Polymer Networks: Recent Developments

Costas S. Patrickios

Summary: Polymer networks have long been the subject of study by chemists, physicists, biologists, material scientists and engineers, aiming to understand the fundamentals of their preparation and behavior, but also to adopt them for a multitude of technologically important applications. This introductory chapter overviews some of this previous knowledge on polymer networks, and also presents recent important developments in the field, as these are detailed in the chapters of this volume.

Keywords: gels; network structure; polymer networks; swelling

Introduction

Although the definition that *polymer networks are three-dimensional polymers* is most frequently used (samples of ‘‘linear’’ or branched polymers are also three-dimensional!), it is more precise to state that *polymer networks are materials in which all constituting polymer chains are connected to each other in some way, either directly or indirectly, via other directly-connected chains*. If this interconnection is via chemical bonds, the networks at hand are called *chemical* or *covalent*, whereas if the bonding is via physical association the networks are called *physical* or *reversible*. The covalent interconnection in chemical networks confers upon them their most characteristic property: the inability to dissolve in any solvent but capability to swell in compatible solvents. Physical networks are more usually encountered swollen in various solvents which promote the non-covalent association between the polymer chains. Water and other polar solvents are particularly good mediators of this association. There are also two other special classes of networks, in which the forces holding the chains together are of a strength intermediate between those in physical and chemical networks. These are the supramolecular and the inorganic networks, where the interconnection is accomplished through hydrogen bonds and coordination bonds, respectively. The classification of these four types of networks with respect to the strength of the bonds holding the chains together is schematically represented in Fig. 1.

Most covalent organic polymer networks are based on highly cross-linked apolar/hydrophobic units, e.g. vulcanized rubber and various coatings.[1] These materials swell slightly in organic solvents but remain shrunk in water. On the other extreme are hydrogels,[2,3] which are lightly cross-linked hydrophilic polymers, and have emerged during the past 3 decades as new materials with growing importance in technology and medicine. These hydrophilic networks greatly swell in water and collapse in apolar organic solvents. The constituting chains of hydrogels can sometimes be particularly hydrophilic, composed of such polar monomer repeating units as ethylene oxide (which is non-ionic), or comprising strong electrolyte monomer units such as diallyldimethylammonium chloride (DADMAC, cationic) or sodium styrene sulfonate (SSS, anionic). Hydrogels based on polyelectrolyte networks are called superabsorbents as they can absorb more than 100 times their dry mass in water, and are, therefore, used for water-retention in agriculture. The same materials can also

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Department of Chemistry, University of Cyprus, P. O. Box 20537, 1678 Nicosia, Cyprus
Fax: (+357) 22892801; E-mail: costasp@ucy.ac.cy

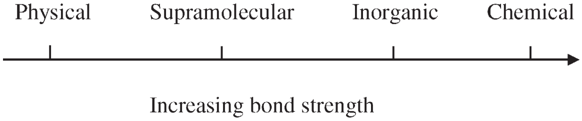

Figure 1.
Network classification according to the strength of the bonds holding the polymer chains together.

hold large amounts of salt-water, urine or blood (30–40 times their dry mass), which results in their use as the absorbing material in baby and hygienic diapers. Swollen superabsorbent networks are highly fragile as they consist of *ca.* 99% water and only 1% polymer. Mechanical stability, necessary to hold the weight of an infant, is conferred to the superabsorbent beads by constructing them of a highly cross-linked thin shell surrounding the internal, loosely cross-linked and highly absorbing core.

Polymer networks with intermediate and tunable hydrophilicity or with coexisting hydrophilicity and hydrophobicity represent two new classes of networks, far more interesting than their purely hydrophobic or purely hydrophilic counterparts. The former category is that of responsive (also known as "intelligent" or "smart") networks,[4] while the latter is that of amphiphilic conetworks.[5] Responsive networks exhibit large changes in their swelling in response to changes in their compatibility with the solvent, effected by changes in temperature, pH, introduction of additives (such as salt) or application of external fields (electric or magnetic). While non-network polymers (e.g. linear or branched) can also be responsive, the response of polymer networks is manifested on the macroscale and can be readily observed visually, but also leads to some of their important modern applications such as in valves and actuators. Equally important is the new class of amphiphilic networks, bearing both hydrophilic and hydrophobic units. Similar to conventional low-molecular-weight surfactants and amphiphilic block copolymers, these materials exhibit a large tendency for aqueous micellization, with the formation of distinct hydrophobic water-free domains and highly hydrated domains, and a resulting large interface between the two types of domains. However, this takes place in the presence of the cross-links which imparts to the material its solid-like texture on the one hand, and on the other hand it imposes constraints to chain conformation which affects the domain size and morphology of the resulting micro- or nano-structures.

Polymer networks find many applications in contemporary technology. Their conventional use (hydrophobic networks) is as structural materials with a range of mechanical properties. Their less conventional use as superabsorbent materials (hydrogels) in baby and hygienic diapers and for water retention in agriculture has already been mentioned. Polymer networks also have increasing importance in medicine and biotechnology for uses as matrices for drug delivery and scaffolds for tissue engineering. Furthermore, responsive polymer networks have found application as modern actuators, valves and artificial muscles for robotics. Finally, state-of-the-art soft contact lenses are advanced amphiphilic networks in which the hydrophilic component ensures aqueous swelling and materials softness providing comfort to the eye, while the hydrophobic components secure mechanical strength and oxygen permeability necessary for the oxygenation of the eye.

Although not necessary for their applications, *structural perfection* is a very important issue for networks in general, but more so for the chemical networks. Fig. 2 illustrates schematic representations of three polymer networks with different degrees of structural perfection. On the left is depicted a *perfect* (or "*model*") network,[6] where the length of the polymer chains between the cross-linking nodes (the so-called elastic chain length) and the number of polymer chains emanating from

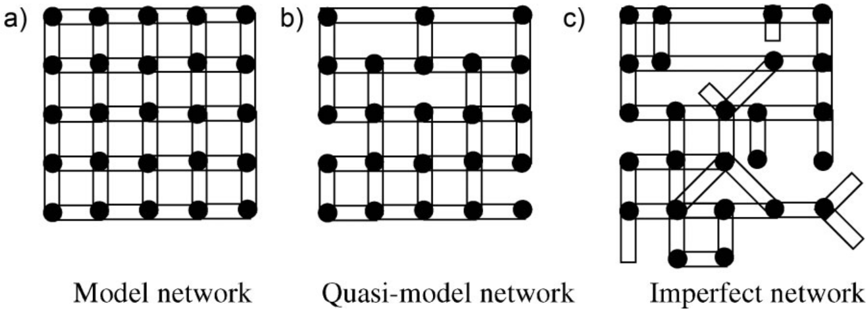

Figure 2.
Polymer networks of different degrees of perfection.

each cross-linking node (known as core functionality) are both well-defined. A network with many defects (*imperfect* network) is drawn on the right. In this network, both the elastic chain lengths and the core functionality are broadly distributed. Furthermore, this network bears other defects, such as dangling (singly-attached) chains. Other possible defects (not shown) are loops and totally unattached (free) chains. In between these two extremes is the structure of an *almost-perfect* (''*quasi-model*'') network shown in the middle of the figure and exhibiting only a small number of defects. The vast majority of polymer networks produced and studied to date are *imperfect* networks, which are readily synthetically accessible via conventional free-radical copolymerization of monomer(s) and cross-linker, or polycondensation between bifunctional and higher monomers. *Model* and *quasi-model* networks can be prepared using living polymerization techniques, including anionic, group transfer and controlled radical polymerizations.

As polymer networks are branched polymer structures, it is worth comparing them with other branched polymer structures.[7] Such structures are those of the star polymers, the dendrimers, the graft polymers and the hyperbranched polymers, schematically illustrated in Fig. 3. Star polymers represent the simplest branched polymer structure comprising several arms emanating from a single branching point. Dendrimers are more complex than star polymers, bearing several branching points, but characterized by a high degree of regularity and perfection. Their preparation, however, requires multiple synthesis and purification steps. Thus, dendrimers are highly ordered branched polymers which are difficult to prepare. This can be contrasted to conventional networks (Fig. 2(c)) which can be very readily synthesized but their structure is very difficult to analyze.

Description of Volume Contents

This volume is organized in four sections. The first section is that on synthesis, followed by that on properties. The third section focuses on theory and simulations,

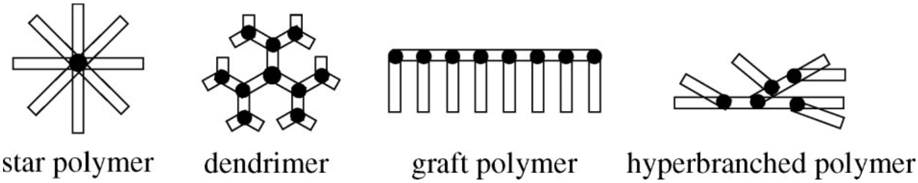

Figure 3.
Branched polymer architectures.

whereas the final section combines applications, bioapplications and biogels. The contents of each section are described in some detail below.

Synthesis

As one of the key themes of the PNG2008 meeting was synthesis by controlled polymerization methods,[8] half of the chapters in this section involve such controlled syntheses, including atom transfer radical polymerization (ATRP), anionic polymerization and group transfer polymerization (GTP). The meeting also covered branched polymer structures, in addition to polymer networks; thus, chapters on star and hyperbranched polymers are also found in this section.

The first chapter comes from **Gao** and **Matyjaszewski** and concerns the **use of ATRP for the preparation of "core cross-linked" star polymers** by the sequential addition of monomer(s) and cross-linker. When the cross-linker is polymerized first, followed by the polymerization of the monomer(s) (**"core-first"** strategy), the initiating sites are directed to the periphery of the star, whereas in the **"arm-first"** approach the polymerization sequence is reversed and the initiating sites are now located in the core of the star. The size of the core relative to that of the arms can be increased in the "arm-first" approach by adding the cross-linker before the monomer is completely consumed; the earlier the cross-linker is added, the larger the core. However, if the **cross-linker is added too early**, a **randomly cross-linked network** would be obtained, also of interest in this symposium volume. Both the "arm-first" and the "core-first" strategies can lead to the formation of star block copolymers if two, rather than one, monomers are sequentially copolymerized. Mikto-arm star copolymers can be readily obtained when a mixture of different macromonomers is copolymerized with cross-linker. The same product is obtained when the macromonomer mixture is replaced by a macroinitiator mixture. All the initiators used in this chapter are monofunctional. Use of bifunctional ATRP initiators would lead to the formation of end-linked networks rather than star polymers.

The next chapter is by **Kiriy** and co-workers, and also concerns the **preparation of star polymers**. A hexafunctional core is employed from which **poly(3-hexylthiophene) arms are grown using nickel-catalyzed coupling** (Kumada polycondensation). Although the present synthesis is of the **step-growth** rather than of the addition type, the **length of the arms** is **well-controlled**. The arms of the present star polymers are **conjugated**, potentially imparting to them such important properties as electrical conductivity. This synthesis is the **first** example of **"core-first"** preparation of **star polymers** with **conjugated arms**. Chloroform solutions of these star polymers deposited on mica resulted in the formation of **fibers** with diameters of 2–4 nm. It would be interesting to interlink these star polymers and compare the properties (morphology and electrical conduction) of the resulting networks to those of the parent material.

The following chapter, co-authored by **Dodds** and **Hutchings**, describes the synthesis of **hyperbranched polymers** with **very long linear branches**, called **hypermacs**. These branches comprised **near-monodisperse polystyrene** of molecular weight (MW) *ca.* 30,000 g mol^{-1}, prepared using living anionic polymerization. With the use of the appropriate initiator and proper end-group modifications, these branches were converted to **AB_2–type** polystyrene **macromonomers** which were subsequently coupled using **etherification** reactions in the presence of cesium carbonate base to result in the hypermacs. The **optimized coupling** is **very efficient**, performed at room temperature, and yields, in addition to **hypermacs** (MW of 10^6 g mol^{-1}), a **very-high-MW soluble fraction** (MW of 10^7 g mol^{-1}) and an **insoluble network fraction** ($\sim$15%).

The chapter by **Georgiou** and co-workers involves both star polymers and polymer networks. In particular, these researchers prepared **star copolymers** and they ***in-situ* interconnected** them to **conetworks**. Both the star polymer synthesis and the star interconnection were effected *via* a multistep, one-pot sequential procedure by GTP. Three binary monomer combinations were used to provide three different series of conetworks: **amphiphilic** (= hydrophilic + hydrophobic), **ampholytic** (= positively + negatively charged) and **double-hydrophobic** (= two different hydrophobic). Each series covered all five possible star architectures: **star-block** (both AB and BA arms), **statistical**, and **heteroarm**, also known as **mikto-arm** (both A-*core*-B and B-*core*-A). The study is complemented by **swelling measurements**.

The contribution by **Lutz** and colleagues involves the **synthesis and characterization of end-linked networks of polystyrene and poly(ethylene oxide)**. The linear precursors are prepared by **living anionic polymerization** and the use of **bifunctional initiators**, followed by appropriate **end-group modifications** to yield the **α,ω-divinyl telechelic polymers**. These polymers are subsequently reacted with **octafunctional silsesquioxanes** to yield the corresponding end-linked networks, which are characterized in terms of their **swelling** and **mechanical properties**.

The chapter by **Cook**, **Bowman** and coworkers reviews recent exciting work on covalent ***photo-plastic*** **polymer networks bearing thiol-ene groups** which are reversibly cleaved by light. The present networks are synthesized by the **free-radical addition** between a **tetra-thiol** and a **divinyl ether** in the presence of **additives** which promote **bond interchange** after the preparation of the network, particularly upon irradiation. **Photo-plasticity** allows the networks to be **readily reshaped** or to **rectify inhomogeneities** in stress distribution, thus **extending their life-span**.

In the following chapter, **Van Duin** and colleagues shed light to the **mechanism** of **peroxide-curing** for the preparation of **ethylene-propylene-diene-monomer (EPDM) rubber**, an extremely important commercial **elastomer** extensively used for outdoor applications, such as **automotive sealing systems** and **roofing for buildings**. The spectroscopic data (GC-MS, EPR and solid state ^{13}C NMR) of these researchers indicate that **H-abstraction** leads to the formation of **alkyl and allyl macro-radicals** which **recombine** in all three possible ways to provide the **cross-links**.

In their chapter, **Fromm** and coworkers present their work on **coordination polymer networks**, comprising **metal ions** interconnected with **organic ligands** via **coordinative** and other weak chemical **bonds**, also known as **metal-organic frameworks** (MOFs). **Crystal structures** of MOFs based on **copper** or **silver ions** and **α,ω-bis(4-pyridine)s** spaced out with **oligo(ethylene oxide)s** are presented. Similar structures differing only in the number of co-crystallizing solvent molecules (**pseudo-polymorphs**), in the ligand layout (**polymorphs**) and in spatial connectivity (**isomers**) are presented.

Properties

The largest section of the volume is that on network properties with 17 chapters. The majority of these chapters are on the characterization of physical and nanocomposite gels and networks, but there are also chapters on liquid crystalline gels and networks, self-healing polymer networks, and interpenetrating networks.

Tournilhac, Leibler and co-workers present novel, **self-healing, supramolecular, rubbery networks**. These materials can be **cut** and then **perfectly mended** by bringing the pieces together and **applying mild pressure** at **room temperature**. The bulding blocks of these materials are **non-toxic amides, ureas and imidazolidones of vegetable origin**, interconnected via **thermally-reversible hydrogen bonds** to **non-crystalline, amorphous rubbers**.

Urayama reviews the work by his group and by others on **stimulus-responsive nematic elastomers** swollen in **non-nematic** and **nematic solvents**. The chapter presents the **swelling**, **mechanical** and **optical properties** of these materials, and illustrates how these properties are affected by **temperature**, **electric fields** and **mechanical stress**. In particular, as the **nematic gels** are **cooled down**, they do not only **shrink** but they also

get elongated. Furthermore, the application of a **strong electric field** can **rapidly** cause a **macroscopic deformation** and a significant **change in the birefringence** of the nematic gels. Finally, nematic gel **stretching normal to the initial director** induces the **director rotation** along the stretching axis.

Heinrich and co-workers review their recent work on the **preparation of rubber nanocomposites** with **improved mechanical and electrical properties**. The car industry uses such materials for **car tire tread** applications. These researchers incorporate in elastomers several novel nanosized fillers, including **layered silicates**, **carbon nanotubes**, and ***in-situ* sol-gel derived silica nanoparticles**, in replacement of the traditionally-used carbon black, and characterize the **physical properties** of the resulting nanocomposites.

Christodoulakis and **Vamvakaki** use emulsion free-radical cross-linking copolymerization to prepare **weakly polyelectrolytic microgels** based either on 2-(diethylamino)ethyl methacrylate (hydrophobic, positively ionizable) or methacrylic acid (hydrophilic, negatively ionizable); the latter units were introduced by the polymerization of *tertiary*-butyl methacrylate followed by deprotection using trifluoroacetic acid. Dynamic light scattering indicated that both types of **microgels** were **pH-responsive**, presenting changes in their **hydrodynamic radii**, typically between **200 and 500 nm**.

Shibayama and **Osaka** investigate, using small-angle neutron scattering (SANS), **aqueous polymer transitions induced,** not only by temperature, **but also by pressure**. A **homopolymer**, a **block copolymer** and a **protein** are studied. Whereas increases of both temperature and pressure promote hydrophobic interactions, some **subtle differences** exist. For instance, at ambient pressure, temperature increases cause, sequentially, the micellization and the precipitation of the block copolymer, whereas, at ambient temperature, a pressure increase can only cause block copolymer precipitation.

In their chapter, **Wu** and co-workers present a two-component synthetic hydrogel (**"double-network"**) with **high fracture toughness** and low surface friction, **mimicking** the mechanical properties of **natural cartilage**. The two pure components of the hydrogel, an **anionic polyelectrolyte network** and a **neutral linear polymer**, possess mechanical properties very different from those of the final robust composite material, with the former component being **hard and brittle**, and the latter being **soft and viscoelastic**. In this contribution, the authors present mechanical measurements on their materials and, based on those, they propose a deformation mechanism qualitatively consistent with their previously proposed one based on neutron scattering measurements.

In the following chapter, **Galina** and co-workers describe the preparation and characterization of **polymer networks** based on cross-linked **liquid crystalline** monomers. The obtained networks are **anisotropic**, a result of their constitution of anisotropic (liquid crystalline) monomers. The introduction of **polyhedral oligomeric silsesquioxanes** in to these networks as **reactive fillers** affects their thermomechanical properties, while preserving their optical anisotropic properties.

Philippova and **Molchanov** present a **physical hydrogel** composed of **hydrophobically modified polyacrylamide** and **long cylindrical surfactant micelles** of potassium oleate. The system, characterized using viscosity and SANS, is **highly responsive to hydrocarbons** whose addition converts the network to a solution due to disruption of the cylindrical micelles. Such systems can be used for **oil recovery**.

In their chapter, **Hourdet** and **Petit** describe in detail the preparation and characterization of **physical hybrid hydrogels** comprising **silica** and **polyacrylamide graft copolymers** with poly(*N*,*N*-dimethylacrylamide) (PDMA), poly(*N*-isopropylacrylamide) (PNIPA) or poly(ethylene oxide) (PEO) grafts. Viscosity and modulus measurements indicated that there is an **optimum silica-polymer stoichiometry** for **hydrogel formation**. The ability of the **grafts** to **promote hydrogel formation** increases in the order **PEO** $<$ **PNIPA** $<$ **PDMA**, coinciding with the **adsorption affinity** of the corresponding linear oligomers for silica surfaces, measured in independent experiments.

In a similar spirit, **Haraguchi** and **Li** present **physical hybrid hydrogels** composed of **exfoliated clay** and **PNIPA**, displaying **substantial surface hydrophobicity**, as indicated by extraordinarily high contact angles for water (100–150°) at ambient temperature, despite the fact that both constituents are hydrophilic. The exact values of the contact angles depended on hydrogel composition. These values were stable in short-term measurements ($\leq$10 s), but during long-term measurements ($\sim$20 min), they underwent unique changes which strongly depended on clay concentration.

Grande and co-workers describe the preparation of **mesoporous networks**, using, as starting materials, **interpenetrating** (IPN) and **semi-interpenetrating** polymer networks (sIPN) whose **one** component is **degradable** and can be eroded away. In this chapter, **poly(D,L-lactide)** served as the erodible component, whereas non-degradable **methacrylate** or **styrenic** networks with **acidic** or **basic** functional groups were employed as the permanent skeletons. The resulting mesoporous networks were fully characterized in terms of their **morphology** and **porosity**.

Koga, **Winnik** and co-workers use SANS to study the **structure** of **associating copolymers** of linear **PNIPA** with two hydrophobic **octadecyl** end-groups in **water**, as a function of **copolymer concentration** and **temperature**. At room temperature (20 °C) and moderate copolymer concentration (10 g L^{-1}), individual **flower-like micelles** are formed, which, above 31 °C, agglomerate to form mesoglobules and larger fractal aggregates. The same behavior is preserved at higher copolymer concentrations (50 g L^{-1}), whereas at lower copolymer concentrations (1 g L^{-1}) no fractal aggregates are observed.

Schmidt and colleagues describe **magnetically-actuated liquid crystalline elastomers**. The present system comprises liquid crystalline elastomers loaded with **superparamagnetic nanoparticles** which, upon the application of an **external alternating magnetic field**, **get heated**, warming up the system and **inducing a nematic-isotropic phase transition** and a **shape change** in the material. The system has a **great application potential** because it can be **remotely actuated** with a relatively **short response time**.

In their chapter, **Richter** and co-workers describe **jamming in filled polymer systems**. **Jammed materials** are all **microscopically disordered** structures that can **support a finite stress** up to a critical value **without plastic deformation or flow**. These are solid-like materials, which include polymer gels and various glasses. The **jamming** in two ***filled*** **polymer systems** is of interest in this study: in **EPDM rubber** filled with **silica particles**, and in a **polycarbonate melt** filled with **carbon nanotubes**. These systems are subjected to **high strains to break** the continuity of the filler network, and are subsequently allowed to **re-equilibrate** so that the **kinetics of filler re-agglomeration** (''jamming back'') **is monitored**.

Schlatter, **Hadziioannou** and co-workers investigate the **formation** of **physical gels** based on **polyrotaxanes** comprising **α-cyclodextrins** (α-CD) **threaded** on to **PEO**. Rheological, spectroscopic, scattering and calorimetric measurements revealed that **gel formation** is **driven** by the **crystallization** of **naked PEO** segments and by the **aggregation** of **α-CDs**. The kinetics of gelation was investigated too.

Susoff and **Oppermann** study the **diffusion** coefficient of **linear** fluorescently-labeled (non-cross-linkable) **polystyrene** ''***tracer***'' chains within a toluene semidilute solution of photo-cross-linkable **polystyrene** ''***matrix***'' chains during the course of photo-cross-linking. In **semidilute solution** (before photo-cross-linking), the **diffusion coefficients** of the polystyrene **tracer** chains **decreased** with their **molecular weights less strongly** than **reptation theory** would dictate, especially when tracer molecular weights were higher than matrix molecular weights. However, upon matrix photo-cross-linking (**gelled systems**), reptation theory was closely followed, with the polystyrene **tracer diffusion coefficients decreasing** with the **square** of their **molecular weight**.

Papadakis and co-workers employ scattering techniques to investigate the **structure in water** of an **ABA triblock copolymer** with a **PNIPA mid-block** and **two deuterated polystyrene end-blocks**. Flower-like micelles are formed in dilute solutions, whereas some bridging between the micelles is also observed at higher copolymer concentrations. The effect of temperature on the sizes of the core and the shell of the micelles is also investigated with a collapse observed above the LCST of PNIPAM.

Theory and Simulations

A small but yet very important section of the volume is that of Theory and Simulations, which hosts six chapters, covering a variety of topics, including Monte Carlo simulations, (analytical) theory, kinetic calculations on gel formation, and solution of a time-variant heat transfer problem in nanocomposite rubbers.

First, **Douglas** presents the **localization model of rubber elasticity**, a simple, analytical model, qualitatively describing aspects of rubber elasticity in both dry and swollen rubbers. As in the classical elasticity theory, the localization model of rubber elasticity also assumes that the network chain segments are localized at the network junctions. However, this model further considers the **chains** to be **localized** along their **contours** by a **local harmonic potential** arising from **interparticle packing interactions**, thus successfully capturing the experimentally well-established **incompressibility of dry rubber** arising from **repulsive interactions** between the chains.

Next, **Dias**, **Costa** and co-workers extend, by the inclusion of divinyl cross-linker, their previous work on the **modeling** of the **kinetics** of **controlled radical polymerization** (**ATRP** and **nitroxide-mediated radical polymerization**) on the preparation of **linear polymers** to cover **branched polymers** and **polymer networks**. By solving the time-dependent **differential equations** for the various **chemical reactions**, along with **species balance** (sometimes almost 30 species were present) and appropriate **kinetic rate constants**, they predicted the **temporal evolution** of **monomer conversion** and branched polymer **molecular weight**. These predictions compare favorably with experiments also performed within this study. Their results indicate that the **branched polymers** produced by **controlled radical polymerization** were **more highly branched** than those produced by **conventional free radical polymerization**, although the latter polymers attained higher molecular weights faster than the former.

Sommer and **Saalwächter** define a **tensorial order parameter** to characterize the **orientational properties** of **chain segments** in **polymer networks**. This parameter is proportional to the network **residual dipolar coupling constant** (RDC) which is directly measurable through **NMR experiments**. Experimentally-measured **RDCs** of polymer networks **swollen to equilirium** scale to the **–1.5 power** of their **volume swelling ratio**, in excellent agreement with theoretical predictions and computer simulations. Useful information can also be extracted by following the **evolution** of the experimentally-measured **RDCs** of polymer networks with respect to the **(non-equilibrium) volume swelling ratio**, from the **dry state** all the way to **swelling equilibrium**. The **data** at the **early stages** of swelling indicate **non-affine** polymer chain segment deformations, while the **trends in the data** at the **later stages** of swelling reveal **trapped entanglements**.

Levi and **Srebnik** use **lattice Monte Carlo simulations** to understand the **imprinting of small globular proteins** on to polymer networks. Such networks, exhibiting specificity toward the binding of a particular protein, can be used for protein purification. The simulation results indicate that the **main factor** determining protein **binding** is **protein charge density**.

Lechowicz and **Galina** use Monte Carlo simulations to examine **network formation from the reaction between A_2 and B_3 monomers at ratios far from the stoichiometric one**. Not surprisingly, no gelation is observed under these conditions. Interestingly, however, **gelation can be induced** if the **majority component** is **added** in **small portions**.

The chapter by **Gottlieb** and co-workers **analyzes numerically the magnetically-induced heating in elastomeric nanocomposites**. This is an important system with a great applications potential. The system, consisting of magnetic nanoparticles embedded in an elastomer, is exposed to an external alternating magnetic field which causes its heating mainly via the relaxation of the internal magnetic moment. Numerical solutions to the time-dependent energy Equation at different geometries indicate a **high temperature rise**, of the order of **100** °C, within a **few microseconds**, in good agreement with experimental results.

Applications, Bioapplications and Biogels

The final section of the volume hosts chapters on network applications (both non-biological and biological) and on the characterization of biological networks based on proteins, polysaccharides, DNA or lipids.

The chapter by **Choulis** and colleagues focuses on the optimization of the power conversion efficiency of **inkjet-printed polymer solar cells**. Polymer solar cells represent an attractive alternative to inorganic solar cells due to their **low fabrication cost** arising from their **low-temperature solution processibility**. The active layer of the system investigated consisted of **poly(3-hexylthiophene)** (electron donor) and a **fullerene** derivative (electron acceptor) deposited from **pristine tetralene solution**.

In their chapter, **Tiller** and co-workers review their research on the **evaluation of amphiphilic polymer conetworks for a series of applications**, exploiting the **phase separation** within these materials on the nanoscale and the resulting **large interfacial area**. The applications explored include **biocatalysis in organic solvents**, **metathesis reactions in water** and **sensing of metabolites or gases**. In all these applications, the conetworks act as **matrices** for **phase transfer reactions**, in which the **substrate(s)** and the **catalyst** or the **two reactants** are located in **opposite conetwork nanophases**, but their **contact** is facilitated by the **huge interfacial area**.

In this chapter, **Bolisay** and **Kofinas** describe the **development of imprinted polymer networks for the recognition and separation of viruses**. These researchers prepared networks of **polyallylamine**, cross-linked with **ethylene glycol diglycidyl ether**, in the presence of **tobacco mosaic virus** as the targeted virus. After washing, the virus binding capacity of the network was determined spectroscopically as a function of time.

Peinado, **Anseth** and co-workers review their recent work on the use of **hyperbranched polymers** and the **networks** resulting from their **photopolymerization**-induced interconnection for various **biomedical applications**, including drug delivery, imaging, molecular imprinting, and, most notably, **tissue engineering** of **valvular interstitial cells**.

In a similar spirit, **Rimmer**'s research team investigates the **adhesion** and **proliferation** of **human dermal fibroplast**, **human corneal epithelial**, or **bovine keratocyte** cells on **networks** derivatized either with the **GRGDS peptide** or with **butylamine**. The GRGDS moieties bind directly to the cells, whereas the butylamine groups promote the non-selective binding of proteins to which the cells adhere.

The chapter by **Puskas and Hoerr** presents **drug release** from **coronary stents** coated with **rubbery hyperbranched polyisobutylene-*block*-polystyrenes**. The results indicated a **dependence** of the **drug release profiles** on both the **copolymer molecular weight** and the **coating (spraying) conditions**.

Takafuji and coworkers use photopolymerization of several **monomers** and **cross-linkers** to freeze the **chiral, fibrillar gel structures** formed by a **novel synthetic**

lipid, **dilauryl-pyrenyl-L-glutamide**. When in benzene, the lipid forms **chiral structures at room temperature**, which, however, **melt at or above 70** °C, as indicated by circular dichroism and fluorescence spectroscopy. A similar behavior is also observed when benzene is replaced by most monomers tested, with styrenics being more structure-forming than (meth)acrylates. After photo-irradiating a lipid-methyl methacrylate mixture, the original chirality of the system was locked in, and was preserved even above 70 °C.

Larreta-Garde and co-workers study the **rheological** properties of **aqueous** solutions of **biopolymer mixtures** composed of a **protein** and a **polysaccharide**. In all cases, the protein is **gelatin** (from collagen), whereas the polysaccharide is either **hyaluronic acid** or **alginate**. In the **gelatin/hyaluronic acid** mixtures, the **latter** component always **facilitates** (gelatin) gel formation without forming its own network. **Selective hydrolysis** of **hyaluronic acid** by **hyaluronidase** converts the rheological properties of the mixture to those of **pure gelatin**. Qualitatively **similar results** were obtained with **gelatin/alginate** mixtures. However, for this pair, under certain conditions, it is possible to prepare an **interpenetrating polymer network**, by **first** forming an **alginate gel**, **followed** by the formation of the **gelatin gel**.

Stokke and co-workers study the **gelation** of **alginate** as induced by **calcium** ions (as opposed to by pH) in the **presence of oligomeric guluronic acid**. **Poly(guluronic acid)** segments are a **component** of native **alginate**. The added **oligo(guluronic acid)** used **competes** with **alginate** for **calcium ion binding** (**Ca^{2+}** acts as **cross-linker**) and **delays** alginate **gelation**, without contributing to the mechanical properties of the alginate gel, as its small size does allow it to become part of the gel formed.

Horkay and colleagues characterize **chemically cross-linked DNA gels** using **swelling**, **SANS** and **osmotic pressure** measurements as a function of **pH** and **calcium ion concentration**. At pH values below 1.2 (NaCl concentration = 40 mM, no added $CaCl_2$) or at $CaCl_2$ concentrations higher than 0.3 mM (NaCl concentration = 40 mM, pH = 7) the DNA gel collapses. Under conditions **just before the collapse** (pH = 1.5 or $CaCl_2$ concentration = 0.2 mM), the **SANS intensity** in the **intermediate *q*-range** (0.08 to 0.8 nm^{-1}) from the DNA gels **increases**, with the **effect of $CaCl_2$** on this increase being **more pronounced** than the pH effect, and leading to a **q^{-1}-dependence** of the intensity within that *q*-range, indicating the formation of **linearly-aligned assemblies**. On the other hand, the **dependence** of the **osmotic pressure** of the gel on the **DNA volume fraction** was **stronger** near the **pH-induced transition** than the $CaCl_2$-concentration induced one.

Finally, **Geissler** and co-workers perform **dynamic light scattering** measurements on semidilute aqueous solutions of high molecular weight **hyaluronan** in the presence of both **monovalent** and **divalent cations**, and prove that the effect of the concentration of the divalent calcium ions can adequately be captured by **ionic strength**. In particular, these researchers show that, at **high salt concentration**, the **osmotic compression modulus**, related to the **polymer diffusion coefficient**, scales as **(hyaluronan concentration)$^{9/4}$ × (ionic strength)$^{-3/4}$**.

Conclusion

Polymer networks continue to be a central theme of intense research in polymer science. These materials can be prepared synthetically or they can be of natural origin (polysaccharides, proteins, DNA, lipids). Regarding synthetic polymer networks, there has recently been a growing effort for their synthesis using living/controlled polymerization methods. This endeavor provides materials with better-controlled structure, whose subsequent physical characterization can lead to the derivation of accurate structure-property relationships. Polymer networks, prepared either by controlled or conventional methods, come with a variety of important properties, including stimulus-responsiveness, liquid-crystallinity, hyperhydrophobicity, amphiphilicity, porosity, internal hierarchical organization, softness, toughness, superabsorbency, and, most lately, self-healing. All these properties can be characterized by a host of techniques, ranging from microscopy, to spectroscopy, scattering, rheology, mechanical testing and swelling measurements. Theoretical and modeling efforts, both analytical and computational, are invaluable and necessary complements to the experimental studies of the properties of polymer networks. Polymer networks are used in many applications, both biological and non-biological. These include water, blood and urine retention, chemical and enzymatic catalysis, separations of small molecules, proteins or even viruses, enzyme and cell immobilization, drug delivery, and tissue engineering. This last application involves the use of degradable polymer networks as erodible scaffolds to process cells. A particular form of tissue engineering is organ regeneration which holds great promise for the future in solving the problem of shortage of transplants.

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