Preparation, Structural Analyses and Swelling Behavior of Amphiphilic Polymer Conetworks and Gels Based on Methacrylic Acid

Ph.D. Theses

Gergely Áron Kali

Doctorate School of Chemistry
Analytical Chemistry, Colloid- and Environmental Chemistry, Electrochemistry Program
Eötvös Loránd Science University, Faculty of Natural Sciences
Budapest, Hungary

Programme Leader

Prof. Gyula Záray

Supervisor

Prof. Béla Iván

2009

I. Introduction and Aims

The investigation of the preparation, structure and properties of amphiphilic conetworks (APCN) as well as their possible applications have great interest in polymer science nowadays. These materials are comprised of covalently bonded, immiscible hydrophilic and hydrophobic polymer chains. Many unique and outsanding properties of APCNs, such as excellent mechanical strength, biocompatibility, swelling in polar and nonpolar solvents and the nanophase separated structures make them applicable easier and in broader fields than homopolymer hydrogels. Another disadvantage homopolymer polyelectrolyte hydrogels on the basis of the literature is that these materials undergo phase transition like gel collapse in the solution of different two or higher valence ions. As a consequence, there is a limitation of application hydrogels in high salt containing (for example some biological) systems.

A special class of APCNs is the group of model APCNs consisting of polymer chains with narrow molecular weight distribution and predetermined composition between the cross-links. The synthesis of model APCNs can be accomplished by the use of living polymerization techniques. Due to the well-known structure of the model APCNs, the structure-property relationships can be investigated better than in the case of randomly cross-linked APCNs. The first aim of this research was the preparation of three different model APCN series based on a well-known anionic polyelectrolyte, the hydrophilic poly(methacrylic acid). In the first case, the hydrophobic segment was the commercially available, glassy poly(methyl methacrylate), while in the second case a non-commercial rubbery poly(2-butyl-1-octyl methacrylate) was used. To the best of my knowledge, there is no any report in the literature on the synthesis and application of 2-butyl-1-octyl methacrylate. The third hydrophobic monomer was a macromonomer, the rubbery polyisobutylene-methacrylate. The living polymerization method used was group transfer polymerization (GTP). The resulting conetwork series were widely investigated. My studies have been focused mostly on the investigation of the precursor chains of APCNs, then the mechanical and swelling properties as well as the phase separated structures. The swelling of these materials was also examined in solvents of biologically relevant salts.

Another aim of this work was the synthesis and swelling investigations of a known amphiphilic conetwork, poly(methacrylic acid)-*l*-polyisobutylene (PMAA-*l*-PIB). The synthesis was carried out by the so-called macromonomer method, and the swelling investigations were carried out in different salt solutions.

In the course of my research, I have also dealt with the problem related to with the hydrophilic monomer, methacrylic acid. In the two different synthesis strategies described above the same protected methacrylic acid cannot be used. Tetrahydropyranyl methacrylate (THPMA) was used in the GTP polymerization. This monomer is thermally instable, so it is useless in the case of free radical polymerization in the macromonomer method. The trimethylsilyl methacrylate, used in the macromonomer method, is useless in GTP, because it can lead to the transfer of the trimethylsilyl group which is crucial in this polymerization process. Considering this problem, I aimed to prepare and use a new monomer, which is might be better suitable for obtaining methacrylic acid containing APCNs.

II. Applied Methods

The macromonomers, based on polyisobutylene were synthesized by quasiliving carbocationic polymerization followed by several end group modification steps. The model conetworks were prepared by sequential monomer and cross-linker addition via Group Transfer Polymerization (GTP). Poly(methacrylic acid)-*l*-polyisobutylene APCNs were synthesized by the macromonomer method via free radical copolymerization.

The linear polymers were analyzed by gel permeation chromatography (GPC) and ^{1}H NMR spectroscopy in terms of their molecular weight, polydispersity and composition. FTIR analyses were used to confirm the complete network formation and hydrolysis of the protective groups. The thermal behavior of the conetworks was investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The mechanical properties were determined by dynamic mechanical analysis (DMA). The nanophase separated structure of the conetworks was investigated by small-angle neutron scattering (SANS) and atomic force microscopy (AFM). Finally, the degree of swelling (R %) was determined gravimetrically and was calculated as the solvent uptake divided by the mass of the dry network.

III. New Scientific Results

1.
Three series of model APCNs were synthesized using sequential monomer and cross-linker addition via GTP. The hydrophilic monomer was methacrylic acid (MAA), while the three different hydrophobic monomers were methyl methacrylate (MMA), 2-butyl-1-octyl methacrylate (BOMA) and polyisobutylene-methacrylate (PIBMA). The MAA units were introduced via the polymerization of tetrahydropyranyl methacrylate (THPMA) followed by the removal of the protecting tetrahydropyranyl group by acid hydrolysis after network formation. The linear conetwork precursors were analyzed by GPC and ^{1}H NMR spectroscopy in terms of their molecular weight and composition, both of which were found to be close to calculated values and the molecular weight distribution was narrow. FTIR spectroscopic analyses indicated complete polymerization of the EGDMA cross-linker vinyl units and complete hydrolysis of the THPMA units.

2.
The degrees of swelling (DS) of the MMA, BOMA and PIBMA based, MAA hydrophilic monomer containing conetworks were measured in water and in an organic solvent as a function of the degree of ionization (DI) of the MAA units. The results indicate that the DS of these conetworks increases by increasing the DI in water, and decreases by increasing the DI in THF. The effect of composition and architecture of the conetworks was studied as well, and it was found that these properties have influence on the DS. The DSs of the fully ionized conetworks in water increase by increasing the MAA content. The effect of the architecture on the swelling behavior is more complex. The DS of the statistical copolymer based conetworks are always higher than that of triblokk copolymer based model conetworks. The pK of the MAA units in the conetwork decreases by increasing the MAA content, but all the conetworks have higher pK values than the homopolymer PMAA network due to the effect of the hydrophobic environment in the conetworks. These results indicate that it is possible to influence the pK values of the conetworks by the hydrophobic content.

3.

The phase mode AFM measurements of the dry MMA and BOMA based conetworks have proved the nanophase separated structure for the model conetworks. SANS measurements have provided complementary information to AFM. The results of SANS investigations indicated phase separated morphology in the case of block copolymer based model conetworks, where the phase sizes (distances between the scattering centers) are depended on the composition. In the less ordered structures, such as statistical copolymer conetwork and randomly cross-linked copolymer network, scattering maxima did not appear, or only slight broad maxima occurred, which means that there is no phase separation in these materials.

4.

The swelling behavior of the conetworks based on MMA and BOMA in the aqueous solution of NaCl, $CaCl_2$ and the mixture of these two salts were also investigated. The results show that these amphiphilic conetworks - in contrast to homopolymer polyelectrolyte hydrogels - do not undergo discontinuous gel collapse even in very high salt concentrations, the change in the DS remains continuous. Thus, it can be concluded that these APCNs can be used in environments with very high salt concentrations.

5.

A series of APCNs were successfully synthesized by the macromonomer method in wide conetwork composition range using the bifunctional methacrylate-telechelic PIB macromonomer and MAA comonomer. The PIB macromonomer and the MAA comonomer have no common solvent, and the THPMA is thermally instable to use in the case of free radical copolymerization. In this case, a protected MAA, the trimethylsilyl methacrylate was used, and the protecting groups were removed by acidic hydrolysis after conetwork formation. The elemental analyses of these poly(methacrylic acid)-*l*-polyisobutylene (PMAA-*l*-PIB) conetworks after the deprotection confirmed that the preparation of this kind of conetwork is reproducible with a variety compositions.

6.

Another protected MAA, the ethoxyethyl methacrylate, described recently in the literature, have also been tried to produce a series of conetworks. Conetworks were successfully synthesized by free radical copolymerization of this comonomer and PIB-dimethacrylate. The deprotection was accomplished by acidic hydrolysis and thermolysis. FTIR investigations indicated better results for acidic hydrolysis. In the case of thermolysis of these conetworks, anhydride formation occurred. The temperatures of deprotection and decomposition were determined by TGA. The DSC graphs show the glass transition temperature of PIB, which result represents phase separation in these conetworks. The swelling behavior verifies the amphiphilic nature of the conetwork series. The APCNs swell in water as well as in hexane. Thus, it can concluded ethoxyethyl methacrylate is a suitable monomer for conetwork synthesis by radical copolymerization with PIB-methacrylate.

7.

The swelling behavior of PMAA-*l*-PIB conetworks was studied in aqueous solutions of Ca^{2+}, Cu^{2+} and La^{3+} salts. In the case of Ca^{2+} salt, the change in the DS remains continuous and lower than that of homopolymer hydrogels. With increasing $CaCl_2$ concentration gel collapse does not occur. In the case of Cu^{2+} and La^{3+} salts, the change in the swelling degree is quite high in the range of small salt concentration, but at higher level the degree of swelling will not change anymore. Thus it can be concluded that the investigated APCNs do not behave as it was expected on the basis of results with homopolymer polyelectrolytes. These new results offer possibilities for these novel materials to be useful in applications in biological systems or for metal binding.

IV. Publications and Presentations

V. 1. Publications

V.1.1. Publications related to this PhD work

1. G. Kali, B. Iván: Swelling Response of Amphiphilic Conetworks to Salt Concentration *Proceedings, International Symposium on Polymer Conetworks,Gels and Membranes*, Ed. B. Iván, Budapest, 2005. szeptember 11-13., pp 66-68.
2. G. Kali, T. K. Georgiou, B. Iván, C. S. Patrickios, E. Loizou, Y. Thomann, J. C. Tiller: Synthesis and Characterization of Anionic Amphiphilic Model Conetworks Based on Methacrylic Acid and

Methyl Methacrylate: Effects of Composition and Architecture
Macromolecules, **2007**, *40*, 2192-2200.

3. G. Kali, T. K. Georgiou, B. Iván, C. S. Patrickios, E. Loizou, Y. Thomann, J. C. Tiller: Synthesis and Characterization of Anionic Amphiphilic Model Conetworks of 2-Butyl-1-Octyl methacrylate and Methacrylic Acid: Effects of Polymer Composition and Architecture
Langmuir, **2007**, *23*, 10746-10755.
4. G. Kali, T. K. Georgiou, B. Iván, C. S. Patrickios, E. Loizou, Y. Thomann, J. C. Tiller: Structural Characterization Of Glassy And Rubbery Anionic Amphiphilic Model Conetworks
Nanoparticles Synthesis, Stabilization, Passivation and Functionalization (eds: R. Nagarajan and T. A. Hatton), *ACS Symposium Series* **2008**, *996*, 286-302.
5. G. Kali, T. K. Georgiou, B. Iván, C S. Patrickios: Anionic Amphiphilic Model Conetworks by the Combination of Quasiliving Carbocationic and Group Transfer Polymerizations
J. Polym. Sci., Part A: Polym. Chem., megjelenés alatt. (2009)

V.1.2. Publications not related to this PhD work

6. B. Iván, G. Erdődi, G. Kali, Gy. Holló-Szabó, Z. Zsebi, M. Szesztay: New functional hyperbranched and star polymers
Polym. Mater. Sci. Eng., **2004**, *91*, 197-198.
7. G. Kali, M. Szesztay, A. Bodor, B. Iván: A New Synthetic Method for the Preparation of Star Shaped Polyisobutylene with Hyperbranched Polystyrene Core
Macromol. Chem. Phys., **2007**, *208*, 1388-1393.
8. B. Iván, G. Erdődi, Á. Hellner, P. W. Groh, G. Kali, Gy. Kasza, I. Szanka, M. Szesztay, A. Soltész: New Ways for the Synthesis of Hyperbranched Polymers
Macromol. Rapid. Comm., **2008**, *29*, F16-18.
9. B. Iván, G. Erdődi, G. Kali, Gy. Kasza, I. Szanka, M. Szesztay, A. Soltész: New Routers Towards Novel Branched Polymer Structures: Star Polymers and ultifunctional Hyperbranched Polymers, *Polym. Prepr*., **2008**, *49*, 66-67.

V. 2. Presentations

V.2.1. Presentations related to this PhD work

1. G. Kali, B. Iván: Polimetakrilsav-*l*-poliizobutilén amfifil polielektrolit kotérhálók szintézise, analízise és duzzadási viselkedésük, MTA Természetes Polimerek és Műanyag Munkabizottsági Ülés, Budapest, 2005. április 26. (előadás)
2. G. Kali, B. Iván: Swelling response of amphiphilic conetworks to salt concentration, Polymer Gels and Networks Conference, Prague, 7-14 July, 2005. (poszter)
3. G. Kali, B. Iván: Swelling esponse of amphiphilic conetworks to salt concentration, International Symposium on Polymer Conetworks, Gels and Membranes, Budapest, 2005. szeptember 11-13. (poszter)
4. G. Kali, T. K. Georgiou, B. Iván, C. S. Patrickios: Group transfer polymerization synthesis of amphiphilic model conetworks based on methacrylic acid, 231. American Chemical Society Meeting, Atlanta, GA USA, 26 – 30 March, 2006. (poszter)
5. G. Kali, T. K. Georgiou, C. S. Patrickios, B. Iván: Swelling behavior of anionic amphiphilic model conetworks in the presence of monovalent and divalent cations, 1st European Chemistry Congress, 27-31 August, 2006. (előadás + poszter)
6. G. Kali, T. K. Georgiou, B. Iván, C. S. Patrickios, E. Loizou, Y. Thomann, J. C. Tiller: Structural characterization of glassy and rubbery anionic amphiphilic model conetworks, 233. American Chemical Society Meeting, Chicago, USA, 25-29 March, 2007. (előadás)
7. G. Kali, B. Iván: Metakrilsav alapú amfifil polimer kotérhálók, X. Doktori Iskola, Mátraháza, 2007. május 7-9. (előadás)
8. G. Kali, T. K. Georgiou, B. Iván, C. S. Patrickios, E. Loizou, Y. Thomann, J. C. Tiller: Metakrilsav-tartalmú amfifil polimer kotérhálók, MTA Kémiai Kutatóközpont, Kutatóközponti Tudományos Napok, Budapest, 2007. május 22-24. (előadás)

9. G. Kali, T. K. Georgiou, B. Iván, C. S. Patrickios: Synthesis of anionic amphiphilic polymer model conetworks by the Combination of quasiliving carbocationic and group transfer polymerizations, European Polymer Congress, Portoroz, Szlovénia, 2-6 Julyj 2007. (poszter)
10. G. Kali, T. K. Georgiou, B. Iván, C. S. Patrickios, E. Loizou, Y. Thomann, J. C. Tiller: Mechanical and structural differences between amphiphilic conetworks containing various hydrophobic segments, 11th Dresden Polymer Discussion, Drezda, 16-19, september 2007. (poszter)
11. G. Kali, T. K. Georgiou, B. Iván, C. S. Patrickios, E. Loizou, Y. Thomann, J. C. Tiller: Nanophase separated amphiphilic conetworks based on methacrylic acid, 9th Conference on Colloid Chemistry, Siófok, 2007, október 3-6. (poszter)
12. G. Kali, C. S. Patrickios, T. K. Georgiou, B. Iván: Biológiailag releváns sók és pH hatásának vizsgálata metakrilsav alapú amfifil kotérhálók duzzadására, VIII. Téli Iskola, Balatonfüred, 2008. február 6-8. (előadás)
13. B. Iván, G. Erdődi, A. Domján, Cs. Fodor, M. Haraszti, G. Kali, P. Mezey, J. Scherble, R. Thomann, R. Mülhaupt: Amphiphilic conetworks: new nanostructured polymers for smart materials, nanohybrids and biomaterials, 9th Austrian Polymer Meeting, Graz, 26-28 March, 2008 (előadás)
14. B. Iván, G. Erdődi, A. Domján, Cs. Fodor, M. Haraszti, G. Kali, P. Mezey, J. Scherble, R. Thomann, R. Mülhaupt: Nanophasic amphiphilic polymer conetworks: a new material platform for nanostructured surfaces and films, 1st Functional Nanocoatings Conference, Budapest, 30 March - 2 April, 2008. (előadás)
15. G. Kali, T. K. Georgou, B. Iván, C. S. Patrickios, E. Loizou, Y. Thomann, J. C. Tiller: Nanophase separated amphiphilic model polymer conetworks, 1st Functional Nanocoatings Conference, Budapest, 30 March - 2 April, 2008 (poszter)
16. G. Kali, B. Iván, T. K. Georgiou, C. S. Patrickios, Y. Thomann, J. C. Tiller: Metakrilsav alapú amfifil polimer kotérhálók: szintézis stratégiák, szekerkezet-tulajdonság összefüggések és kollpszusmentes sóhatás vizes közegű duzzadásra, Magyar Tudományos Akadémia, Anyagtudományi Nap, Budapest, 2008. május 9. (előadás)
17. G. Kali, T. K. Georgiou, B. Iván, C. S. Patrickios, E. Loizou, Y. Thomann, J. Tiller: Synthesis, swelling behavior and morphology investigations of poly(methacrylic acid)-based amphiphilic conetworks with various hydrophobic segments, Polymer Networks Group conference, Larnara, Cyprus, 22-26 June, 2008 (előadás)
18. G. Kali, B. Iván: Swelling behavior of amphiphilic conetworks in physiologically relevant salts solutions, Polymer Networks Group conference, Larnara, Cyprus, 22-26 June, 2008 (poszter)

V.2.2. Presentations related to this PhD work

19. B. Iván, G. Erdődi, G. Kali, Gy. Holló-Szabó, Z. Zsebi, M. Szesztay: New functional hyperbranched and star polymers, 228. American Chemical Society Meeting, Philadelphia, USA, 22-26 August, 2004. (előadás)
20. G. Kali, M. Szesztay, A. Bodor, B. Iván: Csillag és hiperelágazásos poliizobutilén előállítása láncvégi sztirol monomeregységek Friedel-Crafts reakciója útján, Vegyészkonferencia 2005, Hajdúszoboszló, 2005. június 28-30. (poszter)
21. T. Podlaviczki; M. Szesztay, T. Erdey Grúz, T. Fónagy; I. Szanka; B. Iván, G. Kali: Polystyrene star polymers by quasiliving atom transfer radical polymerization, 1st European Chemistry Congress, 27-31 August, 2006. (poszter)
22. Cs. Fodor, G. Kali, B. Iván: Poly(N-vinylimidazole)-*l*-poly(propylene oxide) amphiphilic conetworks, 1st European Chemistry Congress, 27-31 August, 2006. (poszter)
23. Cs. Fodor, G. Kali, K. Z. Perényi, B. Iván: N-vinil-imidazol alapú amfifil kotérhálók szintézise, analízise és réz(II)-ion megkötő képességének vizsgálata, MTA Kémiai Kutatóközpont, Kutatóközponti Tudományos Napok, Budapest, 2007. május 22-24. (előadás)
24. A. Domján, K. Hódi, J. Varga, P. Mezei, Cs. Fodor, G. Kali, B. Iván: Makromolekulák és összetett polimerrendszerek vizsgálata szilárd fázisú NMR-módszerekkel, MTA Kémiai Kutatóközpont, Kutatóközponti Tudományos Napok, Budapest, 2007. május 22-24. (előadás)
25. Cs. Fodor, G. Kali, K. Perényi, B. Iván: Synthesis, characterization and metal ion binding of N-vinylimidazole based amphiphilic conetworks, European Polymer Congress, Portoroz, Szlovénia, 2-6, july 2007. (poszter)

26. G. Kali, M. Szesztay, A. Bodor, B. Iván: Synthesis Of New Branched Polyisobutylene Structures By Quasiliving Carbocationic Polymerization, IUPAC International Symposium on Ionic Polymerization, Kloster Banz, 9-11 September, 2007. (poszter)
27. Cs. Fodor, G. Kali, K. Z. Perényi, B. Iván: Synthesis, Characterization And Copper(II) Ion Coordination Studies Of Amphiphilic Conetworks Based On N-Vinylimidazole, 11th Dresden Polymer Discussion, Drezda, 16-19 September, 2007. (poszter)
28. B. Iván, G. Erdődi, P. W. Groh, G. Kali, Gy. Kasza, A. Soltész, I. Szanka, M. Szesztay: New methods for new multifunctional hyperbranched polymers, 3rd International Symposium on "Reactive Polymers in Inhomogeneous Systems, in Melts, and at Interfaces", Dresden, 23-25, september 2007. (poszter)
29. Cs. Fodor, G. Kali, K. Z. Perényi, B. Iván: Metal ion binding by water swollen poly(N-vinylimidazole-*l*-poly(tetrahydrofuran), a novel amphiphilic conetwork, 9th Conference on Colloid Chemistry, Siófok, 2007, október 3-6. (poszter)
30. G. Erdődi, Cs. Fodor, P. W. Groh, M. Haraszti, B. Iván, G. Kali, P. Mezey, V. Pálfi, A. Soltész, L. S. Szabó, I. Szanka, Gy. Szarka, K. Verebélyi: Új nanoszerkezetű polimer rendszerek, mint új nanohibrid anyagok platformja, A Magyar Tudomány Ünnepe 2007, Budapest, 2007. november 12. (poszter)
31. G. Erdődi, Cs. Fodor, P. W. Groh, M. Haraszti, Á. Hellner, B. Iván, G. Kali, P. Mezey, V. Pálfi, A. Soltész, L. S. Szabó, I. Szanka, Gy. Szarka, K. Verebélyi: Nanoszerkezetű polimereken alapuló új nanohibrid anyagok, ELTE Innovációs Nap, Budapest, 2008. február 05. (poszter)
32. Cs. Fodor, G. Kali, A. Domján, K. Z. Perényi, B. Iván: N-vinil-imidiazol alapú amfifil kotérhálók szintézise és alkalmazhatósága nehézfémionok megkötésében, VIII. Téli Iskola, Balatonfüred, 2008. február 6-8. (előadás)
33. A. Soltész, Gy. Kasza, I. Szanka, P. W. Groh, M. Szesztay, G. Kali, B. Iván: Multifunkciós hiperelágazásos polimerek mint fogtömő és módosító alapanyagok, VIII. Téli Iskola, Balatonfüred, 2008. február 6-8. (előadás)
34. B. Iván, G. Erdődi, Á. Hellner, P. W. Groh, G., Gy. Kasza, A. Soltész, I. Szanka, M. Szesztay: New ways for the synthesis of hyperbranched polymers, Makromolekulares Kolloquium, Freiburg, 28 february – 1 march 2008. (előadás)
35. Cs. Fodor, G. Kali, K. Z. Perényi, A. Domján, B. Iván, R. Thomann, R. Mülhaupt: Heavy metal ion chelating by water swollen n-vinylimidazole based nanophasic amphiphilic conetwork films, 1st Functional Nanocoatings Conference, Budapest, 30 march- 2 april, 2008 (poszter)
36. G. Kali, Gy. Kasza, A. Soltész, I. Szanka, M. Szesztay, B. Iván: Hiperelágazásos polimerek szintézise láncvégi és láncmenti reakciókkal - új potenciális energiatakarékos adalékoktól új fogtömőanyagokig, MKE Vegyészkonferencia, Hajduszoboszló, 2008. június 19-21. (poszter)
37. Cs. Fodor, G. Kali, K. Z. Perényi, A. Domján, R. Mülhaupt, R. Thomann, B. Iván: Preparation, characterization of polymer conetworks as metal ion chelating agents, Polymer Networks Group conference, Larnara, Cyprus, 22-26 June, 2008 (poszter)
38. Gy. Kasza, G. Kali, M. Szesztay, B. Iván: The effect of reaction conditions on the formation of hyperbranched polystyrene by quasiliving carbocationic polymerization, Kolozsvár, 13-15, november 2008. (poszter)