CHAPTER 1

Thirty Years of Amphiphilic Polymer Co-networks

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1.1 Introduction

Self-assembly is the autonomous organisation of matter, ranging from molecular (crystals) to planetary (weather systems) dimensions. It also encompasses biological systems, involving cell (self-) replication at the micrometre scale, but also lipid bilayer formation, DNA base pairing and protein folding within the nanometre range.[1] Of particular interest to chemistry is the self-assembly of synthetic (as well as the above-mentioned biological) surfactants[2] and segmented (block or graft) amphiphilic copolymers[3,4] to a variety of organised structures, such as micelles, cylinders, lamellae and gyroids. An intriguing complication in the self-assembly is introduced if the aforementioned surfactant or segmented copolymer systems are interconnected *via* chemical crosslinks in the disordered state before they are allowed to self-organise. The imposed crosslinks constitute constraints to the self-organisation that is to follow, not letting the system to subsequently equilibrate to the same lowest energy configuration as it would have in the un-crosslinked state, thereby reaching a (slightly) higher energy state, possessing a modified morphology with blurred interfaces. At the same time, the existence of crosslinks

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confers upon the segmented copolymer system an increased rigidity, and improvement in the mechanical properties. Furthermore, the presence of the hydrophobic segments reduces aqueous swelling, further enhancing the mechanical properties in water. The system of chemically crosslinked amphiphilic polymer co-networks (APCN)[5–8] is exactly the subject matter of this chapter and this book.

Figure 1.1 schematically illustrates various APCN designs. The hydrophilic segments are coloured blue, whereas the hydrophobic segments are red. A first possibility involves the random interconnection of segmented amphiphilic linear copolymers (designs 2 and 6), whereas a second possibility is given by the random interconnection of amphiphilic graft copolymers (design 4). Other possibilities, leading to better-defined APCN architectures, result from the combination of hydrophilic with hydrophobic linear homopolymers, either *via* random side interconnection (design 8) or *via* end-linking (design 3). Design 7 is similar to design 3, which involves the end-linking of two types of four-arm star, rather than linear, homopolymers. Finally, designs 1 and 5 depict the architectures obtained from the end-linking of amphiphilic block copolymers, attained by the reaction of ABA or BAB linear amphiphilic triblock copolymers with a low molecular weight tetra-functional crosslinker, or by the end-linking of AB or BA four-arm amphiphilic star block copolymers.

Due to the different polarity of the constituting segments, these APCNs would microphase separate when swollen in a selective solvent, *e.g.* water or *n*-hexane. If segment incompatibility is sufficiently high, microphase

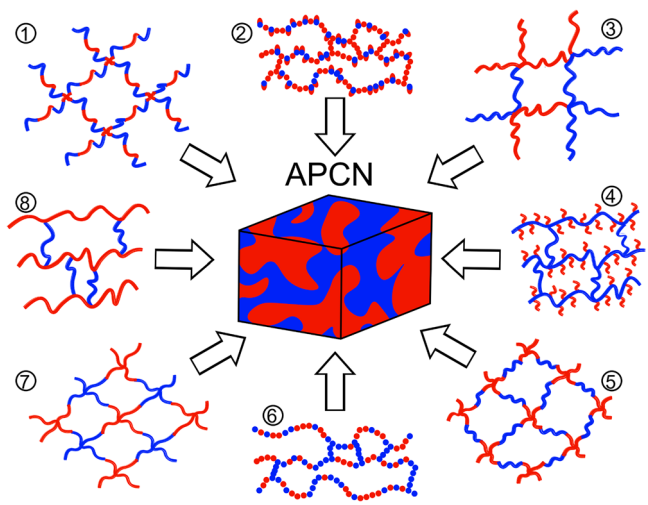

Figure 1.1 Various APCN designs and their microphase separated morphology. The hydrophilic and hydrophobic segments are in blue and red, respectively. Taken from Chapter 7 (K. R. McLeod and G. N. Tew), Figure 7.1.

separation may also occur in the solid state. However, owing to the presence of the crosslinks and the architectural imperfections (not perfect block structure and random crosslinking), the obtained morphologies are not as well-defined as in the case of free (non-crosslinked) linear or star block copolymers, but are characterised by patchy irregular domains (see centre of Figure 1.1) and blurred interfaces. It is highly desirable to attain microphase separation with long-range order in APCNs, as this is expected to improve their properties (mechanical, transport). This has recently been attained in some cases involving well-defined building blocks.

The rest of this introductory chapter is organised as follows. First, we give a brief historical overview of the APCN field, as established independently by Kennedy[9] and Stadler[10,11] in 1988. Next, we provide a preview of all the chapters in the book. We then summarise important APCN work not covered in the book. Finally, we present the conclusions and an outlook towards future developments in the area.

1.2 Historical Overview

Although there are some earlier literature reports on amphiphilic polymer co-networks,[12,13] the first systematic studies on the subject were published in 1988 by Stadler[10,11] and Kennedy.[9] It is noteworthy that these latter studies highly relied on the availability of living polymerisation techniques[14] and, in particular, living anionic polymerisation[15] and quasi-living cationic polymerisation.[16] In fact, Kennedy is the inventor of the quasi-living cationic polymerisation of isobutylene, whereas Stadler regularly employed sequential living anionic polymerisation to prepare block copolymers and study their bulk structures.

In their seminal paper, Kennedy and co-workers[9] used α,ω-dimethacrylated polyisobutylene (PIB, hydrophobic component, prepared by quasi-living cationic polymerisation) of two different molecular weights, about 5 and 10 kDa, which they subsequently free-radically copolymerised in various proportions with the hydrophilic 2-(dimethylamino)ethyl methacrylate (DMAEMA). Thus, this APCN system comprised hydrophobic PIB segments and hydrophilic poly[2-(dimethylamino)ethyl methacrylate] (PDMAEMA) segments, with the former type of segment possessing a well-defined size, and the latter characterised by a statistical size distribution. The resulting APCNs were found to swell both in water (degrees of swelling, DS, ranged from 1.2 to 2.7) and in *n*-heptane (DS varied from 2.7 to 1.4). Differential scanning calorimetry (DSC) indicated two glass transition temperatures (T_g) for dried APCNs, one at −60 °C (corresponding to the PIB segments) and the other at 30 °C (corresponding to the PDMAEMA segments), consistent with microphase separation in the bulk. Bulk APCNs were also characterised in terms of their mechanical properties in tension, and found to exhibit tensile strengths and elongations of up to 5.6 MPa and 200%, respectively.

In their pioneering work, Weber and Stadler[10,11] first carefully optimised APCN preparation[10] and subsequently characterised the properties of the APCNs prepared.[11] The APCN components used were polybutadiene (PB, hydrophobic component, molecular weight of 34 kDa) and poly(ethylene glycol) (PEG, hydrophilic component, molecular weights of 200 and 600 Da), all synthesised by living anionic polymerisation. Both termini of the (linear) PEGs were quantitatively functionalised with 1,2,4-triazoline-3,5-dione groups in a seven-step synthetic procedure.[10] These groups are highly reactive toward the allyl groups in PB. APCN formation took place by mixing 5% solutions of the two components in tetrahydrofuran (THF) at different ratios, at room temperature. Although both starting components of this APCN system were of well-defined size, the attachment of the PEG chain ends took place at random locations in the PB chains. This led to precise lengths between crosslinks only for the hydrophilic PEG segments, and a statistical length distribution between crosslinks for the hydrophobic PB segments.

The resulting APCNs were then characterised in terms of their various properties.[11] This included characterisation of the equilibrium DSs in THF (a non-selective solvent for both APCN components), cyclohexane (selective solvent for PB), and water (selective solvent for PEG). The DSs in tetrahydrofuran and cyclohexane decreased with the APCN content in PEG, as a higher PEG content was accompanied by a higher crosslinking density. In contrast, the DSs in water presented a maximum with respect to the PEG content, arising from the more pronounced effect of PEG aqueous solubility on the DS in water at lower PEG contents and the stronger effect of crosslinking density (*via* the PEG content) on the aqueous DS at higher PEG contents. Microphase separation within dried APCNs was shown using DSC, which indicated two T_g values, one at −90 °C (corresponding to the PB segments) and the other at −20 °C (corresponding to the PEG segments). Microphase separation was also confirmed using transmission electron microscopy on selected APCN samples, which revealed a bicontinuous morphology with channel sizes of 2–4 nm. This is in good agreement with the PEG (minority component) molecular dimensions. Finally, bulk APCNs were subjected to tensile testing, which revealed stresses and elongations at break of up to 0.6 MPa and 150%, respectively, and Young's moduli of up to 2.5 MPa.

1.3 Chapter Previews

This book focuses on new developments in the field of APCNs and is organised in to four sections: synthesis, properties, modelling and applications. In addition to the wide-spread APCN syntheses based on radical copolymerisation of hydrophobic or hydrophilic macro-crosslinkers with monomers of opposite philicity (design 8 in Figure 1.1), other more modern APCN synthetic strategies are also presented, including the 'clicking' of hydrophobic and hydrophilic end-functionalised homopolymers (design 3) and the end-linking of linear amphiphilic ABA triblock copolymers and

star block copolymers (designs 1 and 5). Properties of interest discussed concern aqueous swelling, thermophysical and mechanical properties, self-assembled structures, ion conductivity, electrical actuation and protein adsorption. Applications described in the book include the use of co-networks as soft contact lenses, scaffolds for drug delivery and tissue engineering, matrices for heterogeneous biocatalysis and membranes of controllable permeability. Finally, an important theory chapter on the modelling of the self-assembly of APCNs is also included.

1.3.1 Synthesis

The first chapter in the *Synthesis* section, Chapter 2, comes from the Hungarian Academy of Sciences in Budapest, authored by Iván and co-workers, and presents the preparation of APCNs based on poly(*N*-vinylimidazole) hydrophilic segments interconnected with α,ω-dimethacrylated polyisobutylene or α,ω-dimethacrylated poly(tetrahydrofuran) hydrophobic macro-crosslinkers. These are the first APCNs containing moieties of imidazole, which is a group of great biological importance. Several APCNs are prepared and are thoroughly characterised in terms of their swelling, morphological and thermophysical properties. Finally, selected APCNs are loaded with silver, and the resulting nanohybrids are evaluated as catalysts and antibacterial materials.

Chapter 3 was contributed by Jewrajka and co-workers from the Central Salt & Marine Chemicals Research Institute in Gujarat, India. The APCNs presented by these authors are multi-component materials, characterised by biodegradability and biocompatibility and are, consequently, appropriate for biomedical applications. Degradability in these APCNs is secured *via* the incorporation of erodible polymers, typically poly(ε-caprolactone). Hydrophilic components, *e.g.* PEG, PDMAEMA, or polysaccharides, such as agarose or dextran, are used. In addition to their biocompatibility and biodegradability, the drug loading capacity of these APCNs is also investigated. The results indicate that these materials represent excellent choices for use in biomedical applications.

The next chapter in the *Synthesis* section, Chapter 4, was written by Rikkou-Kalourkoti and Patrickios from Frederick University, Cyprus and the University of Cyprus, respectively. This chapter presents the synthesis, characterisation and degradation of APCNs based on dimethacrylate-end-linked linear amphiphilic ABA triblock copolymers prepared using labile bifunctional initiators. Three co-network families are presented, each synthesised using three different 'living'/controlled polymerisation techniques: group transfer polymerisation (GTP), atom transfer radical polymerisation (ATRP) and reversible addition–fragmentation chain transfer (RAFT) polymerisation, employing the appropriate labile bifunctional initiator. The kinetics of degradation, the nature of the degradation products and the evolution of the swelling degree are reported. A small-angle neutron scattering study is also

presented, revealing two (changing) correlation peaks: one due to the scattering centres within the degrading APCNs and the other due to the scattering by the polymeric degradation products, which are amphiphilic star block copolymers.

1.3.2 Properties

The first chapter in the *Properties* section, Chapter 5, is authored by K. Mortensen of the University of Copenhagen, Denmark. This chapter introduces the reader to the methods employed to characterise the structures obtained upon the self-assembly of (linear) block copolymers and how this can be extended for the characterisation of the structures formed by microphase separated (crosslinked) block copolymer gels and networks. The latter is illustrated through the structural characterisation of particular examples of such block copolymer gels and networks. These examples are based thermo-responsive, end-linked, four-arm star block copolymers of PEG and poly(propylene glycol) (Tetronics).

The next chapter in the *Properties* section, Chapter 6, was written by Li and Sakai of the University of Tokyo, Japan. This chapter presents the preparation, structure and physical properties of model APCNs with PEG four-arm star homopolymers (tetraPEG stars) as their hydrophilic component, and poly(ethyl glycidyl ether) four-arm star homopolymers (tetraPEGE stars), poly[(ethyl glycidyl ether)-*co*-(methyl glycidyl ether)] four-arm star random copolymers (tetraPEGE-PMGE stars), or polydimethylsiloxanes (PDMS) as the hydrophobic components. In addition to their formation, the aqueous swelling (including swelling and shrinking kinetics), microphase separated structure and mechanical properties of these APCNs are also presented and discussed.

The following chapter in this section, Chapter 7, comes from McLeod and Tew of the University of Massachusetts at Amherst, USA and presents the preparation and properties of APCNs comprising α,ω-bis(norbornene)-functionalised hydrophilic PEGs and hydrophobic poly(styrene)s or PDMSs 'clicked' onto tetra-thiol crosslinkers. The PEG-PDMS APCNs exhibit high resilience, whereas the PEG-PSty APCNs display morphological co-continuity over a broad composition window, with the latter type of co-networks being able to serve as excellent matrices for solid polymer electrolytes for lithium ion batteries.

Chapter 8 was written by Guzman and Cakmak of Purdue University, Indiana, USA and Nugay of Boğaziçi University, Istanbul, Turkey. The APCNs presented in this chapter possess hydrophilic segments based on *N*,*N*-dimethylacrylamide (DMAAm) and hydrophobic PDMS segments. The PDMS segments have the novel feature that they consist of two populations, one with a lower (17 kDa) and the other with a higher (117 kDa) molecular

weight. The latter PDMS component greatly enhances the mechanical properties of the co-networks, whereas both PDMS components control the other co-network properties. The swelling and mechanical properties of these APCNs are presented, whereas their bulk and surface morphologies are also reported, including real-time structural evolution during drying. Finally, the chapter explores the adsorption of plasma proteins onto these co-networks, and the use of co-network films as soft contact lenses capable of releasing an antibiotic drug.

The next chapter in the *Properties* section, Chapter 9, comes from China, and is written by Fu and Sun from Sun Yat-sen University in Guangzhou and Xi'an Polytechnic University, respectively. This chapter introduces mechanically robust (tough and ultra-stretchable) APCNs based on α,ω-diacrylated Pluronic F127 [(ethylene glycol)$_{99}$-*b*-(propylene glycol)$_{65}$-*b*-(ethylene glycol)$_{99}$] macro-crosslinker copolymerised with acrylamide. Due to the presence of the Pluronic macro-crosslinker, these co-networks are thermo-responsive. However, they can also acquire salt- and pH-responsiveness *via* the incorporation of a cationic monomer or both a cationic and an anionic monomer. Co-networks of the latter type, equilibrated in a salt solution, can be actuated by an electric field, presenting a fast response and proving themselves as potential materials for use in sensors, actuators, switches and artificial muscles.

Chapter 10 is written by our research team at the University of Cyprus and proposes an efficient method to toughen APCNs. This can be particularly useful in the cases when the APCNs are not mechanically robust from the beginning of their preparation. The concept explored in this work is that of double-network hydrogels, *via* the interpenetration of the initial APCN with a second polymeric hydrogel. Indeed, this approach was shown to be successful as it led to a several-fold improvement of the mechanical properties of the original APCNs. In the examples presented, the second hydrophilic networks were prepared *via* conventional free radical photo-polymerisation of monomer and crosslinker, within the first APCN network prepared by RAFT polymerisation.

1.3.3 Modelling

Chapter 11 is from F. Schmid of the University of Mainz, Germany and is the single, but extremely important, contribution to the volume in the *Modelling* section, dealing with the prediction of self-organisation within APCNs. The chapter first introduces polymer modelling in general and then elaborates on the modelling of the self-assembly of (linear) block copolymer melts. Next, the focus shifts onto polymer co-networks and their self-assembly, examining two particular systems, randomly crosslinked A/B co-networks and amphiphilic polymer co-networks.

1.3.4 Applications

The first chapter in the *Applications* section, Chapter 12, comes from industry and is written by S. J. Diamanti of CooperVision in California, USA. This chapter deals with the most wide-spread application of APCNs, which is their use in the form of 'silicone hydrogels' as the materials for the fabrication of extended-wear soft contact lenses. The size of the related industry can be appreciated by considering that more than 100 million people worldwide wear contact lenses. The chapter first provides a historical overview of contact lenses, starting with the original conception and drawings by DaVinci. It then follows onto the earliest (1900s) commercial contact lenses that were made of hand-blown glass, then onto polymer-based hard and soft contact lenses and culminates in the creation of silicone hydrogel-based soft contact lenses used today. The latter materials provide an excellent combination of comfort, breathability, affordability and ocular health, which would have been unimaginable to patients wearing glass-blown lenses at the turn of the 20th century. The clinical needs that led to the development of these state-of-the art soft contact lenses are provided and some of the technological challenges necessary to be overcome to create these modern materials are given. Finally, the chapter concludes with a brief look at the frontier of contact lens technology.

The next chapter in the *Applications* section, Chapter 13, comes from Qiao's research group at the University of Melbourne, Australia. Having in mind important hydrogel biomedical applications, such as drug delivery and tissue engineering, these authors recognise the need for mechanical strength in these materials. Therefore, they review recent literature on robust hydrogels in general and robust APCNs in particular. They also present strategies to produce such materials with enhanced mechanical properties.

The next *Applications* chapter, Chapter 14, was written by Krumm and Tiller of the Technical University of Dortmund, Germany. This chapter illustrates a special APCN application: their use as matrices for heterogeneous enzyme catalysis. This application exploits the biphasic structure of the co-networks and the large interfacial area between the hydrophilic and lipophilic nanophases, with the aim to catalyse chemical reactions in organic solvents residing in the lipophilic phase by the enzyme residing within the hydrophilic phase. First, the advantages of this approach in enzyme catalysis are given. Then, the different ways to incorporate the enzymes in a molecularly dispersed fashion within the co-networks is described, including incorporation during APCN formation (polymerisation), or *via* diffusion, post-polymerisation. Afterward, several examples of biocatalysis by the enzyme (in the hydrophilic nanophase) of reactions in organic solvents (in the hydrophobic nanophase) through the co-network interfacial area are given. Finally, the concept of chiral biocatalysis, *via* chirality within the APCN, is introduced.

Chapter 15 is the last chapter in the *Applications* section and is also the last chapter in the book. It is written by Bruns and co-workers from the University of Fribourg, Switzerland (the lead corresponding author is now at Strathclyde University, Scotland, United Kingdom). This chapter presents the employment of APCNs as functional membranes and illustrates related applications. The chapter describes the co-network structural features rendering them as ideal membrane materials and then details the preparation of co-network membranes based on stimuli-responsive polymers and their functionalisation. Finally, the applications of such functionalised, stimuli-responsive APCNs as membranes with light-regulated permeability and self-sealable films are described.

1.4 Further Work in the APCN Field

In their important work, Wooley and co-workers developed APCNs comprising a hydrophobic core of a hyperbranched aromatic fluoropolymer, cross-linked with linear hydrophilic PEGs,[17–32] as schematically depicted in Figure 1.2.[30] Films based on these novel APCNs exhibited very low adhesion, with this property arising from the low adhesiveness of the two individual components, the hydrophobic fluoropolymer and the hydrophilic PEG. Therefore, these materials were mainly explored as anti-biofouling coatings.[17–19,24–29] These APCNs have also been shown that they can serve as good release matrices,[20] whereas it was most recently found that they can act as efficient anti-icing coatings,[30–32] a property arising from the ability of these materials to depress the melting temperature of water. Furthermore, these intriguing APCNs exhibited exceptional mechanical properties, even when equilibrium-swollen in water, with tensile stresses at break up to 2 MPa and tensile strains at break up to 120%.[22] Some variants of these APCNs possessed a dendritic,[24] rather than a hyperbranched, hydrophobic core, whereas some others also contained PDMS.[29] In the latest studies,[31,32] liquid crystalline segments were also introduced into these APCNs, so as to further enhance their dynamic properties. Finally, a particular study involved a detailed investigation of the

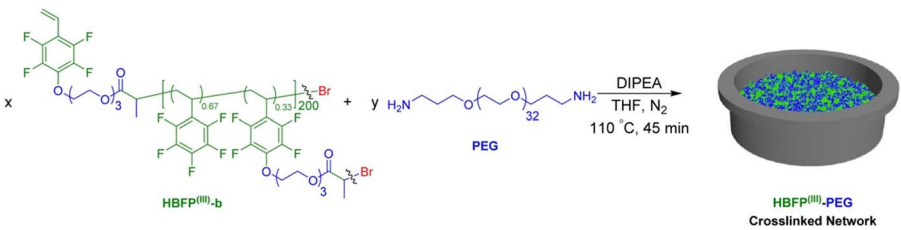

Figure 1.2 Synthetic route followed for the preparation of APCNs from the cross-linking of a hyperbranched aromatic fluoropolymer using a linear PEG.[30] Reproduced from ref. 30 with permission from John Wiley and Sons, © 2015 Wiley Periodicals, Inc.

aqueous self-assembly of the non-crosslinked (and water-soluble) amphiphilic analogues, based on the hyperbranched fluoropolymer core, functionalised with PEG.[23]

He and colleagues developed APCNs, whose common feature was the presence of a hydrophobic PDMS or/and polymethylhydrosiloxane (PMHS) segments,[33–41] as illustrated in Figure 1.3.[33] As hydrophilic segments, various polymers were used, including PDMAAm,[33,38] poly(2-hydroxyethyl methacrylate),[34] PDMAEMA,[35] P(DMAEMA-sulfobetaine),[36] poly(vinyl pyrrolidone)[38] and PEG.[39–41] In some cases, the hydrophilic components were introduced *via* controlled radical polymerisation, either ATRP[33–36] or RAFT polymerisation.[38] The resulting APCNs were evaluated for a variety of applications, including anti-biofouling,[36,39–41] drug delivery,[34,35] and materials for selective membranes[35,37] and cell culture.[33,38] Most of the APCNs[33–35,37,38,40] were characterised in terms of their tensile mechanical properties, which were found to be excellent, typically reaching strengths between 1.5 and 5.5 MPa and strains at break from 150% to 250%.

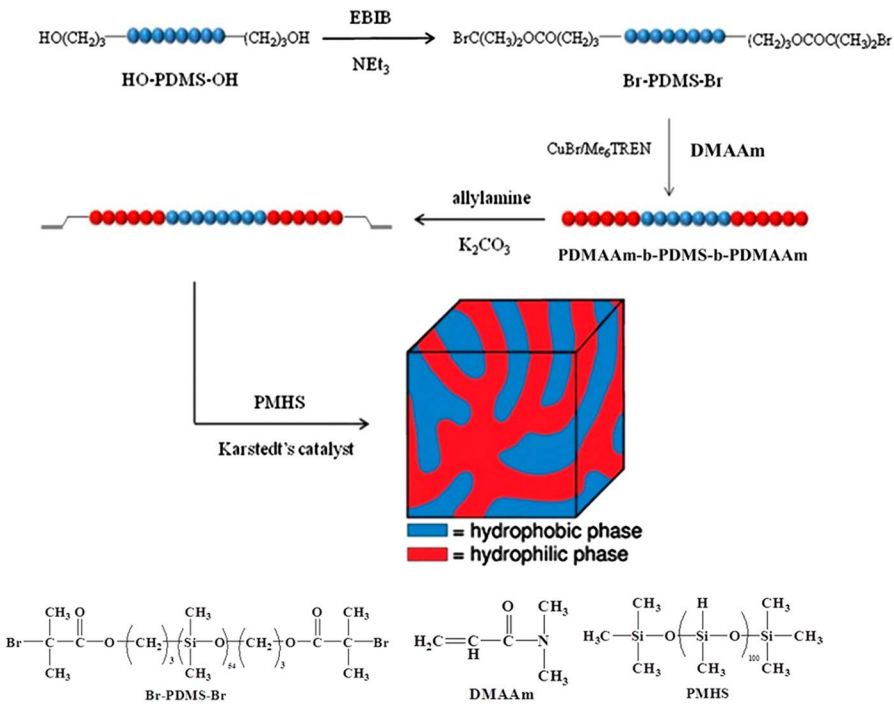

Figure 1.3 Synthetic route followed for the preparation of APCNs, comprising linear PDMS-containing amphiphilic pentablock terpolymers prepared by ATRP, crosslinked using PMHS.[33] Reproduced from ref. 33 with permission from American Chemical Society, Copyright 2014.

1.5 Conclusions and Outlook

APCNs represent the network analogues to polymeric surfactants or, conversely, the surfactant analogues to simple hydrophilic polymer networks. Therefore, these materials combine internal self-organisation with semi-solid nature and enhanced mechanical strength. Since their birth about 30 years ago, much progress has taken place in the APCN field, synthesis, properties, modelling and applications, as laid out in the chapters of this book. The synthesis of these materials can greatly benefit from the development of new controlled polymerisation methods and new 'click' chemistries. Furthermore, as new hydrophilic and hydrophobic segments are employed for their fabrication, new APCN properties emerge. Properties of current interest for these materials include, in addition to simple swelling behaviour, microphase separated morphologies, mechanical properties (strength, stretchability, stiffness), gas, nutrient, drug and protein permeability, cell and protein attachment, biocompatibility, and degradability. Predicting these properties using theoretical models and simulations is an area where more progress is needed.[42]

Silicone hydrogels, an important type of APCNs, is the material from which extended-wear soft contact lenses are made and represent the most widespread application of APCNs. Other emerging applications of APCNs include their use as matrices for drug delivery, tissue engineering and heterogeneous (bio)catalysis, membranes with selective permeability and anti-biofouling coatings. It is noteworthy, that modern extended-wear soft contact lenses (silicone hydrogel APCNs) are already used for ocular drug (ophthalmic antibiotics, mainly) delivery, thereby serving not only for vision correction but also for eye treatment.[43] Most recently, miniature electronic circuits comprising conducting polymers[44] have been engineered into contact lenses to also render them as electronic screens from which one may watch TV or read their electronic mail.[45,46]

During most of the past 30 years, much imperfection was tolerated within the molecular structure of APCNs, possibly leading to suboptimal properties. The use of well-defined building blocks, interconnected in a precise way, would result in model APCNs,[47] which may display improved properties. This is confirmed from studies performed in the last five years, in which the produced model APCNs indeed exhibited microphase separation with long-range order,[48–51] enhanced mechanical properties[48,52–54] and improved electrical (ionic) conductivity[54] of utmost importance in the fabrication of the separator membrane in the highly celebrated lithium ion battery.[55] Therefore, the preparation of APCNs with a structure as perfect as possible would help these intriguing materials reach their full potential.

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