



## Interpenetrating polymer networks: So happy together?

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### ARTICLE INFO

Dedicated to Professor Moshe Narkis, mentor, colleague, friend, who entangled me in IPN and immersed me in emulsions.

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### ABSTRACT

A typical description of interpenetrating polymer networks (IPN) can be surprisingly simple, systems that consist of two crosslinked polymer networks that are physically entangled but not chemically linked. That simplistic description, however, successfully encompasses a wide range of synthesis processes and macromolecular architectures that can include “semi-IPN” (IPN-like systems containing only one crosslinked polymer) and interconnected polymer networks (IPN-like systems that also include a limited amount of inter-network chemical links). The macromolecular topologies of these systems combine kinetically entrapped molecular-level mixing with limited phase separation into a continuous range of nanodomain compositions. This perspective-review presents the family of IPN systems, describes the synthesis parameters used to generate a variety of macromolecular topologies, and discusses the damping properties, the ability to process latex IPN, the mechanical robustness of double network hydrogels, and IPN as templates for porous polymers, as well as recent innovations and cutting-edge applications. The wide gamut of macromolecular topological options described herein will serve as a guide to realizing synergistic behaviors by combining polymers in IPN-like structures.

### 1. Introduction: Oh, what a tangled web we weave

Hermann Staudinger's "On Polymerization" article in 1920 insightfully described the true nature of the chemical bonding within the molecules produced by polymerization reactions [1,2]. Staudinger also contributed insight into the structure and nature of polymer networks, describing polyisoprene networks in the same 1922 article in which he coined the term “makromolekel” (macromolecule) [3] and describing copolymer networks (styrene and divinylbenzene (DVB)) in 1934 [4]. This perspective-review celebrates contemporary polymer science and engineering on the 100th anniversary of "On Polymerization" by describing the complex macromolecular architectures and arrangements inherent in interpenetrating polymer networks (IPN).

A typical description of IPN can be surprisingly simple, systems that consist of two crosslinked polymer networks that are physically entangled but not chemically linked [5]. That simplistic description, however, successfully encompasses a wide range of synthesis processes and macromolecular architectures, many of which are described in various reviews [6–13]. The term IPN includes simultaneous (sim) synthesis processes, sequential (seq) synthesis processes, and “semi-IPN”, systems that consist of a linear (i.e., non-crosslinked) polymer that is physically entangled within a crosslinked polymer network. The macromolecular architectures of these complex systems are generated through the combination of kinetically entrapped molecular-level mixing with

thermodynamically driven, but macromolecular-mobility-limited, phase separation. The description of interconnected polymer networks (ICN) is similar to that of IPN, but with one important difference. ICN consist of IPN-like systems that also include a limited amount of inter-network chemical links.

One early, principal, and prolific proponent of the importance of IPN was L.H. Sperling, whose irrepressible and infectious enthusiasm for IPN was emulated by his colleagues and students. Sperling's 1981 book, “Interpenetrating Polymer Networks and Related Material”, was a relatively comprehensive description of the state of IPN at the time, describing the place of IPN in the rapidly developing world of polymers (1960s and 1970s). At the time, novel polymer systems were being generated by combining distinct homopolymers into multi-polymer systems dominated by blends, grafts, and blocks [5]. While IPN may have seemed to play a relatively low-key role, compared to the more elegant and more common multi-polymer systems, the combination of polymers in IPN enabled access to unique macromolecular topologies and properties. Sperling's book gathered together a large body of IPN research and development, as stated in the Preface [5]: “One of the objectives of this book is to point out the wealth of work done on IPNs or closely related materials. Since many papers and patents actually concerned with IPNs are not so designated, this literature is significantly larger than first imagined. It may also be that many authors will meet each other for the first time on these pages and realize that they are

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working on a common topology.” In the pioneering work on IPN, the structure and properties were usually investigated using a combination of transmission electron microscopy (TEM), differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), and stress-strain tests.

## 2. Sequential and simultaneous: Which comes first?

The most common synthesis routes for IPN, semi-IPN, and ICN are depicted schematically in Fig. 1. In the scheme,  $M_i$  represents monomer  $i$ ,  $X_i$  represents the crosslinker for monomer  $i$ ,  $P_i$  represents polymer  $i$ ,  $xP_i$  represents crosslinked polymer  $i$ , and  $R_i$  represents the reaction used to polymerize  $M_i$  and  $X_i$ .  $R_1$  and  $R_2$  are two reactions in a sequential synthesis, and therefore, they can entail the same polymerization mechanism.  $R_1$  and  $R_3$ , on the other hand, are two reactions in a simultaneous synthesis, and therefore, they must be mutually exclusive polymerization mechanisms.  $RX$  is a selective IPN-forming reaction that crosslinks the linear polymer in a semi-IPN.  $RC$  is a selective ICN-forming reaction that generates a limited number of inter-network bonds.

Sequential IPN are synthesized in a multi-stage process, and therefore, the same polymerization mechanism can be used to synthesize  $xP_1$  and  $xP_2$ . In brief,  $M_1$  and  $X_1$  are polymerized to form  $xP_1$ .  $xP_1$  is swollen in  $M_2$  and  $X_2$ , which are then polymerized to form  $xP_2$ . There are many variations possible in this multi-stage process. If the synthesis takes place without  $X_1$  (but with  $X_2$ ), then a semi-1-IPN is formed. If the synthesis takes place without  $X_2$  (but with  $X_1$ ), then a semi-2-IPN is formed. If  $xP_1$  is only partially swollen in  $M_2$  and  $X_2$  and their polymerization rate is faster than the diffusion of  $M_2$  and  $X_2$  into  $xP_1$ , then an IPN with a gradient in its macromolecular topology results. Simultaneous IPN are synthesized in a one-stage, one-pot process using two mutually exclusive polymerization mechanisms for  $xP_1$  and  $xP_3$  (e.g.

chain-growth and step-growth). Since the reaction rates may not be the same, the faster reaction can produce an increase in the viscosity of the system. The macromolecular structure generated by the slower reaction will, therefore, be affected by the limitations on the mobilities of the growing macromolecules and of the monomers that are imposed by the increase in viscosity. If either  $X_1$  or  $X_3$  is not used, then the result is a semi-IPN.

Unless stated otherwise, the general descriptions of the synthesis mechanisms and processes herein will, by default, be describing the combination of two covalent networks in IPN. Usually, the same descriptions of the synthesis mechanisms and processes can be applied to the synthesis of semi-IPN, simply by omitting one of the two crosslinkers. A comparison of an IPN formed by combining  $xP_1$  and  $xP_2$  with a random copolymer will be conceptually based on a monomer mixture that contains the same amounts of  $M_1$  and  $X_1$  as in  $xP_1$  and the same amounts of  $M_2$  and  $X_2$  as in  $xP_2$ . A comparison of an IPN formed by combining  $xP_1$  and  $xP_2$  with a polymer blend will be conceptually based on a coagulated mixture of individual  $xP_1$  and  $xP_2$  latices that were synthesized using emulsion polymerization.

The scheme in Fig. 1 provides a framework for classifying the different types of macromolecular architectures that can be generated from  $M_1$ ,  $M_2$ , and  $M_3$ . Obviously, real systems would be much more complex than these simplistic descriptions. An example of real monomers could have: styrene as  $M_1$ , DVB as  $X_1$ ,  $n$ -butyl acrylate as  $M_2$ , ethylene glycol dimethacrylate as  $X_2$ , a combination of a polyether diol and toluene diisocyanate as  $M_3$ , and a polyether triol as  $X_3$ . In such examples, while the  $P_i$  are homopolymers, the  $xP_i$  are clearly copolymers. In the description of IPN systems herein, the copolymeric nature of the  $xP_i$  and the inhomogeneities that exist within the  $xP_i$  will not be emphasized. The effects of adding  $X_i$  to  $M_i$  on the macromolecular structure and properties (e.g., the glass transition temperature ( $T_g$ ) and the mechanical behavior) will not be discussed in detail. The

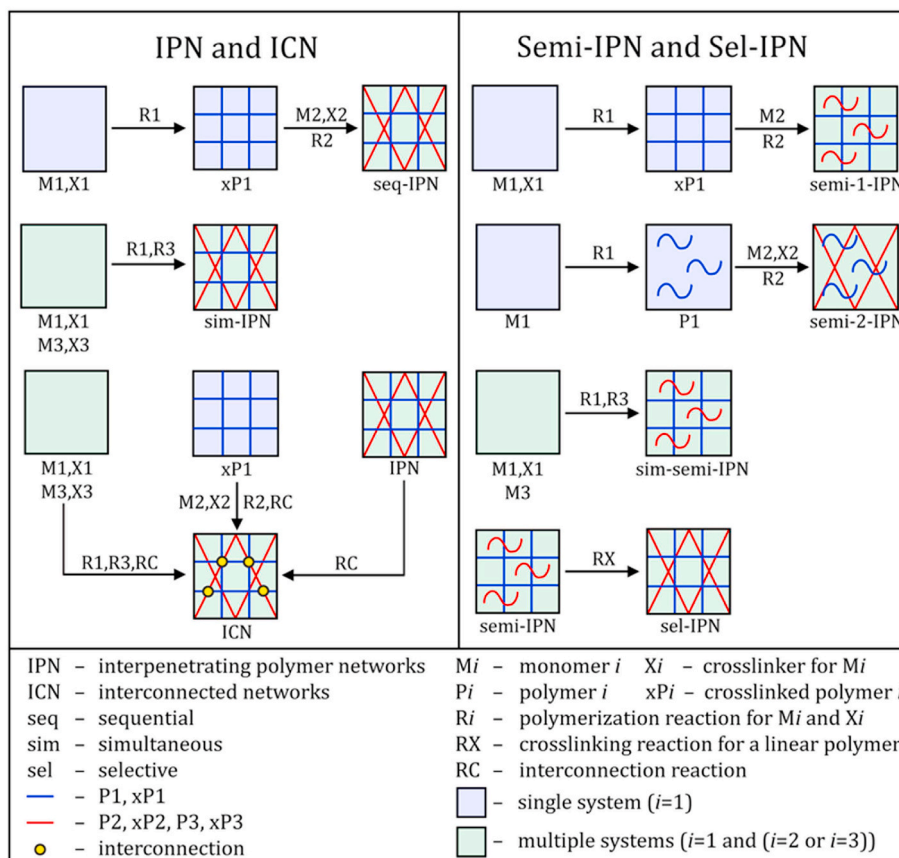


Fig. 1. A schematic depiction of the most common synthesis routes for IPN, semi-IPN, and ICN.

dependence of a copolymer's macromolecular structure and network structure upon the polymerization mechanism, the reactivity ratios, and the complexities of network topologies (the presence of dangling strands, entanglements, and loops) have been discussed in detail elsewhere [14–23]. This perspective-review will focus upon the synergisms attainable through the complex macromolecular topologies produced when combining polymers in IPN.

### 3. Macromolecular architecture: Mix and separate

The underpinning concept in IPN is the synergistic combination of two incompatible polymers with very different sets of properties that is achieved by generating, and then entrapping, molecular-level mixing. While the two polymers are thermodynamically driven to undergo phase separation, they are topologically prevented from doing so through the entanglement of their individual networks. In an “ideal” IPN, the entrapped mixing of the networks would generate a homogeneous composition at the molecular level that would be, in some ways, equivalent to that generated by random copolymerization. Most IPN, however, are far from ideal. Limited nanoscale phase separation takes place during and following synthesis, producing a broad spectrum of domain compositions that can range continuously from xP1-rich to xP2-rich, as shown schematically in Fig. 2. The resulting macromolecular architectures and properties are, therefore, quite different from those of random copolymers and quite different from those of the more elegant and more controlled copolymer architectures such as blocks, grafts, stars, and brushes that can be achieved through controlled/“living” polymerizations. While IPN, semi-IPN, and ICN were originally based on two synthetic, covalently crosslinked, organic polymers, systems have also been developed that are based on: renewable resource networks (such as natural oils [24–27], polysaccharides [28], cellulose [29], hyaluronic acid [30], and collagen [31,32]); supramolecular networks [33]; and inorganic networks [34–40].

An in-depth, detailed monograph written by Y.S. Lipatov that focuses on phase separation in IPN describes the structures and properties through the prism of the thermodynamic and kinetic factors involved, discussing thermodynamics and phase separation, heterogeneous structures and morphologies, relaxation transitions and viscoelasticity, chemical kinetics and phase separation, and compatibilization [41]. Lipatov relates that it became clear early-on that IPN were phase-separated materials and were quite different from the “ideal” of two crosslinked networks entangled homogeneously on the

macromolecular level. The uniqueness of IPN compared to polymer blends, therefore, lies in the interpenetrating structures that exists within the quasi-equilibrium phases formed under forced compatibilization. This is also reflected in Sperling's use of a synthesis-based definition of IPN as “a combination of two polymers in network form, at least one of which is synthesized and/or cross-linked in the immediate presence of the other” [42] rather than a topological-based definition.

The unusual properties often associated with IPN are directly related to the unusual macromolecular architectures that combine molecular-scale mixing with a continuous compositional range of nanoscale phase-separated domains. One example is the broad damping temperature range that results when a polymer with a low  $T_g$  (e.g., xP1) and a polymer with a high  $T_g$  (e.g., xP2) are combined. The effects on the DMTA storage modulus ( $E'$ ) and  $\tan \delta$  of combining xP1 and xP2 in a 1/1 ratio are illustrated schematically in Fig. 3. xP1 is depicted as having a  $T_g$  of around  $-100^\circ\text{C}$  and a low modulus at room temperature, while xP2 is depicted as having a  $T_g$  of around  $150^\circ\text{C}$  and a high modulus at room temperature. The  $T_g$  and modulus of a random copolymer of M1, X1, M2, and X2, with an (M1+X1) to (M2+X2) ratio of 1/1, is also included in Fig. 3. The copolymer  $T_g$ , predicted to be  $25^\circ\text{C}$  by the Fox equation [43], is shown between the  $T_g$ s of xP1 and xP2.

At their  $T_g$ s, the homopolymer, copolymer, and blend curves in Fig. 3 all exhibit relatively rapid decreases in  $E'$  and relatively narrow  $\tan \delta$  peaks. The 1/1 blend of xP1 and xP2 in Fig. 3 represents the formation of a bicontinuous structure that is conceptually similar to the structure formed by a 1/1 blend of immiscible P1 and P2, which exhibits the  $T_g$ s of the phase-separated component polymers. The modulus between the xP1 and xP2  $T_g$ s would be  $\sim 50\%$  of the high- $T_g$  polymer modulus since the load-bearing component only constitutes 50% of the blend.

The characteristic IPN curves in Fig. 3, from a 1/1 combination of xP1 and xP2, are quite different from the homopolymer, copolymer, and blend curves. The IPN curves reflect both the presence of entrapped molecular-level mixing and the presence of nanoscale phase-separated domains with a continuous range of compositions. The modulus decreases gradually between the  $T_g$ s associated with xP1 and xP2 and the  $\tan \delta$  peak is relatively broad and relatively low. The relatively wide breadth of the IPN  $\tan \delta$  peak is associated with the continuous range of nanodomain  $T_g$ s that corresponds to the continuous range of phase-separated nanodomain compositions. The relatively low height of the IPN  $\tan \delta$  peak is associated with the additional limitations on macromolecular mobility. These additional limitations, imposed by the mutually entrapped macromolecular topology, are even more stringent

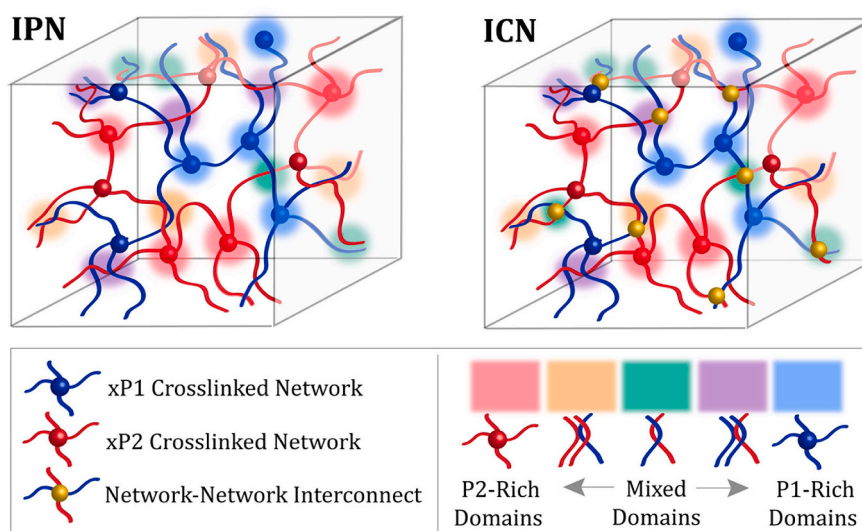
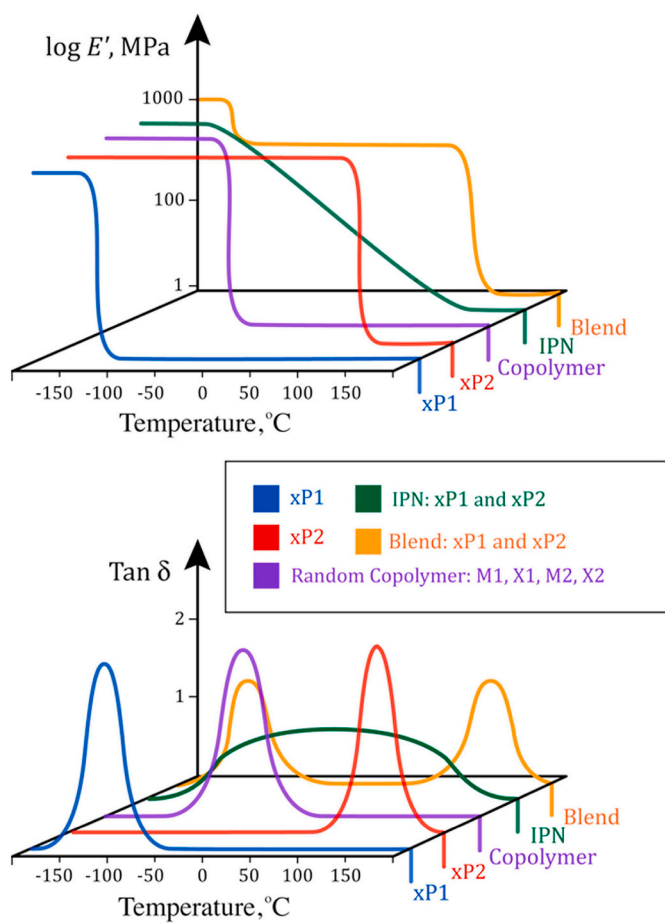


Fig. 2. Schematic illustrations showing two physically entangled macromolecular networks, highlighting the broad spectrum of domain compositions that can range continuously from xP1-rich to xP2-rich, for IPN (left) and ICN (right).



**Fig. 3.** Schematic illustrations of  $E'$  and  $\tan \delta$  curves produced by the representative polymer systems (after Fig. 5 in Ref. [48]). These systems have a fixed M1/X1 ratio and/or a fixed M2/X2 ratio. The random copolymer, IPN, and blend have a (M1+X1)/(M2+X2) ratio of 1/1. From front to back: xP1 (blue); xP2 (red); a random copolymer of M1, X1, M2, and X2 (purple); an IPN based on xP1 and xP2 (green); a blend of xP1 and xP2 (orange). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

than those imposed by the individual crosslinking of P1 and P2. The effects of IPN formation on chain conformation [44], on combining two elastomeric polymers [45,46], and on combining elastomeric polymers with brittle polymers [47] have been investigated in some detail.

#### 4. Begin at the beginning: Over and over and over again

The IPN macromolecular topology seems to have been continually reinvented in the patent literature. Sperling has described examples of syntheses going back as far as 1914 that involved the formation of IPN, sometimes even unbeknownst to those concerned [5,10,49,50]. The first recorded IPN work seems to have been that by J.W. Aylsworth, the chief chemist in Thomas A. Edison's laboratory. The platter phonograph records, introduced to replace wax cylinders, were made of Bakelite, a brittle phenol-formaldehyde resin. Aylsworth added natural rubber and sulfur to enhance impact resistance, thus forming two independent polymer networks that combined a glassy polymer and a rubbery polymer in a simultaneous IPN [51]. The visual distortion that appeared in crosslinked amorphous polymers (polystyrene (PS) and poly(methyl methacrylate) (PMMA)) was eliminated by swelling the crosslinked polymer in the same monomer mixture and polymerizing, thus forming a sequential IPN (xP1 with xP1), in work by J.J.P. Staudinger (the son of Hermann Staudinger!) and H.M. Hutchinson in 1951 [52]. Swelling the

crosslinked polymer stretched the first network and the stretched network topology was "locked-in" by the second polymerization. Enhanced ion exchange resins, synthesized by using the IPN topology to intimately mix a negatively charged network with a positively charged network, were produced by G.S. Solt in 1955 [53].

The term IPN was coined by J. Millar in 1960 who was investigating beads produced using multiple polymerizations of styrene-DVB mixtures [54]. The in-depth investigations of IPN began to intensify in the late 1960s with the first works by Sperling [6], by H.L. Frisch, D. Klemperer, and K.C. Frisch [55], by K. Shibayama [56], and by Lipatov [57] and the field became well-established in the 1980s. The aspects of IPN explored in those initial works included phase-separation thermodynamics, dynamic mechanical behavior as a function of frequency and temperature, mechanical behavior, and damping. Several variations on the IPN theme were also investigated. In latex IPN (LIPN), the IPN were synthesized using emulsion polymerization, where the presence of the emulsion's external phase can affect the macromolecular structure. In "thermoplastic IPN", the crosslinks are physical, and therefore, can enable flow at elevated temperatures [5]. Highly porous IPN were produced by cryo-gelation [58–61] and by templating within the continuous phase of high internal phase emulsions (HIPEs), emulsions containing over 74% dispersed internal phase [62–65]. In emulsion templating, the locus of initiation (within the external phase or at the oil-water interface) in almost identical reaction systems can affect the macromolecular structure. In double network elastomers, the first network is oriented (stretched) during the formation of the second network [66–68]. More recently, the advantageous physical combination of two individual polymer networks has been brought to the forefront of cutting-edge polymer research and development once again by J.P. Gong's work on double network (DN) hydrogels [69–74]. Tables summarizing various aspects of IPN, from synthesis to application, have been compiled in a number of reviews, with some focusing on hydrophobic IPN [6,10] and others focusing on hydrogel IPN [7,9,13].

#### 5. Latex IPN: Complex structures, itty bitty living space

While IPN are usually synthesized using bulk polymerizations and using batch processes, they can also be synthesized using sequential emulsion polymerizations to produce LIPN [5,6,10]. LIPN syntheses usually take place in oil-in-water (o/w) emulsions. The presence of an aqueous external phase can affect the macromolecular topology and enable the generation of a wide variety of complex multiphase structures, including core-shell (C/S) nanoparticles (NPs) with IPN cores, as described by Sperling [75–78] and demonstrated by M. Narkis and Y. Talmon [79–82]. LIPN syntheses can take place using batch processes, where all the components are added at the beginning of the reaction, or using semi-batch processes, where the monomers (and often the surfactants and/or initiators) are added slowly and continuously throughout the reaction [83].

The morphology of the monomer-swollen polymer particles in emulsion polymerization is not necessarily straightforward, even in a relatively simple one-monomer, single-stage synthesis (e.g., the emulsion polymerization of styrene). On one hand, a uniform morphology would be expected from uniformly monomer-swollen polymer particles [84,85], while on the other hand, a C/S structure would be expected from a polymer-rich core surrounded by a monomer-rich shell [86–89]. C/S structures can also be formed during single-stage emulsion copolymerizations. A core that is rich in the more hydrophobic monomer and a shell that is rich in the more hydrophilic monomer could be produced in one scenario, while a core that is rich in the more reactive monomer and a shell that is rich in the less reactive monomer could be produced in a different scenario.

The two-stage emulsion polymerizations that are usually used to synthesize LIPN can be used to produce a wide variety of latex particle morphologies, reflecting the large number of synthesis parameters involved. The structures that can be generated using two-stage



sequential emulsion polymerizations depend on the polymer-polymer compatibility and on the degree of seed crosslinking and can include C/S, inverted C/S [90], raspberry-like (phase-separated domains at the surface) [91,92], Janus (crescent-moon-like or half-moon-like) [93,94], and dumbbell structures. One well-known example is the synthesis of acrylonitrile-butadiene-styrene (ABS) using emulsion polymerization. During the synthesis, grafted styrene-acrylonitrile (SAN) inclusions are produced within the polybutadiene (PBd) particles and then "wart-like" SAN protrusions are produced on the PBd surface that, with further polymerization, become SAN shells around the SAN-filled PBd cores [95–97].

For LIPN, the first synthesis stage consists of generating a seed latex through the polymerization of M1 and X1 in the presence of a water-soluble surfactant and a water-soluble initiator. For IPN formation, M2 and X2 are added to the seed latex, often with additional surfactant and initiator, and then polymerized. As indicated previously, variations on the same synthesis procedures can also be used to synthesize semi-IPN. In monolithic IPN generated using bulk sequential syntheses, the intimacy of macromolecular mixing, and the degree of phase separation is determined by the solubilities of M2, X2, and xP2 in xP1 and by the ability of xP1 to be swollen by M2 and X2. In LIPN syntheses, the monomer hydrophilicity becomes an additional factor in determining the multiphase structure owing to the presence of an aqueous external phase. In addition to the hydrophobic LIPN that are synthesized by two-stage polymerization within o/w emulsions, hydrogel LIPN can be synthesized through two-stage polymerizations within water-in-oil emulsions [98].

The formation of an LIPN structure based on xP1 seed latex particles is illustrated schematically in Fig. 4. If the xP1 seed particles do not swell in M2 and X2, then xP2 will form a shell around an xP1 core. If, however, xP1 swells in M2 and X2, then the resulting structure will be more complex. An IPN latex particle can be formed at relatively low M2 and X2 contents (75/25 in Fig. 4). The macromolecular topology within the latex particles can combine entrapped molecular-level mixing, phase-separated nanodomains, and a continuous range of compositions, as described for monolithic IPN [80,99,100]. Eventually, as the M2 and X2 content increases, the core will not be able to swell further and incorporate more M2 and X2. An xP2 shell will then form around the IPN core by the polymerizing M2 and X2 that cannot be incorporated within the monomer-swollen xP1 particle.

The approach to combining two polymers within a latex particle was used by H. Hopff in 1935, who polymerized vinyl monomers that were added to a natural rubber seed latex [10,101]. The resulting latex was coagulated and was then crosslinked using sulfur, producing semi-IPN. A series of LIPN for noise and vibration damping applications, modifying the viscoelastic behaviors by combining rubbery and glassy polymers (PS, PBd, polyacrylates, polymethacrylates (PMAs), and poly(vinyl chloride)), were developed by Sperling [75–78,102,103]. LIPN have been applied as coatings, adhesives, resins, golf ball threads, sealable films, damping materials, and impact-resistant thermoplastics, and have been applied as additives in paints, toners, and rubber crumb [10].

Narkis demonstrated that LIPN particles with diameters between 50

and 200 nm can have significant applicative advantages compared to the same IPN that is synthesized as a monolith. IPN are thermosets, and in principle, cannot be processed following synthesis. Above the  $T_g$ s of both xP1 and xP2, however, IPN become rubbery and deformable. This deformability is advantageous in LIPN, enabling the IPN latex particles to be processed using standard thermoplastic techniques and equipment (e.g., compression molding, injection molding) [48,82,104]. The deformable LIPN particles can "flow" via plug flow, motion that can maintain the individual identities of the crosslinked particles. The macromolecules at the surfaces of neighbouring particles can entangle and form phase-separated inter-particle domains during plug flow, as illustrated schematically in Fig. 5. The high- $T_g$  phase-separated inter-particle domains can then become glassy physical crosslinks upon cooling, binding the crosslinked particles together and generating a strength-forming mechanism. The particle nature of LIPN adds processability and re-processability to the advantageous properties available from IPN systems. A processable LIPN in which the low- $T_g$  polymer is dominant is the equivalent of a thermoplastic elastomer, while a processable LIPN in which the high- $T_g$  polymer is dominant is the equivalent of a high-impact thermoplastic.

## 6. IPN-templated porous polymers: Less is more

Porous polymers are produced by generating empty volumes within the polymer and then fixing them in place [105–109]. The approaches used to produce porous polymers include macromolecular design, self-assembly, phase separation, templating (solid and liquid), sol-gel formation, and foaming. Many of these approaches use the formation of networks to fix the polymer around a volume that is either filled with a gas or filled with a removable porogen. As early as 1929, crosslinking was used to entrap air within a rubber latex, producing foam rubber [110]. Staudinger, investigating the copolymerization of styrene and DVB in organic solvents, concluded that the resulting materials were three-dimensional networks containing solvent-filled pores [105,111]. In "On Polymerization", Staudinger also described two techniques now commonly used to produce porous polymers, solvent induced phase separation (SIPS) and non-solvent induced phase separation (NIPS) [1].

Nano-scale porosity has been generated in polymers through the removal of sacrificial porogens in a variety of systems, ranging from block copolymers [107,109,112] to low-k dielectrics [113,114]. Similarly, the IPN and semi-IPN topologies can be used as templates for the formation of porous polymers through a judicious selection of the components. In this scenario, one of the polymers is used as a sacrificial porogen that can be removed using selective degradation and/or selective extraction. To prevent collapse, it is essential that the framework polymer remains rigid and unaffected by the removal of the porogenic polymer. Sperling developed the sacrificial network concept during his investigation of IPN structures. He synthesized seq-IPN containing one network that was crosslinked using DVB and another network that was crosslinked using acrylic anhydride (AAn), a labile crosslinker [115, 116]. Porous structures were generated by removing the AAn-containing network through de-crosslinking (hydrolysis in an NaOH solution) and selective extraction.

Porous polymers can be generated within semi-IPN simply through the selective removal of the linear polymer, since de-crosslinking is not needed. D. Grande, an early proponent of this approach, generated porous polymers through selective solvent extraction of sim-semi-IPN based on polylactide (PLA) and a crosslinked PMMA, investigating the effects of crosslinking and polymer-polymer miscibility [117–119]. In other work, sim-semi-IPN were synthesized by combining the ring opening polymerization (ROP) of  $\epsilon$ -caprolactone with the free radical copolymerization of styrene and DVB [120]. Porous P(S-co-DVB) monoliths were then generated by removing the linear poly( $\epsilon$ -caprolactone) (PCL) through hydrolysis. The porous structure was based on the extent of phase separation, which was modified by varying the relative rates of polymerization through variations in the concentration

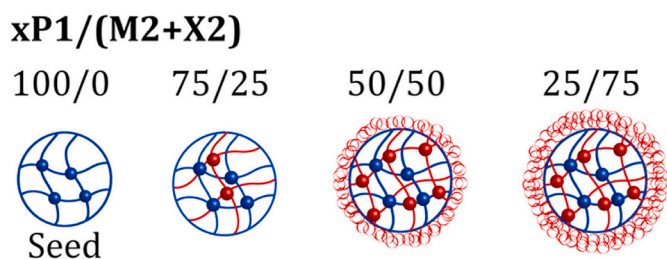


Fig. 4. A schematic illustration of LIPN synthesis showing a seed particle (100/0), an xP1-xP2 IPN particle (75/25), and an xP2 shell around an IPN core (50/50 and 25/75) (after Figure 13 in Ref. [82]).

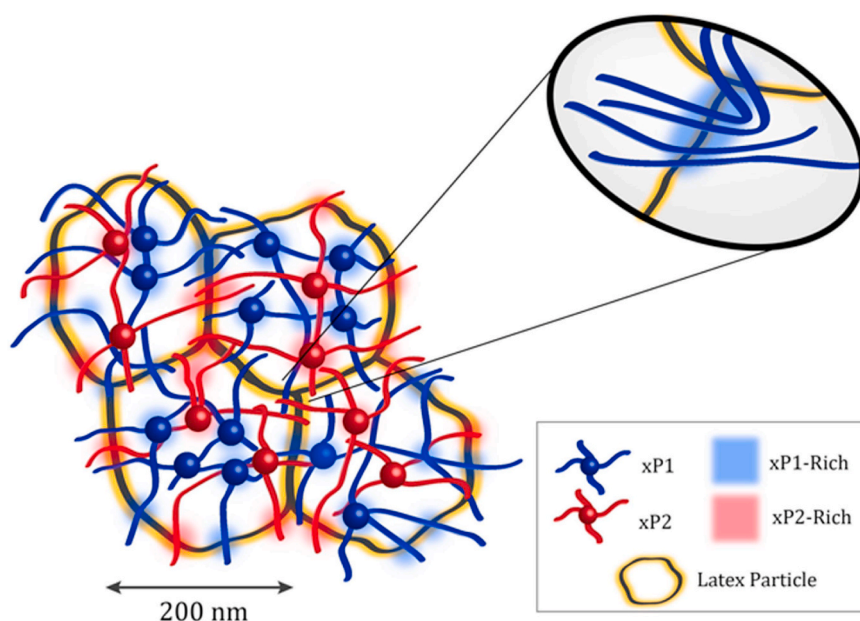


Fig. 5. A schematic illustration of a molded LIPN showing two physically entangled macromolecular networks within the IPN latex particles (highlighted) and indicating the presence of both intra-particle nanodomains and inter-particle strength-forming nanodomains (after Figure 14 in Refs. [82]).

of the ROP catalyst. Pores of around 2  $\mu\text{m}$  were generated when phase separation occurred before gelation, at faster ROP rates (higher catalyst concentrations). Pores of around 50 nm and a significant increase in specific surface area were generated when gelation occurred before phase separation, at slower ROP rates (lower catalyst concentrations). The porous structures generated from IPN and semi-IPN can, therefore, be fine-tuned by modifying the polymerization sequence, the relative polymerization rates, the polymer-polymer miscibility, the composition, and the degree(s) of crosslinking, all of which influence the extent of phase separation [121,122].

Selective electron beam degradation has also been used to generate porous polymers from multiple network systems based on dissolving a low density polyethylene (PE) in a solution of methacrylates [123–125]. The radical polymerization and crosslinking of the methacrylates at a lower temperature was followed by the radical crosslinking of the PE at a higher-temperature. This combination of radical reactions also produced some covalent links between the two networks, generating ICN rather than IPN. Under electron beam irradiation, the PMA underwent degradation, while the PE underwent crosslinking. Porous, crosslinked PE membranes were produced by extracting the degraded PMA. Here, again, the porous structure was templated by the phase-separated structure produced by the thermodynamic drive to phase separate, on one hand, and by the kinetic ability to do so, on the other.

## 7. Double networks: Re-booting IPN

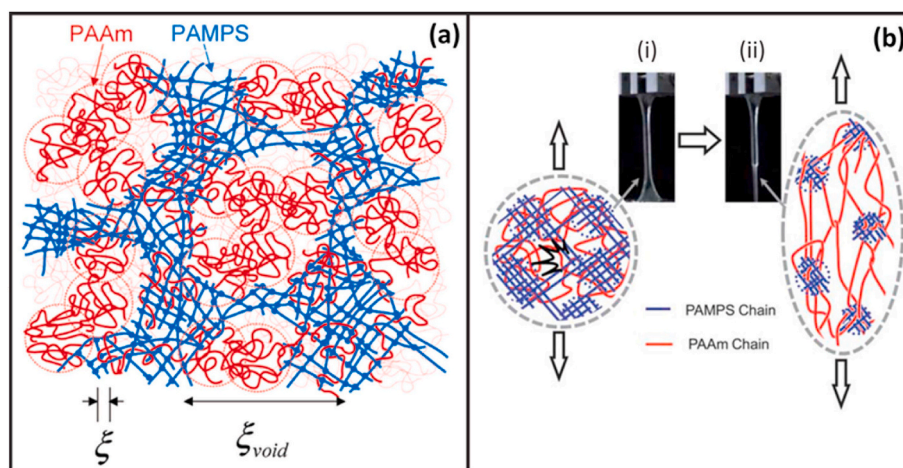
Hydrogels are water-swollen networks of hydrophilic polymers that are either crosslinked through reversible physical bonds (e.g. hydrogen bonds or hydrophobic interactions) or through permanent covalent bonds. In the 1960s, hydrogels were developed as polymer systems for biomedical applications such as contact lenses. The high water content in hydrogels was expected to produce more favourable interactions with living tissues than were produced by the standard hydrophobic polymers being investigated at the time [126]. The pervasive uses of hydrogels today include applications for hygiene, cosmetics, contact lenses, drug delivery, agriculture, food, wound care, and tissue engineering. Most of the work on IPN and semi-IPN described previously involves hydrophobic polymers. The formation of IPN within hydrogels, therefore, will involve polymers that were usually not included in IPN research (e.g. non-ionic water-soluble polymers and polyelectrolytes

(anionic, cationic, zwitterionic)). Hydrogel IPN will also involve polymer-water interactions and polymer-polymer interactions that can produce novel macromolecular architectures and properties.

While hydrogels have exhibited great promise for a wide variety of biomedical applications [127–133], there are still certain practical limitations on their use. Hydrogels are usually friable (easily crumbled) due to their relatively high water contents, limiting their use in applications that require the ability to bear loads and deformations without failing [134,135]. The need for robust hydrogels has inspired research on hydrogel systems that involve complex load-bearing and deformation mechanisms [136]. These systems include nanocomposite hydrogels [135,137–143], hydrogels with complex macromolecular architectures (slide-ring hydrogels [144], hydrogel IPN and semi-IPN [8,9,145–152], highly porous hydrogels [153–159], and combinations thereof [160–162].

Gong's development of double network (DN) hydrogels have brought the macromolecular topologies that result from combining two hydrogel networks to the forefront of cutting-edge polymer research and development. The original DN hydrogels combined a highly crosslinked polyelectrolyte (poly(2-acrylamido-2-methylpropanesulfonic acid), PAMPS) as the first network with a lightly crosslinked uncharged polymer (polyacrylamide, PAAm) as the second network, where the molar ratio of the second network to first network was ten or more [69–74,163]. This specific method of combining two hydrophilic polymers produced hydrogels containing 60–90% water that had fracture strengths higher than 10 MPa and high wear resistances [69]. DN synthesis is, for the most part, sequential, with xP1 swollen in an aqueous solution of M2 and X2, which are then polymerized. The macromolecular architecture of a representative DN system with a PAMPS network as the first polymer and a linear PAAm as the second polymer is illustrated schematically in Fig. 6a [73]. The PAMPS network has a mesh size ( $\xi$ ) of several nanometres and large “voids” whose size ( $\xi_{\text{void}}$ ) is much larger than  $\xi$ . The PAAm, entangled with the PAMPS network, is largely found in PAAm-rich “crack-stopping” domains that are formed within the voids that exist in the PAMPS network.

This specific method of combining two hydrogels produced exceptional improvements in mechanical strength compared to the two component hydrogels. The enhancement in mechanical properties results from the ability of the second network to prevent the crack growth that can lead to catastrophic failure. As seen for IPN, both entrapped



**Fig. 6.** Schematic illustration of a representative DN: (a) macromolecular architecture (Reproduced with permission from Ref. [73], copyright 2005, American Chemical Society); (b) the effect of deformation on the macromolecular architecture (i) before necking and (ii) after necking (Reproduced with permission from Refs. [164], copyright 2010, Royal Society of Chemistry).

molecular-level mixing and phase separation play important roles. Here, the formation of phase-separated xP2-rich domains is promoted by the existence of local volumes with low polymer densities in the inhomogeneous xP1 network structure. While the DN hydrogels originally consisted of two covalently crosslinked networks, a number of variations have been investigated including DN with hydrogen bonding and supramolecular crosslinking that can be used to effect self-healing [165–170], DN with ionic coordination crosslinking [171], DN with strong hydrophobic interactions [172], and DN with physical crosslinking [173,174]. Variations on the basic DN structure include systems with a single network that is combined with a linear polymer and systems where both polymers are linear and semicrystalline, with the polymer crystals acting as physical crosslinks [175].

Several models have been used to explain the toughness of DN including a mechanism of local yielding and hardening during deformation, a mechanism of energy dissipation by xP2 that has a shielding effect and keeps the DN from failing, and a mechanism whereby fractured clusters of the relatively brittle xP1, formed during deformation, act as sliding crosslinks for the more deformable xP2 [136,145,164]. The expected changes in the macromolecular architectures of DN hydrogels upon deformation are illustrated schematically in Fig. 6b [164]. In Fig. 6b(i), below the critical stress, the structure is as described in Fig. 6a. Above the critical stress, in Fig. 6b(ii), the relatively brittle PAMPS fractures and forms clusters that behave as sliding crosslinks for the more deformable PAAm and the hydrogel becomes softer.

Gong has recently extended the hydrogel-toughening DN concept to hydrophobic elastomers [176] by generating a hydrophilic-hydrophobic hybrid DN combining a brittle, hydrophilic polyelectrolyte network with a stretchable, hydrophobic polyacrylate network. The synthesis procedure included polymerizing water-soluble monomers in an aqueous solution to generate a polyelectrolyte network, incorporating acrylates through a series of solvent exchanges, polymerizing the acrylates, and solvent removal. The significant enhancement in elastomer toughness was ascribed to energy-dissipative polyelectrolyte chain-scission during deformation. The development, structures, properties, and applications of DN hydrogels have been described in a number of recent reviews [13, 72,131,133–136,145,164,177]. J. Zheng's list of some emerging DN frontiers includes peptide polymers, triple networks, physical bonding, dynamic covalent bonding, adapting the sacrificial network concept to other polymer systems, and additive manufacturing [13].

## 8. Applications: Two are better than one

The applicative adoption of polymers that are combined through IPN

formation continually renews itself with the advances in polymer science and engineering, offering routes to “tune” the properties of novel polymers of interest through combinations with other polymers that offer synergistic advantages. Many of the applications originally associated with IPN were focused upon their damping behavior and their enhanced mechanical properties [10]. There is now an increasing interest in IPN for novel and niche biomedical applications where an “established” material is lacking. Under such circumstances, the added value of the IPN material can outweigh the additional costs associated with the more complex materials system. IPN have been applied as films for burn healing with advantageous transport properties and as soft contact lenses with advantageous refractive index gradients [10]. DN hydrogels have also been applied for a variety of biomedical applications [8,9,132,178].

Advances in polymer synthesis chemistries and in macromolecular structures are often rapidly adopted into novel IPN systems for previously unforeseen applications, taking advantage of novel polymers with properties that were previously inaccessible (e.g., conductivity, semiconductivity, and luminescence) and combining them with polymers having orthogonal properties [10]. Thus, IPN formation enables leveraging the properties of interest in one polymer into systems that can provide applicative advantages. In stretchable electronics, the IPN architecture was used to provide a combination of extensibility and compatibility with the conductive moiety [179,180]. The formation of IPN actuators based on electromechanical polymers and highly elastic polymers was used to support pre-strain and eliminate external supporting structures [181,182]. Sequential IPN of amorphous polymers and crosslinked liquid-crystalline polymer networks were used to control the mechanical and photo-responsive properties, yielding soft actuator films with a homogeneous alignment of mesogens [183]. IPN and semi-IPN are being applied as fuel cells membranes with advantageous proton conductivities, methanol permeabilities, and stabilities. IPN systems have combined a linear conductive polyelectrolyte with a hydrophilic matrix to entrap a hydrophobic fluorinated linear polymer within a conductive polyelectrolyte network, to combine a hydrophobic fluorinated polymer network with a conductive polyelectrolyte network, and to combine a linear conductive polyelectrolyte with a more hydrophobic polymer in a hydrophilic-hydrophobic hybrid IPN [7]. Hydrophilic-hydrophobic hybrid IPN and semi-IPN have also been investigated as solid anion-exchange membranes for positive air electrodes in energy conversion and storage systems [184,185]. Hydrophilic-hydrophobic hybrid IPN can also be generated by synthesizing hydrophobic IPN containing a polymer that can be rendered hydrophilic through subsequent modification (e.g., the hydrolysis of poly



(*t*-butyl acrylate) to poly(acrylic acid)) [64,186].

## 9. IPN update: Back to the future

Recent IPN research often involves investigating innovative and cutting-edge polymer systems for advanced applications using experimental frameworks that are similar to those originally developed during the pioneering work on IPN. For the most part, recent research continues to include a focus on synthesis and the development of novel monomers, reaction mechanisms, interpenetration routes, and crosslinking strategies. Interestingly, a relatively large percentage of recent publications seems to involve hydrogels, both synthetic and natural, and also seems to involve bio-related applications. The types of systems investigated now include hydrophobic, hydrogel, hydrophilic-hydrophobic hybrids, and organic-inorganic hybrids. Some research focuses on understanding the macromolecular topology and its implications, combining experimental work with computer modelling. The overwhelming majority of research, however, emphasizes applications. Recent investigations are not only driven by the enhancement in mechanical properties, but are also driven by the new challenges associated with energy-related applications, 3D printing, separation processes, and “high tech” applications (e.g., sensors, actuators). A brief description of a limited selection of recent IPN papers, loosely arranged into topics, is included below. These papers, reflecting the state of the current challenges, the novel polymers developed, and the innovative synthesis strategies introduced, will serve to inspire future work.

### 9.1. IPN structure and behavior

Hydrogel IPN, with both networks based on poly(sodium acrylate), were swollen in salt solutions to investigate the effects of topology on the macromolecular mobility in water and on the partitioning of salt [187]. Low crystallinity hydroxyapatite was used to provide energy-dissipative sacrificial bonds to toughen DN hydrogels that were based on a fully pre-stretched, densely crosslinked, rigid, brittle polyelectrolyte and a loosely cross-linked, soft, stretchable neutral polymer [188].

### 9.2. Bio-related IPN

A one-pot, biodegradable, thermoresponsive shape memory semi-IPN for tissue engineering was generated by combining a crosslinked PCL diacrylate with either PLA or a poly(lactide-*co*-glycolide) [189]. Sim-IPN fillers generated *in-situ* for corneal defects were based on collagen (azide-alkyne cycloaddition crosslinking) and hyaluronic acid (thiol-ene Michael click crosslinking) [190]. An injectable, one-pot IPN used for *in-situ* tissue regeneration was based on peptide self-assembly and on chitosan (covalently crosslinked using a *N*-hydroxysuccinimide-terminated poly(ethylene glycol) (PEG)) [191]. An artificial ionic skin with multimodal sensation, high toughness, stretchability, and ambient stability and transparency was produced by assembling two DN, each combining a physically crosslinked agarose, a covalently crosslinked PAAm, and one of two oppositely charged polyelectrolytes [192]. Cartilage mimics based on a porous PCL framework were generated by 3D printing hydrogel sim-IPN that combined alginate (CaCl<sub>2</sub> crosslinking) and gelatin methacryloyl (photoinitiated crosslinking) [193].

### 9.3. Responsive IPN

A temperature-switchable, light-scattering-based, bright whiteness was generated in IPN that combined agarose (physically crosslinked, then subsequently removed) and a chemically crosslinked thermoresponsive poly(*N*-isopropylacrylamide) (PNiPAAm) [194]. On-demand-release drug carriers with thermal and pH responsiveness were generated in bicontinuous microemulsions by polymerizing and crosslinking an acrylate in the organic phase while simultaneously

polymerizing a hydrophilic monomer in the aqueous phase, swelling the resulting multiphase polymer in a second hydrophilic monomer, and then polymerizing and crosslinking the second monomer [195]. Photoswitchable sol-gel transitions and catalysis were generated by combining a reversible supramolecular PEG network (linked by metal-organic cages) and a covalently crosslinked PEG network [33]. Thermoresponsive shape-memory seq-IPN hydrogels were generated by polymerizing and crosslinking acrylamide in a solution containing an elastin-like polypeptide whose physical crosslinking was reversible [196].

### 9.4. Energy and “high tech” applications

The mechanical durability of the donor-acceptor active layer in organic photovoltaic devices was enhanced by the *in-situ* photoinitiated thiol-ene generation of semi-IPN based on multi-functional acrylates [197]. Semi-IPN hydrogels with high conductivities for solid-state zinc-air batteries were synthesized by combining a covalently crosslinked polyelectrolyte with an alkaline solution of methyl cellulose [198]. Seq-IPN proton exchange fuel cell membranes with enhanced conductivities and selectivities were generated by crosslinking sulfonated poly(vinyl alcohol) in the presence of a PAMPS network [199]. The color activation in a mechanochromic polymer was enhanced by generating a tough DN combining a mechanochromic polyacrylate network and a (non-mechanochromic) polyacrylate network [200].

## 10. Perspective: United we stand

The IPN family occupies a niche within the wide range of macromolecular topologies that are available for generating multi-polymer systems with synergistic properties. Unlike the copolymer systems (blocks, grafts, stars, and brushes) that combine individual polymers using covalent bonds, the individual polymers in IPN are physically entwined but not covalently linked. Unlike polymer blends, in which immiscible polymers can undergo extensive phase separation, the incompatible polymers in IPN are unable to undergo extensive phase separation. Initially, IPN applications were focused on the extraordinary damping properties that originated in the broad range of phase-separated domain compositions. More recently, IPN were applied to synergistically combine polymers with very different, often orthogonal, properties (for example, hydrophilic-hydrophobic hybrid IPN) and to form mechanically robust hydrogels and elastomers. In addition, porous polymers can be generated from IPN and semi-IPN containing a polymeric porogen by using the kinetically-limited phase-separated structure as a template.

The macromolecular architectures in IPN can be varied extensively through variations in the multiplicity of synthesis parameters that are involved. These parameters include the polymerization sequence, the polymerization rates, the polymer compatibility, the polymerization mechanisms, the polymer ratio, and the extents of crosslinking. These parameters affect the macromolecular topology through their effects on the network homogeneity, the entrapped molecular-level mixing, and the extent of phase separation. In LIPN, the monomer and polymer hydrophilicities also play an important role and the generation of nanoscale latex particles enables processing and re-processing using standard thermoplastic techniques and equipment.

The macromolecular topologies associated with the combination of two polymers through the formation of IPN, semi-IPN, and ICN are, in many ways, ubiquitous. As Sperling noted in 1981, the widespread use of these macromolecular topologies may not even be recognized as such by those concerned in their development. These interpenetrating topologies do, however, play an important role in producing synergistic properties and their significance should not be underestimated. One recent example is the exceptional augmentation in hydrogel mechanical properties achieved through the formation of DN. The wide gamut of macromolecular topological options described herein will serve as a



guide to the realization of synergistic behaviors attainable by combining polymers in IPN-like structures.

### Declaration of competing interest

The author declares that he has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### References

- [1] H. Staudinger, Über polymerisation, *Ber. Dtsch. Chem. Ges.* 53 (6) (1920) 1073–1085.
- [2] H. Frey, T. Johann, Celebrating 100 years of “polymer science”: Hermann Staudinger’s 1920 manifesto, *Polym. Chem.* 11 (1) (2020) 8–14.
- [3] H. Staudinger, J. Fritsch, Über Isopren und Kautschuk. 5. Mitteilung. Über die Hydrierung des Kautschuks und über seine Konstitution, *Helv. Chim. Acta* 5 (5) (1922) 785–806.
- [4] H. Staudinger, W. Heuer, Über hochpolymere Verbindungen, 94. Mitteil.: Über ein unlösliches Poly-styrol, *Ber. Dtsch. Chem. Ges.* 67 (7) (1934) 1164–1172.
- [5] L.H. Sperling, *Interpenetrating Polymer Networks and Related Material*, Plenum, New York, 1981.
- [6] L.H. Sperling, *Interpenetrating Polymer Networks*, Encyclopedia of Polymer Science and Technology, John Wiley and Sons, 2004, pp. 272–311.
- [7] L. Chikh, V. Delhorbe, O. Fichet, (Semi-)Interpenetrating polymer networks as fuel cell membranes, *J. Membr. Sci.* 368 (1) (2011) 1–17.
- [8] P. Matricardi, C. Di Meo, T. Coviello, W.E. Hennink, F. Alhaique, Interpenetrating Polymer Networks polysaccharide hydrogels for drug delivery and tissue engineering, *Adv. Drug Deliv. Rev.* 65 (9) (2013) 1172–1187.
- [9] E.S. Dragan, Design and applications of interpenetrating polymer network hydrogels. A review, *Chem. Eng. J.* 243 (2014) 572–590.
- [10] L.H. Sperling, R. Hu, Interpenetrating polymer networks, in: L. Utracki, C. Wilkie (Eds.), *Polymer Blends Handbook*, Springer, Dordrecht, 2014, pp. 677–724.
- [11] C.M. Roland, Interpenetrating polymer networks (IPN): structure and mechanical behavior, in: S. Kobayashi, K. Müllen (Eds.), *Encyclopedia of Polymeric Nanomaterials*, Springer Berlin Heidelberg, Berlin, Heidelberg, 2015, pp. 1004–1011.
- [12] E.S. Dragan, Advances in interpenetrating polymer network hydrogels and their applications, *Pure Appl. Chem.* 86 (11) (2014) 1707.
- [13] Q. Chen, H. Chen, L. Zhu, J. Zheng, Engineering of tough double network hydrogels, *Macromol. Chem. Phys.* 217 (9) (2016) 1022–1036.
- [14] G. Odian, *Principles of Polymerization*, John Wiley & Sons, New York, NY, 2004, pp. 464–543.
- [15] S.L. Rosen, *Fundamental Principles of Polymer Materials*, John Wiley & Sons, New York, NY, 1993, pp. 200–213.
- [16] A. Rudin, *The Elements of Polymer Science and Engineering*, Academic Press, Orlando, FL, 1982, pp. 262–302.
- [17] K. Matyjaszewski, Advanced materials by atom transfer radical polymerization, *Adv. Mater.* 30 (23) (2018) 1706441.
- [18] H. Gao, K. Matyjaszewski, Synthesis of functional polymers with controlled architecture by CRP of monomers in the presence of cross-linkers: from stars to gels, *Prog. Polym. Sci.* 34 (4) (2009) 317–350.
- [19] M.L. Coote, T.P. Davis, The mechanism of the propagation step in free-radical copolymerisation, *Prog. Polym. Sci.* 24 (9) (1999) 1217–1251.
- [20] B.B. Noble, M.L. Coote, First principles modelling of free-radical polymerisation kinetics, *Int. Rev. Phys. Chem.* 32 (3) (2013) 467–513.
- [21] Y. Gu, J. Zhao, J.A. Johnson, Polymer networks: from plastics and gels to porous frameworks, *Angew. Chem. Int. Ed.* 59 (13) (2020) 5022–5049.
- [22] J.P. Wang, R. Wang, Y.W. Gu, A. Sourakov, B.D. Olsen, J.A. Johnson, Counting loops in sidechain-crosslinked polymers from elastic solids to single-chain nanoparticles, *Chem. Sci.* 10 (20) (2019) 5332–5337.
- [23] T.-S. Lin, R. Wang, J.A. Johnson, B.D. Olsen, Revisiting the elasticity theory for real Gaussian phantom networks, *Macromolecules* 52 (4) (2019) 1685–1694.
- [24] P. Tan, *Interpenetrating Polymer Networks from Castor Oil Polyurethane and Vinyl Copolymers*, Interpenetrating Polymer Networks, American Chemical Society, 1994, pp. 595–614.
- [25] H.-Q. Xie, J.-S. Guo, G.-G. Wang, Properties of two kinds of room temperature cured interpenetrating polymer networks based on castor oil polyurethane, *Eur. Polym. J.* 29 (12) (1993) 1547–1551.
- [26] N. Devia, J.A. Manson, L.H. Sperling, A. Conde, Simultaneous interpenetrating networks based on castor oil elastomers and polystyrene. 2. Synthesis and systems characteristics, *Macromolecules* 12 (3) (1979) 360–369.
- [27] N. Devia-Manjarres, J.A. Manson, L.H. Sperling, A. Conde, Simultaneous interpenetrating networks based on castor oil polyesters and polystyrene, *Polym. Eng. Sci.* 18 (3) (1978) 200–203.
- [28] M. Kurisawa, M. Terano, N. Yui, Doublestimuli-responsive degradable hydrogels for drug delivery: interpenetrating polymer networks composed of oligopeptide-terminated poly(ethylene glycol) and dextran, *Macromol. Rapid Commun.* 16 (9) (1995) 663–666.
- [29] M. Kamath, J. Kincaid, B.K. Mandal, Interpenetrating polymer networks of photocrosslinkable cellulose derivatives, *J. Appl. Polym. Sci.* 59 (1) (1996) 45–50.
- [30] P. Giusti, L. Callegaro, Biomaterial Comprising Hyaluronic Acid and Derivatives Thereof in Interpenetrating Polymer Networks (IPN), US Patent 5,644,049, 1997.
- [31] C.W. Peak, S. Nagar, R.D. Watts, G. Schmidt, Robust and degradable hydrogels from poly(ethylene glycol) and semi-interpenetrating collagen, *Macromolecules* 47 (18) (2014) 6408–6417.
- [32] B.K. Chan, C.C. Wippich, C.-J. Wu, P.M. Sivasankar, G. Schmidt, Robust and semi-interpenetrating hydrogels from poly(ethylene glycol) and collagen for elastomeric tissue scaffolds, *Macromol. Biosci.* 12 (11) (2012) 1490–1501.
- [33] N.J. Oldenhuis, K.P. Qin, S. Wang, H.-Z. Ye, E.A. Alt, A.P. Willard, T. Van Voorhis, S.L. Craig, J.A. Johnson, Photoswitchable sol–gel transitions and catalysis mediated by polymer networks with coumarin-decorated Cu<sub>24</sub>L<sub>24</sub> metal–organic cages as junctions, *Angew. Chem. Int. Ed.* 59 (7) (2020) 2784–2792.
- [34] H. Tai, A. Sergienko, M.S. Silverstein, Organic-inorganic networks in foams from high internal phase emulsion polymerizations, *Polymer* 42 (10) (2001) 4473–4482.
- [35] A. Slusznay, M.S. Silverstein, S. Kababya, A. Schmidt, M. Narkis, Novel semi-IPN through vinyl silane polymerization and crosslinking within PVC films, *J. Polym. Sci., Part A: Polym. Chem.* 39 (1) (2001) 8–22.
- [36] M.S. Silverstein, H.W. Tai, A. Sergienko, Y.L. Lumelsky, S. Pavlovsky, PolyHIPE: IPNs, hybrids, nanoscale porosity, silica monoliths and ICP-based sensors, *Polymer* 46 (17) (2005) 6682–6694.
- [37] J. Normatov, M.S. Silverstein, Silsesquioxane-cross-linked porous nanocomposites synthesized within high internal phase emulsions, *Macromolecules* 40 (23) (2007) 8329–8335.
- [38] J. Normatov, M.S. Silverstein, Porous interpenetrating network hybrids synthesized within high internal phase emulsions, *Polymer* 48 (22) (2007) 6648–6655.
- [39] J. Normatov, M.S. Silverstein, Highly porous elastomer-silsesquioxane nanocomposites synthesized within high internal phase emulsions, *J. Polym. Sci., Part A: Polym. Chem.* 46 (7) (2008) 2357–2366.
- [40] J. Normatov, M.S. Silverstein, Interconnected silsesquioxane-organic networks in porous nanocomposites synthesized within high internal phase emulsions, *Chem. Mater.* 20 (4) (2008) 1571–1577.
- [41] Y.S. Lipatov, T.T. Alekseeva, Phase-separated interpenetrating polymer networks, *Adv. Polym. Sci.* 208 (2007) 1–227.
- [42] L.H. Sperling, Recent developments in interpenetrating polymer networks and related materials, in: D.R. Paul, L.H. Sperling (Eds.), *Multicomponent Polymer Materials*, American Chemical Society, Washington, DC, 1985, pp. 21–56.
- [43] T.G. Fox Jr., P.J. Flory, Second-order transition temperatures and related properties of polystyrene. I. Influence of molecular weight, *J. Appl. Phys.* 21 (6) (1950) 581–591.
- [44] E. Ducrot, H. Montes, C. Creton, Structure of tough multiple network elastomers by small angle neutron scattering, *Macromolecules* 48 (21) (2015) 7945–7952.
- [45] P. Millereau, E. Ducrot, J.M. Clough, M.E. Wiseman, H.R. Brown, R.P. Sijbesma, C. Creton, Mechanics of elastomeric molecular composites, *Proc. Natl. Acad. Sci. Unit. States Am.* 115 (37) (2018) 9110.
- [46] M. Bacca, C. Creton, R.M. McMeeking, A model for the mullins effect in multinet network elastomers, *J. Appl. Mech.* 84 (12) (2017).
- [47] E. Ducrot, C. Creton, Characterizing large strain elasticity of brittle elastomeric networks by embedding them in a soft extensible matrix, *Adv. Funct. Mater.* 26 (15) (2016) 2482–2492.
- [48] M.S. Silverstein, M. Narkis, Elastomeric latex domain-interpenetrating polymer networks - physical and rheological properties, *Polym. Eng. Sci.* 29 (12) (1989) 824–834.
- [49] L.H. Sperling, Interpenetrating polymer networks: an overview, in: D. Klempner, L.H. Sperling, L.A. Utracki (Eds.), *Interpenetrating Polymer Networks*, American Chemical Society, Washington, DC, 1994, pp. 3–38.
- [50] L.H. Sperling, History of interpenetrating polymer networks starting with bakelite-based compositions, in: E.T. Strom, S.C. Rasmussen (Eds.), *100+ Years of Plastics. Leo Baekeland and beyond*, American Chemical Society, 2011, pp. 69–82.
- [51] J.W. Aylsworth, *Plastic Composition*, 1914. US1111284A, United States.
- [52] J.J.P. Staudinger, H.M. Hutchinson, Process for the Production of Strain-free Masses from Crosslinked Styrene-type Polymers, 1951. US2539377A, United States.
- [53] G.S. Solt, Improvements Relating to the Production of Ion-Exchange Resins, 1955. GB728508A, United Kingdom.
- [54] J.R. Millar, 263. Interpenetrating polymer networks. Styrene-divinylbenzene copolymers with two and three interpenetrating networks, and their sulphonates, *J. Chem. Soc.* (1960) 1311–1317.
- [55] H.L. Frisch, D. Klempner, K.C. Frisch, A topologically interpenetrating elastomeric network, *J. Polym. Sci. B Polym. Lett.* 7 (11) (1969) 775–779.
- [56] K. Shibayama, Y. Suzuki, Viscoelastic properties of multiple network polymers. IV. Copolymers of styrene and divinylbenzene, *Rubber Chem. Technol.* 40 (2) (1967) 476–483.

- [57] Y.S. Lipatov, L.M. Sergeeva, Synthesis and properties of interpenetrating networks, *Russ. Chem. Rev.* 45 (1) (1976) 63–74.
- [58] E.S. Dragan, A.I. Cocarta, Smart macroporous IPN hydrogels responsive to pH, temperature, and ionic strength: synthesis, characterization, and evaluation of controlled release of drugs, *ACS Appl. Mater. Interfaces* 8 (19) (2016) 12018–12030.
- [59] E.S. Dragan, A.I. Cocarta, M. Gierszewska, Designing novel macroporous composite hydrogels based on methacrylic acid copolymers and chitosan and in vitro assessment of lysozyme controlled delivery, *Colloids Surf. B Biointerfaces* 139 (2016) 33–41.
- [60] E.S. Dragan, M.M. Lazar, M.V. Dinu, F. Doroftei, Macroporous composite IPN hydrogels based on poly(acrylamide) and chitosan with tuned swelling and sorption of cationic dyes, *Chem. Eng. J.* 204–206 (2012) 198–209.
- [61] M.V. Dinu, M.M. Perju, E.S. Dragan, Porous semi-interpenetrating hydrogel networks based on dextran and polyacrylamide with superfast responsiveness, *Macromol. Chem. Phys.* 212 (3) (2011) 240–251.
- [62] H. Tai, A. Sergienko, M.S. Silverstein, High, internal phase emulsion foams: copolymers, and interpenetrating polymer networks, *Polym. Eng. Sci.* 41 (9) (2001) 1540–1552.
- [63] Y. Lumelsky, J. Zoldan, S. Levenberg, M.S. Silverstein, Porous polycaprolactone-polystyrene semi-interpenetrating polymer networks synthesized within high internal phase emulsions, *Macromolecules* 41 (4) (2008) 1469–1474.
- [64] Y. Lumelsky, I. Lalush-Michael, S. Levenberg, M.S. Silverstein, A degradable, porous, emulsion-templated polyacrylate, *J. Polym. Sci., Part A: Polym. Chem.* 47 (24) (2009) 7043–7053.
- [65] Y. Lumelsky, M.S. Silverstein, Biodegradable porous polymers through emulsion templating, *Macromolecules* 42 (5) (2009) 1627–1633.
- [66] P.H. Mott, C.M. Roland, Mechanical and optical behavior of double network rubbers, *Macromolecules* 33 (11) (2000) 4132–4137.
- [67] J. Wang, G.R. Hamed, K. Umetsu, C.M. Roland, The payne effect in double network elastomers, *Rubber Chem. Technol.* 78 (1) (2005) 76–83.
- [68] P.G. Santangelo, C.M. Roland, Role of strain crystallization in the fatigue resistance of double network elastomers, *Rubber Chem. Technol.* 76 (4) (2003) 892–898.
- [69] J.P. Gong, Y. Katsuyama, T. Kurokawa, Y. Osada, Double-network hydrogels with extremely high mechanical strength, *Adv. Mater.* 15 (14) (2003) 1155–1158.
- [70] Y.-H. Na, T. Kurokawa, Y. Katsuyama, H. Tsukeshiba, J.P. Gong, Y. Osada, S. Okabe, T. Karino, M. Shibayama, Structural characteristics of double network gels with extremely high mechanical strength, *Macromolecules* 37 (14) (2004) 5370–5374.
- [71] A. Nakayama, A. Kakugo, J.P. Gong, Y. Osada, M. Takai, T. Erata, S. Kawano, High mechanical strength double-network hydrogel with bacterial cellulose, *Adv. Funct. Mater.* 14 (11) (2004) 1124–1128.
- [72] Y. Tanaka, J.P. Gong, Y. Osada, Novel hydrogels with excellent mechanical performance, *Prog. Polym. Sci.* 30 (1) (2005) 1–9.
- [73] H. Tsukeshiba, M. Huang, Y.-H. Na, T. Kurokawa, R. Kuwabara, Y. Tanaka, H. Furukawa, Y. Osada, J.P. Gong, Effect of polymer entanglement on the toughening of double network hydrogels, *J. Phys. Chem. B* 109 (34) (2005) 16304–16309.
- [74] K. Yasuda, J. Ping Gong, Y. Katsuyama, A. Nakayama, Y. Tanabe, E. Kondo, M. Ueno, Y. Osada, Biomechanical properties of high-toughness double network hydrogels, *Biomaterials* 26 (21) (2005) 4468–4475.
- [75] L.H. Sperling, T.-W. Chiu, C.P. Hartman, D.A. Thomas, Latex interpenetrating polymer networks, *Int. J. Polym. Mater. Polym. Biomater.* 1 (4) (1972) 331–341.
- [76] L.H. Sperling, T.W. Chiu, D.A. Thomas, Glass transition behavior of latex interpenetrating polymer networks based on methacrylic/acrylic pairs, *J. Appl. Polym. Sci.* 17 (8) (1973) 2443–2455.
- [77] L.H. Sperling, D.A. Thomas, J.E. Lorenz, E.J. Nagel, Synthesis and behavior of polyvinyl chloride based latex interpenetrating polymer networks, *J. Appl. Polym. Sci.* 19 (8) (1975) 2225–2233.
- [78] J. Sionakidis, L.H. Sperling, D.A. Thomas, Morphology and mechanical-behavior of poly(vinyl chloride)-poly(butadiene-co-acrylonitrile) latex interpenetrating polymer networks, *J. Appl. Polym. Sci.* 24 (5) (1979) 1179–1190.
- [79] Y. Talmon, M. Narkis, M. Silverstein, Radiation-damage to latex-particles as an analytical tool in polymer science, *Ultramicroscopy* 14 (4) (1984), 380–380.
- [80] M. Narkis, Y. Talmon, M. Silverstein, Properties and structure of elastomeric 2-stage emulsion interpenetrating networks, *Polymer* 26 (1985) 1359–1364.
- [81] Y. Talmon, M. Narkis, M. Silverstein, Electron-beam radiation-damage to organic inclusions in ice as an analytical tool for polymer science, *J. Electron. Microsc. Tech.* 2 (6) (1985) 589–596.
- [82] M.S. Silverstein, M. Narkis, Elastomeric domain-type interpenetrating polymer networks, *J. Appl. Polym. Sci.* 33 (7) (1987) 2529–2547.
- [83] F.A. Bovey, I.M. Kolthoff, A.I. Medalia, E.J. Meehan, *Emulsion Polymerization*, Interscience, New York, NY, 1955.
- [84] J.L. Gardon, Mechanism of emulsion polymerization, *Rubber Chem. Technol.* 43 (1) (1970) 74–94.
- [85] J.L. Gardon, Evidence for and against concentration gradients in polymerizing latex particles, *J. Polym. Sci. Polym. Chem. Ed.* 11 (1) (1973) 241–251.
- [86] M.R. Grancio, D.J. Williams, The morphology of the monomer–polymer particle in styrene emulsion polymerization, *J. Polym. Sci. Polym. Chem. Ed.* 8 (9) (1970) 2617–2629.
- [87] P. Kusch, D.J. Williams, Equilibrium encapsulation of polystyrene latex particles, *J. Polym. Sci. Polym. Chem. Ed.* 11 (1) (1973) 143–162.
- [88] D.J. Williams, Particle morphology in emulsion polymerization, *J. Polym. Sci. Polym. Chem. Ed.* 11 (1) (1973) 301–303.
- [89] D.J. Williams, Latex particle morphology during polymerization and at saturation equilibrium, *J. Polym. Sci. Polym. Chem. Ed.* 12 (9) (1974) 2123–2132.
- [90] S. Muroi, H. Hashimoto, K. Hosoi, Morphology of core-shell latex particles, *J. Polym. Sci. Polym. Chem. Ed.* 22 (6) (1984) 1365–1372.
- [91] M. Okubo, A. Yamada, T. Matsumoto, Estimation of morphology of composite polymer emulsion particles by the soap titration method, *J. Polym. Sci. Polym. Chem. Ed.* 18 (11) (1980) 3219–3228.
- [92] T.I. Min, A. Klein, M.S. El-Aasser, J.W. Vanderhoff, Morphology and grafting in polybutylacrylate-polystyrene core-shell emulsion polymerization, *J. Polym. Sci. Polym. Chem. Ed.* 21 (10) (1983) 2845–2861.
- [93] M. Okubo, Y. Katsuta, T. Matsumoto, Studies on suspension and emulsion. li. peculiar morphology of composite polymer particles produced by seeded emulsion polymerization, *J. Polym. Sci., Polym. Lett. Ed.* 20 (1) (1982) 45–51.
- [94] I. Cho, K.-W. Lee, Morphology of latex particles formed by poly(methyl methacrylate)-seeded emulsion polymerization of styrene, *J. Appl. Polym. Sci.* 30 (5) (1985) 1903–1926.
- [95] K. Kato, Die elektronenmikroskopischen Darstellungen von ABS-Kunststoffen, *Kolloid-Z. Z. Polym.* 220 (1) (1967) 24–31.
- [96] S.L. Rosen, The physical limits of grafting in two-phase polymerization reactions, *J. Appl. Polym. Sci.* 17 (6) (1973) 1805–1811.
- [97] V.J. Stabenow, F. Haaf, Morphologie von ABS-Pfropfkautschuken, *Die Angewandte Makromolekulare Chemie* 29 (1) (1973) 1–23.
- [98] D.E. Owens, Y. Jian, J.E. Fang, B.V. Slaughter, Y.-H. Chen, N.A. Peppas, Thermally responsive swelling properties of polyacrylamide/poly(acrylic acid) interpenetrating polymer network nanoparticles, *Macromolecules* 40 (20) (2007) 7306–7310.
- [99] M.S. Silverstein, Y. Talmon, M. Narkis, Microstructure of polyacrylate polystyrene 2-stage lattices, *Polymer* 30 (3) (1989) 416–424.
- [100] N. Nemirovski, M.S. Silverstein, M. Narkis, Latex interpenetrating polymer networks: from structure to properties, *Polym. Adv. Technol.* 7 (4) (1996) 247–256.
- [101] H. Hopff, Patent 623,351, Germany, 1935.
- [102] J.A. Grates, D.A. Thomas, E.C. Hickey, L.H. Sperling, Noise and vibration damping with latex interpenetrating polymer networks, *J. Appl. Polym. Sci.* 19 (6) (1975) 1731–1743.
- [103] J.E. Lorenz, D.A. Thomas, L.H. Sperling, Viscoelastic properties of acrylic latex interpenetrating polymer networks as broad temperature span vibration damping materials, *ACS Symp. Ser.* 24 (1976) 306–329.
- [104] M.S. Silverstein, M. Narkis, Capillary extrusion of elastomeric emulsion crosslinked interpenetrating networks, *Polym. Eng. Sci.* 25 (5) (1985) 257–263.
- [105] H.-P. Hentze, M. Antonietti, Porous polymers and resins, in: F. Schiith, K.S. W. Sing, J. Weitkamp (Eds.), *Handbook of Porous Solids*, WILEY-VCH Verlag GmbH, Weinheim, 2008, pp. 1964–2013.
- [106] M.S. Silverstein, N.R. Cameron, M.A. Hillmyer, *Porous Polymers*, John Wiley & Sons, New York, NY, 2011.
- [107] D. Wu, F. Xu, B. Sun, R. Fu, H. He, K. Matyjaszewski, Design and preparation of porous polymers, *Chem. Rev.* 112 (7) (2012) 3959–4015.
- [108] S. Qiu, T. Ben, *Porous Polymers: Design, Synthesis and Applications*, Porous Polymers: Design, Synthesis and Applications, Royal Society of Chemistry, Cambridge, UK, 2016.
- [109] M.S. Silverstein, *The Chemistry of porous polymers: the holey grail*, *Isr. J. Chem.* 60 (1–2) (2020) 140–150.
- [110] W.H. Chapman, D.W. Pounder, E.A. Murphy, E.W.B. Owen, *Manufacture of Goods of Rubber or Similar Material*, BP 332,525, Dunlop Rubber Co, Ltd, Great Britain, 1929.
- [111] H. Staudinger, E. Husemann, Über hochpolymere Verbindungen, 116. Mitteil.: Über das begrenzt quellbare Poly-styrol, *Ber. Dtsch. Chem. Ges.* 68 (8) (1935) 1618–1634.
- [112] E.M. Todd, M.A. Hillmyer, Porous polymers from self-assembled structures, in: M. S. Silverstein, N.R. Cameron, M.A. Hillmyer (Eds.), *Porous Polymers*, John Wiley & Sons, New York, NY, 2011, pp. 31–78.
- [113] M.S. Silverstein, M. Shach-Caplan, B.J. Bauer, R.C. Hedden, H.J. Lee, B.G. Landes, Nanopore formation in a polyphenylene low-k dielectric, *Macromolecules* 38 (10) (2005) 4301–4310.
- [114] M.S. Silverstein, B.J. Bauer, R.C. Hedden, H.J. Lee, B.G. Landes, SANS and XRR porosimetry of a polyphenylene low-k dielectric, *Macromolecules* 39 (8) (2006) 2998–3006.
- [115] J.M. Widmaier, L.H. Sperling, Phase continuity in sequential poly(n-butyl acrylate)/polystyrene interpenetrating polymer networks, *Macromolecules* 15 (2) (1982) 625–631.
- [116] J.-M. Widmaier, L.H. Sperling, The use of labile crosslinker for morphological studies in interpenetrating polymer networks, *Br. Polym. J.* 16 (1) (1984) 46–48.
- [117] G. Rohman, D. Grande, F. Lauprêtre, S. Boileau, P. Guérin, Design of porous polymeric materials from interpenetrating polymer networks (IPNs): poly(dilactide)/poly(methyl methacrylate)-based semi-IPN systems, *Macromolecules* 38 (17) (2005) 7274–7285.
- [118] G. Rohman, F. Lauprêtre, S. Boileau, P. Guérin, D. Grande, Poly(d,l-lactide)/poly(methyl methacrylate) interpenetrating polymer networks: synthesis, characterization, and use as precursors to porous polymeric materials, *Polymer* 48 (24) (2007) 7017–7028.
- [119] T.-X. Lav, B. Carbonnier, M. Guerrouache, D. Grande, Porous polystyrene-based monolithic materials templated by semi-interpenetrating polymer networks for capillary electrochromatography, *Polymer* 51 (25) (2010) 5890–5894.
- [120] P. Uroša, E. Žagar, S. Kovacic, D. Pahovnik, Porous polystyrene monoliths prepared from in situ simultaneous interpenetrating polymer networks:

- modulation of morphology by polymerization kinetics, *Macromolecules* 52 (3) (2019) 819–826.
- [121] D. Grande, Macro-, meso-, and nanoporous systems designed from IPNs, in: S. Thomas, D. Grande, U. Cvelbar, K.V.S.N. Raju, R. Narayan, S.P. Thomas, A. H (Eds.), *Micro- and Nano-structured Interpenetrating Polymer Networks: from Design to Applications*, John Wiley & Sons, New York, NY, 2016, pp. 127–143.
- [122] D. Grande, G. Rohman, Oligoester-derivatized (Semi-)Interpenetrating polymer networks as nanostructured precursors to porous materials with tunable porosity, *Chem. Afr. 2* (2) (2019) 253–265.
- [123] J. Hu, G. Pompe, U. Schulze, J. Pionteck, Synthesis, electron irradiation modification and characterization of polyethylene/poly(butyl methacrylate-co-methyl methacrylate) interpenetrating polymer network, *Polym. Adv. Technol.* 9 (10–11) (1998) 746–751.
- [124] J. Hu, U. Schulze, J. Pionteck, Degradation of interpenetrating polymer networks based on PE and polymethacrylates by electron beam irradiation, *Polymer* 40 (19) (1999) 5279–5284.
- [125] J. Pionteck, J. Hu, U. Schulze, Membrane properties of microporous structures prepared from polyethylene/polymethacrylate IPN, *J. Appl. Polym. Sci.* 89 (7) (2003) 1976–1982.
- [126] O. Wichterle, D. Lím, Hydrophilic gels for biological use, *Nature* 185 (4706) (1960) 117–118.
- [127] D.Y. Ko, U.P. Shinde, B. Yeon, B. Jeong, Recent progress of in situ formed gels for biomedical applications, *Prog. Polym. Sci.* 38 (3–4) (2013) 672–701.
- [128] J.-A. Yang, J. Yeom, B.W. Hwang, A.S. Hoffman, S.K. Hahn, In situ-forming injectable hydrogels for regenerative medicine, *Prog. Polym. Sci.* 39 (12) (2014) 1973–1986.
- [129] E. Caló, V.V. Khutoryanskiy, Biomedical applications of hydrogels: a review of patents and commercial products, *Eur. Polym. J.* 65 (2015) 252–267.
- [130] M.C. Koetting, J.T. Peters, S.D. Steichen, N.A. Peppas, Stimulus-responsive hydrogels: theory, modern advances, and applications, *Mater. Sci. Eng. R Rep.* 93 (2015) 1–49.
- [131] A.M.S. Costa, J.F. Mano, Extremely strong and tough hydrogels as prospective candidates for tissue repair – a review, *Eur. Polym. J.* 72 (2015) 344–364.
- [132] M.S. Salehi Dashtebayaz, M.S. Nourbakhsh, Interpenetrating networks hydrogels based on hyaluronic acid for drug delivery and tissue engineering, *Int. J. Polym. Mater. Polym. Biomater.* 68 (8) (2019) 442–451.
- [133] S.A. Young, H. Riahinezhad, B.G. Amsden, In situ-forming, mechanically resilient hydrogels for cell delivery, *J. Mater. Chem. B* 7 (38) (2019) 5742–5761.
- [134] C. Creton, 50th anniversary perspective: networks and gels: soft but dynamic and tough, *Macromolecules* 50 (21) (2017) 8297–8316.
- [135] M.A. Haq, Y. Su, D. Wang, Mechanical properties of PNIPAM based hydrogels: a review, *Mater. Sci. Eng. C* 70 (2017) 842–855.
- [136] J.A. Johnson, N.J. Turro, J.T. Koberstein, J.E. Mark, Some hydrogels having novel molecular structures, *Prog. Polym. Sci.* 35 (3) (2010) 332–337.
- [137] K. Haraguchi, T. Takehisa, Nanocomposite hydrogels: a unique organic-inorganic network structure with extraordinary mechanical, optical, and swelling/deswelling properties, *Adv. Mater.* 14 (16) (2002) 1120–1124.
- [138] K. Haraguchi, R. Farnworth, A. Ohbayashi, T. Takehisa, Compositional effects on mechanical properties of nanocomposite hydrogels composed of poly(*N,N*-dimethylacrylamide) and clay, *Macromolecules* 36 (15) (2003) 5732–5741.
- [139] K. Haraguchi, H.J. Li, K. Matsuda, T. Takehisa, E. Elliott, Mechanism of forming organic/inorganic network structures during in-situ free-radical polymerization in PNIPAA-clay nanocomposite hydrogels, *Macromolecules* 38 (8) (2005) 3482–3490.
- [140] C.M. Paranhos, B.G. Soares, R.N. Oliveira, L.A. Pessan, Poly(vinyl alcohol)/clay-based nanocomposite hydrogels: swelling behavior and characterization, *Macromol. Mater. Eng.* 292 (5) (2007) 620–626.
- [141] P. Schexnailder, G. Schmidt, Nanocomposite polymer hydrogels, *Colloid Polym. Sci.* 287 (1) (2009) 1–11.
- [142] L. Wu, M. Ohtani, S. Tamesue, Y. Ishida, T. Aida, High water content clay–nanocomposite hydrogels incorporating guanidinium-pendant methacrylamide: tuning of mechanical and swelling properties by supramolecular approach, *J. Polym. Sci., Part A: Polym. Chem.* 52 (6) (2014) 839–847.
- [143] A. Alam, Y. Zhang, H.-C. Kuan, S.-H. Lee, J. Ma, Polymer composite hydrogels containing carbon nanomaterials—morphology and mechanical and functional performance, *Prog. Polym. Sci.* 77 (2018) 1–18.
- [144] Y. Okumura, K. Ito, The polyrotaxane gel: a topological gel by figure-of-eight cross-links, *Adv. Mater.* 13 (7) (2001) 485–487.
- [145] C.W. Peak, J.J. Wilker, G. Schmidt, A review on tough and sticky hydrogels, *Colloid Polym. Sci.* 291 (9) (2013) 2031–2047.
- [146] R. Singhal, K. Gupta, A review: tailor-made hydrogel structures (classifications and synthesis parameters), *Polym. Plast. Technol. Eng.* 55 (1) (2016) 54–70.
- [147] C.A. Schoener, H.N. Hutson, G.K. Fletcher, N.A. Peppas, Amphiphilic interpenetrating networks for the delivery of hydrophobic, low molecular weight therapeutic agents, *Ind. Eng. Chem. Res.* 50 (22) (2011) 12556–12561.
- [148] B.V. Slaughter, A.T. Blanchard, K.F. Maass, N.A. Peppas, Dynamic swelling behavior of interpenetrating polymer networks in response to temperature and pH, *J. Appl. Polym. Sci.* 132 (24) (2015).
- [149] C. Echeverría, N.A. Peppas, C. Mijangos, Novel strategy for the determination of UCST-like microgels network structure: effect on swelling behavior and rheology, *Soft Matter* 8 (2) (2012) 337–346.
- [150] J. Zhang, N.A. Peppas, Synthesis and characterization of pH- and temperature-sensitive poly(methacrylic acid)/poly(*N*-isopropylacrylamide) interpenetrating polymeric networks, *Macromolecules* 33 (1) (2000) 102–107.
- [151] C.A. Schoener, H.N. Hutson, N.A. Peppas, Amphiphilic interpenetrating polymer networks for the oral delivery of chemotherapeutics, *AIChE J.* 59 (5) (2013) 1472–1478.
- [152] L.F. Gudeman, N.A. Peppas, Preparation and characterization of pH-sensitive, interpenetrating networks of poly(vinyl alcohol) and poly(acrylic acid), *J. Appl. Polym. Sci.* 55 (6) (1995) 919–928.
- [153] O. Kulygin, M.S. Silverstein, Porous poly(2-hydroxyethyl methacrylate) hydrogels synthesized within high internal phase emulsions, *Soft Matter* 3 (12) (2007) 1525–1529.
- [154] S. Kovačić, M.S. Silverstein, Superabsorbent, high porosity, PAMPS-based hydrogels through emulsion templating, *Macromol. Rapid Commun.* 37 (22) (2016) 1814–1819.
- [155] M. Ovidia, M.S. Silverstein, High porosity, responsive hydrogel copolymers from emulsion templating, *Polym. Int.* 65 (3) (2016) 280–289.
- [156] S. Kovacic, M.S. Silverstein, Hydrogels through emulsion templating: sequential polymerization and double networks, *Polym. Chem.* 8 (40) (2017) 6319–6328.
- [157] T. Zhang, M.S. Silverstein, Doubly-crosslinked, emulsion-templated hydrogels through reversible metal coordination, *Polymer* 126 (2017) 386–394.
- [158] K.J. France, F. Xu, T. Hoare, Structured macroporous hydrogels: progress, challenges, and opportunities, *Adv. Healthc. Mater.* 7 (1) (2018).
- [159] T. Zhang, M.S. Silverstein, Robust, highly porous hydrogels templated within emulsions stabilized using a reactive, crosslinking triblock copolymer, *Polymer* 168 (2019) 146–154.
- [160] L. Toledo, B.F. Urbano, Poly(2-hydroxyethyl methacrylate)-based porous hydrogel: influence of surfactant and SiO<sub>2</sub> nanoparticles on the morphology, swelling and thermal properties, *Eur. Polym. J.* 81 (2016) 316–326.
- [161] Y. Hu, W. Han, Y. Chen, R. Zou, Y. Ouyang, W. Zhou, Z. Yang, C. Wang, One-pot fabrication of poly( $\epsilon$ -caprolactone)-incorporated bovine serum albumin/calcium alginate/hydroxyapatite nanocomposite scaffolds by high internal phase emulsion templates, *Macromol. Mater. Eng.* 302 (4) (2017) 1600367.
- [162] L. Song, M. Zhu, Y. Chen, K. Haraguchi, Temperature- and pH-sensitive nanocomposite gels with semi-interpenetrating organic/inorganic networks, *Macromol. Chem. Phys.* 209 (15) (2008) 1564–1575.
- [163] R.E. Webber, C. Creton, H.R. Brown, J.P. Gong, Large strain hysteresis and Mullins effect of tough double-network hydrogels, *Macromolecules* 40 (8) (2007) 2919–2927.
- [164] J.P. Gong, Why are double network hydrogels so tough? *Soft Matter* 6 (12) (2010) 2583–2590.
- [165] L. Tang, D. Zhang, L. Gong, Y. Zhang, S. Xie, B. Ren, Y. Liu, F. Yang, G. Zhou, Y. Chang, J. Tang, J. Zheng, Double-network physical cross-linking strategy to promote bulk mechanical and surface adhesive properties of hydrogels, *Macromolecules* 52 (24) (2019) 9512–9525.
- [166] Z. Tang, Q. Chen, F. Chen, L. Zhu, S. Lu, B. Ren, Y. Zhang, J. Yang, J. Zheng, General principle for fabricating natural globular protein-based double-network hydrogels with integrated high mechanical properties and surface adhesion on solid surfaces, *Chem. Mater.* 31 (1) (2019) 179–189.
- [167] H. Chen, Y. Liu, B. Ren, Y. Zhang, J. Ma, L. Xu, Q. Chen, J. Zheng, Super bulk and interfacial toughness of physically crosslinked double-network hydrogels, *Adv. Funct. Mater.* 27 (44) (2017) 1703086.
- [168] X. Yan, Q. Chen, L. Zhu, H. Chen, D. Wei, F. Chen, Z. Tang, J. Yang, J. Zheng, High strength and self-healable gelatin/polycrylamide double network hydrogels, *J. Mater. Chem. B* 5 (37) (2017) 7683–7691.
- [169] X. Li, Q. Yang, Y. Zhao, S. Long, J. Zheng, Dual physically crosslinked double network hydrogels with high toughness and self-healing properties, *Soft Matter* 13 (5) (2017) 911–920.
- [170] F. Chen, Q. Chen, L. Zhu, Z. Tang, Q. Li, G. Qin, J. Yang, Y. Zhang, B. Ren, J. Zheng, General strategy to fabricate strong and tough low-molecular-weight gelator-based supramolecular hydrogels with double network structure, *Chem. Mater.* 30 (5) (2018) 1743–1754.
- [171] Q. Chen, X. Yan, L. Zhu, H. Chen, B. Jiang, D. Wei, L. Huang, J. Yang, B. Liu, J. Zheng, Improvement of mechanical strength and fatigue resistance of double network hydrogels by ionic coordination interactions, *Chem. Mater.* 28 (16) (2016) 5710–5720.
- [172] Q. Chen, L. Zhu, H. Chen, H. Yan, L. Huang, J. Yang, J. Zheng, A novel design strategy for fully physically linked double network hydrogels with tough, fatigue resistant, and self-healing properties, *Adv. Funct. Mater.* 25 (10) (2015) 1598–1607.
- [173] Q. Chen, L. Zhu, L. Huang, H. Chen, K. Xu, Y. Tan, P. Wang, J. Zheng, Fracture of the physically cross-linked first network in hybrid double network hydrogels, *Macromolecules* 47 (6) (2014) 2140–2148.
- [174] Q. Chen, L. Zhu, C. Zhao, Q. Wang, J. Zheng, A robust, one-pot synthesis of highly mechanical and recoverable double network hydrogels using thermoreversible sol-gel polysaccharide, *Adv. Mater.* 25 (30) (2013) 4171–4176.
- [175] X. Zhang, X. Guo, S. Yang, S. Tan, X. Li, H. Dai, X. Yu, X. Zhang, N. Weng, B. Jian, J. Xu, Double-network hydrogel with high mechanical strength prepared from two biocompatible polymers, *J. Appl. Polym. Sci.* 112 (5) (2009) 3063–3070.
- [176] T. Matsuda, T. Nakajima, J.P. Gong, Fabrication of tough and stretchable hybrid double-network elastomers using ionic dissociation of polyelectrolyte in nonaqueous media, *Chem. Mater.* 31 (10) (2019) 3766–3776.
- [177] Q. Chen, H. Chen, L. Zhu, J. Zheng, Fundamentals of double network hydrogels, *J. Mater. Chem. B* 3 (18) (2015) 3654–3676.
- [178] M.A. Haque, T. Kurokawa, J.P. Gong, Super tough double network hydrogels and their application as biomaterials, *Polymer* 53 (9) (2012) 1805–1822.
- [179] F. Vidal, C. Plesse, D. Teyssié, C. Chevrot, Long-life air working conducting semi-IPN/ionic liquid based actuator, *Synth. Met.* 142 (1) (2004) 287–291.



- [180] L.J. Goujon, A. Khaldi, A. Maziz, C. Plesse, G.T.M. Nguyen, P.-H. Aubert, F. Vidal, C. Chevrot, D. Teyssié, Flexible solid polymer electrolytes based on nitrile butadiene rubber/poly(ethylene oxide) interpenetrating polymer networks containing either LiTFSI or EMITFSI, *Macromolecules* 44 (24) (2011) 9683–9691.
- [181] R. Ma, S.-Y. Chou, Y. Xie, Q. Pei, Morphological/nanostructural control toward intrinsically stretchable organic electronics, *Chem. Soc. Rev.* 48 (6) (2019) 1741–1786.
- [182] S.M. Ha, W. Yuan, Q. Pei, R. Pelrine, S. Stanford, Interpenetrating networks of elastomers exhibiting 300% electrically-induced area strain, *Smart Mater. Struct.* 16 (2) (2007) S280–S287.
- [183] T. Ube, Development of novel network structures in crosslinked liquid-crystalline polymers, *Polym. J.* 51 (10) (2019) 983–988.
- [184] F. Ghamouss, M. Mallouki, B. Bertolotti, L. Chikh, C. Vancaeyzeele, S. Alfonsi, O. Fichet, Long lifetime in concentrated LiOH aqueous solution of air electrode protected with interpenetrating polymer network membrane, *J. Power Sources* 197 (2012) 267–275.
- [185] B. Bertolotti, H. Messaoudi, L. Chikh, C. Vancaeyzeele, S. Alfonsi, O. Fichet, Stability in alkaline aqueous electrolyte of air electrode protected with fluorinated interpenetrating polymer network membrane, *J. Power Sources* 274 (2015) 488–495.
- [186] S. Livshin, M.S. Silverstein, Enhancing hydrophilicity in a hydrophobic porous emulsion-templated polyacrylate, *J. Polym. Sci., Part A: Polym. Chem.* 47 (18) (2009) 4840–4845.
- [187] L. Arens, D. Barther, J. Landsgesell, C. Holm, M. Wilhelm, Poly(sodium acrylate) hydrogels: synthesis of various network architectures, local molecular dynamics, salt partitioning, desalination and simulation, *Soft Matter* 15 (48) (2019) 9949–9964.
- [188] K. Fukao, K. Tanaka, R. Kiyama, T. Nonoyama, J.P. Gong, Hydrogels toughened by biominerals providing energy-dissipative sacrificial bonds, *J. Mater. Chem. B* 8 (24) (2020) 5184–5188.
- [189] M.R. Pfau, K.G. McKinzey, A.A. Roth, M.A. Grunlan, PCL-based shape memory polymer semi-IPNs: the role of miscibility in tuning the degradation rate, *Biomacromolecules* 21 (6) (2020) 2493–2501.
- [190] F. Chen, P. Le, K. Lai, G.M. Fernandes-Cunha, D. Myung, Simultaneous interpenetrating polymer network of collagen and hyaluronic acid as an in situ-forming corneal defect filler, *Chem. Mater.* 32 (12) (2020) 5208–5216.
- [191] S. Ishikawa, K. Iijima, D. Matsukuma, Y. Asawa, K. Hoshi, S. Osawa, H. Otsuka, Interpenetrating polymer network hydrogels via a one-pot and in situ gelation system based on peptide self-assembly and orthogonal cross-linking for tissue regeneration, *Chem. Mater.* 32 (6) (2020) 2353–2364.
- [192] B. Ying, Q. Wu, J. Li, X. Liu, An ambient-stable and stretchable ionic skin with multimodal sensation, *Mater. Horiz.* 7 (2) (2020) 477–488.
- [193] R. Shipani, S. Scheurer, R. Florentin, S.E. Critchley, D.J. Kelly, Reinforcing interpenetrating network hydrogels with 3D printed polymer networks to engineer cartilage mimetic composites, *Biofabrication* 12 (3) (2020), 035011.
- [194] A. Eklund, H. Zhang, H. Zeng, A. Priimagi, O. Ikkala, Fast switching of bright whiteness in channeled hydrogel networks, *Adv. Funct. Mater.* 30 (28) (2020) 2000754.
- [195] C. Bombonnel, C. Vancaeyzeele, G. Guérin, F. Vidal, Fabrication of bicontinuous double networks as thermal and pH stimuli responsive drug carriers for on-demand release, *Mater. Sci. Eng. C* 109 (2020) 110495.
- [196] Y. Zhang, M.S. Desai, T. Wang, S.-W. Lee, Elastin-based thermoresponsive shape-memory hydrogels, *Biomacromolecules* 21 (3) (2020) 1149–1156.
- [197] Z. Hu, C. Sun, A. Lin, J. Jackson, T. Terlier, D. Owolabi, H. Mei, Y. Li, Y. Wang, S. Sidhik, F. Hao, Y. Yao, A.D. Mohite, R. Verduzco, Improved mechanical durability of high-performance OPVs using semi-interpenetrating networks, *Adv. Opt. Mater.* (2020) 2000516.
- [198] N. Sun, F. Lu, Y. Yu, L. Su, X. Gao, L. Zheng, Alkaline double-network hydrogels with high conductivities, superior mechanical performances, and antifreezing properties for solid-state zinc–air batteries, *ACS Appl. Mater. Interfaces* 12 (10) (2020) 11778–11788.
- [199] H.Q. Li, X.J. Liu, H. Wang, H. Yang, Z. Wang, J. He, Proton exchange membranes with cross-linked interpenetrating network of sulfonated polyvinyl alcohol and poly(2-acrylamido-2-methyl-1-propanesulfonic acid): excellent relative selectivity, *J. Membr. Sci.* 595 (2020) 117511.
- [200] W. Qiu, P.A. Gurr, G.G. Qiao, Regulating color activation energy of mechanophore-linked multinet network elastomers, *Macromolecules* 53 (10) (2020) 4090–4098.