a keen interest in the biological, especially in the medical field. These polymeric structures are used as carriers of drugs, contact lenses, implants and as scaffolds for tissue engineering. [1]. An important class of homopolymers, the polyelectrolytes, has some undesirable properties which are not compatible with the bioapplications mentioned above. One of the unwanted features is the solution and swelling behavior of linear and cross-linked polyelectrolytes in the solution of bi- and multivalent metal ions. In the presence of such ions, polyelectrolytes, such as poly(acrylic acid), poly(methacrylic acid) or polyalginates undergoes various phase transitions [2–4]. Specifically, the linear polyelectrolytes precipitate in the solution of multivalent salts [2], while homopolymer polyelectrolyte gels collapse at a certain concentration of bi- or multivalent metal salts in the swelling media [3,4]. The

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precipitation of the linear homopolymers, as well as the contraction of the gels occurring at a critical concentration, mainly depend on the number/concentration of the charged groups of the polyelectrolyte [3(b),5]. Here, it should be noted that, although the volume phase transition of these polyelectrolytes is disadvantageous for bioapplications, but it makes these materials desirable for application in valves and actuators.

Recently, Horkay et al. have investigated the swelling of cross-linked negative polyelectrolytes, namely polyacrylates and polymethacrylates in the solutions of physiologically relevant salts [4]. These hydrogels undergo volume contracting by increasing the amounts of different cations, and this change in the swelling degree has depended on the valence of the metal ion. In the case of monovalent ions (such as Na^+), this contraction was smooth and continuous, while in the solution of bi- and multi-valent ions (Ca^{2+} , Mg^{2+} , La^{3+}) the swelling behavior, was completely different. At a critical concentration of the multivalent salt, the volume change of the gels became non-continuous, and rapid gel collapse occurred, most probably due to the physical cross-link formation by the bivalent cations and the negatively charged polyelectrolytes. For homopolymer polyelectrolyte hydrogels, this phenomenon excludes these materials from many application possibilities in biological systems which contain bio-relevant multivalent metal salts, for example, Ca(II) . Calcium is a biologically significant inorganic material, stored mostly in the bones, but the intra- and extracellular matrices also contain Ca^{2+} around 1 and above 2 mM concentration, respectively [6].

Amphiphilic polymer conetworks (APCN) are bi-, or multicomponent polymeric materials with both some similarity and differences from homopolymer hydrogels [7]. In contrast to homopolymer hydrogels, the APCNs has not only hydrophilic but hydrophobic component as well, covalently connected to each other. As a result, these materials can swell in both polar and nonpolar solutes. Beyond their amphiphilic nature, APCNs have some other unusual properties, such as their nanophase separated structure [8,9], biocompatibility [10,11], and excellent mechanical strength [9,12,13]. This last property, their improved mechanical stability befalls not only in the dry but the highly swollen state as well, which is a great advantage, compared to the fragile and mechanically unstable homopolymer hydrogels [1–4]. Due to these advantageous properties, the application of APCNs in biological systems or medical field is well known as matrices for controlled drug delivery [14], scaffolds for tissue engineering [11(b),15,16] and implants, materials for soft contact lenses [17–19] and also for other biorelevant application possibilities [11(a),20]. It seems to be evident, that APCNs are possible candidates to replace homopolymer hydrogels in many fields. Considering the advantageous properties and the wide range of bioapplication possibilities of APCNs, it is surprising that there is no any report on the swelling behavior of these novel materials in solutions of physiologically relevant salts.

The structure of APCNs can be varied by using various interconnected hydrophobic and hydrophilic polymers. In our case, the lipophilic part was the highly hydrophobic, biocompatible, fully saturated polyisobutylene (PIB). PIB is a rubbery polymer with low glass transition temperature (T_g), which property makes APCNs with PIB as hydrophobic component mechanically and chemically stable [21]. The hydrophilic part of the used conetworks can be neutral polymer or even polyelectrolytes, such as poly(methacrylic acid) (PMAA), even there are only a few examples of anionic APCNs reported in the literature [9,12,22–24]. PMAA is a well-known glassy, hydrophilic polyelectrolyte, which forms mechanically nonstable hydrogel. The synthesis and the intelligent swelling behavior of PMAA based APCNs were investigated and described earlier. The swelling of these conetworks was studied in hydrophobic solvents and in water as well as a function of pH [9,12,13(b),22–25], but the swelling behavior of polyelectrolyte APCNs in salt solutions has not been described yet.

In this work, we report on the synthesis of a series of poly(methacrylic acid)-*l*-polyisobutylene (PMMA-*l*-PIB) APCNs (*l* stands for *linked by*) and their unexpected swelling behavior in the solutions of the biologically relevant NaCl and CaCl_2 salts over a wide range of concentrations.

2. Experimental

2.1. Materials and methods

Methylmagnesium bromide (3.0 M solution in diethyl ether), 5-*tert*-butylisophthalic acid (98%), ammonium chloride (puriss), titanium tetrachloride (TiCl_4 , 99.9%), 1,1,4,4-tetramethylethylenediamine (99.5%, TMEDA), 9-borabicyclo [3.3.1]nonane (9-BBN; 0.5 M solution in THF), hydrogen peroxide (35% solution in water), methacryloyl chloride (97%, MACl), trimethylsilyl methacrylate (TMSMA; 98%), calcium hydride (CaH_2 , 90–95%) and aluminium oxide (activated, neutral) were all purchased from Aldrich. Hexane (96%) was obtained from Scharlau S. A., Spain. Dichloromethane (DCM, 99.8%), tetrahydrofuran (THF; 99.8%) and methanol (99.8%) were purchased from Chemolab. Isobutylene (IB, 99.8%) and hydrogen chloride (HCl, 99.8%) were obtained from Messer Griesheim, Germany. Triethylamine (Et_3N , 99%) and potassium hydroxide (98%) were purchased from Merck, while calcium chloride (anhydrous), allyltrimethylsilane (ATMS, 97%) and α,α' -azobisisobutyronitrile (AIBN; 98+%) were purchased from Fluka.

2.2. Preparation of the bifunctional cationic initiator and the macromonomer

The *tert*-butyldicymyl chloride bifunctional carbocationic initiator was obtained by the esterification of 5-*tert*-butylisophthalic acid, followed by a Grignard reaction, and a hydrochlorination step as reported before [26].

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