

## **QI** Interpenetrating Polymer Networks (IPN): Structure and Mechanical Behavior

C. M. Roland\*

Chemistry Division, Naval Research Laboratory, Washington, DC, USA

### **Synonyms**

[Co-continuous networks](#); [Macrocylic catenanes](#); [Polymer blend network](#)

### **Definition**

Interpenetrating polymer network (IPN) refers to a type of elastomer in which two chemically distinct networks coexist, ideally having a structure that is homogeneous down to the segmental level [1]. The two components are present as co-continuous, interlocking networks (catenanes). This co-continuity can be achieved by kinetic retention of an initially miscible mixture of the monomers used to form the network chains, with phase segregation inhibited by the network structure, or be the result of thermodynamically compatible of the constituent polymers. A specific type of IPN relies on solvent to promote miscibility of the two polymers. Hydrogel IPNs, which use water as the solvent, are not included in this review (see related entry ► [Double Network Hydrogels: Soft and Tough IPN](#)).

### **Introduction**

The defining characteristic of polymers is the enormous size of the constituent molecules (“macromolecules”), consisting of subunits that repeat thousands of times. If these chain molecules are flexible, the material exhibits rubbery behavior, in particular high elasticity. This term refers to the ability of the material to recover its original dimensions after large deformations. Optimizing this recoverability, as well as enhancing the modulus and strength of a rubbery polymer, requires chemical bonding of the constituent chains to one another (cross-linking) to form a network. Since the length scale associated with the properties of a rubber is much larger than the chemical repeat units comprising the chains, the mechanical behavior of rubbery networks is general; that is, elastomers exhibit qualitatively the same stress-strain relationship, at least up through strains of a few hundred percent extension, independent of their chemical structure [2]. The modulus can be increased by increasing the concentration of cross-links, but except at very low degrees of cross-linking, an increase in modulus causes a decrease in the strength and other failure properties such as resistance to crack growth. This is the result of the increases in network integrity from the cross-linking being countervailed by increases in local overstressing and eventually embrittlement. Thus, for a given elastomer, a compromise exists between its stiffness and strength.

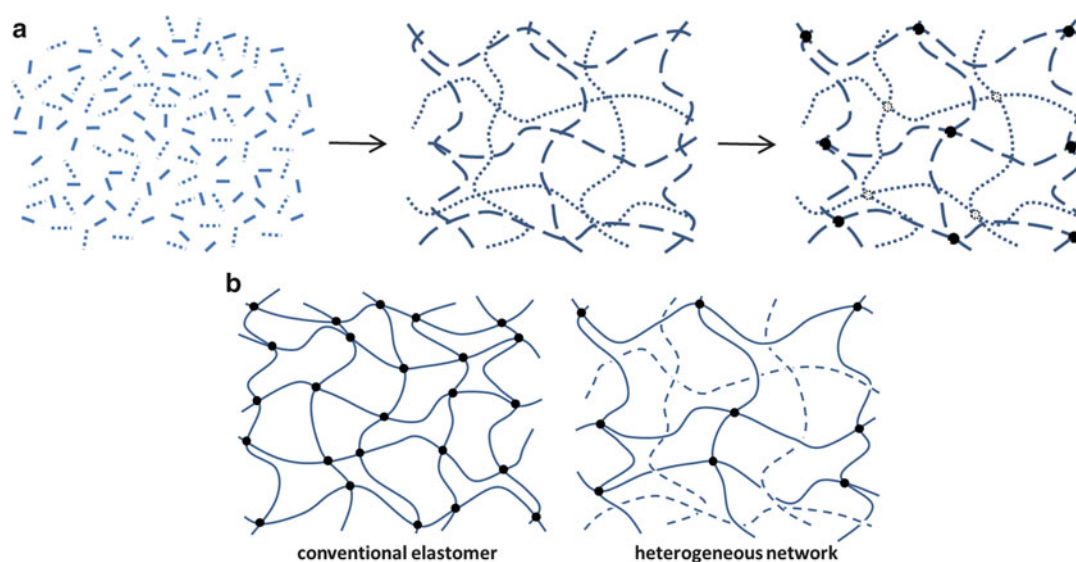
One route to circumventing this trade-off is by modifying the network structure, and there are different approaches that have shown varying degrees of success: using mechanically labile bonding

---

\*Email: roland@nrl.navy.mil

of the chains, which can then dissociate on extension to mitigate local overstressing; having a bimodal distribution of network chain lengths, wherein short network strands enhance the modulus and long chains provide extensibility; using intrinsically oriented “double networks,” prepared by two-step cross-linking in which the initial network is strained during the second cross-linking; and interpenetrating polymer networks. Commonly a material is regarded as an IPN based on its method of preparation – simultaneous or sequential cross-linking of two polymers in a blend. However, strictly speaking an IPN consists of two polymers that are intimately mixed with minimal bonding to each other, both present as a continuous phase; such a morphology can be achieved in different ways. Typical domain sizes in IPNs range from several tens of nm and larger, but it is the dual phase continuity that enables this quasi-homogeneous morphology to give rise to properties that are not a simple average of the component properties. Analytical methods to characterize the morphology include scattering (both X-ray and neutron), optical and electron microscopy, and calorimetry. For sufficiently small morphological heterogeneities (less than *ca.* 20 nm), only a single  $T_g$  is observed, intermediate between those of the neat components. This implies the composition is uniform over distances equal to or larger than the range of correlated motions of the chain segments. A special class of IPNs uses a solvent to homogenize the blend; for example, hydrogel IPNs contain water to achieve miscibility of the components. More generally, IPNs are neat polymer blends without solvents that rely on their method of preparation to achieve phase homogeneity. Even highly incompatible polymers, such as organic-inorganic blends, can be prepared with a homogenous morphology through the IPN approach [3].

IPNs are referred to as semi- and full IPNs, depending on whether one or both of the respective components are cross-linked. They can be prepared by mixing two monomers, which are subsequently (and often simultaneously) polymerized and cross-linked (Fig. 1a), or by dissolving a monomer in a polymer network; the former then reacted to form the second interpenetrating network (Fig. 1b). A third route to IPNs is by blending two polymers that are thermodynamically miscible, followed by cross-linking.



**Fig. 1** (*Upper*) Simultaneous IPN, prepared by polymerization and cross-linking of a mixture of two monomers or two linear prepolymers, with phase separation suppressed due to the rapidly increasing viscosity; (*lower*) sequential IPN, in which a network is swollen in monomers, the subsequent polymerization and cross-linking of which yields an IPN; phase separation is usually greater for sequential IPNs

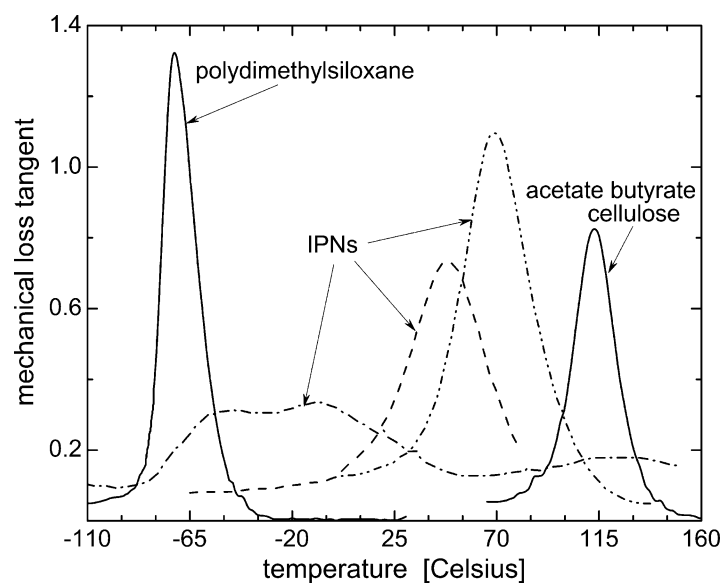
## Full IPNs

Both components of a full IPN are present as cross-linked networks, although there is negligible bonding between the two polymers. These can be prepared sequentially or simultaneously (Fig. 1). Although the constituent polymers are incompatible, phase segregation is constrained by network formation, leading to small phase domains, and hence the potential for homogenization of the properties. Because of the small domains, IPNs can yield transparent materials even if the components have large refractive index differences [4]. Since the glass transition temperature becomes size dependent for small domains, only one transition is expected for IPNs. However, a distribution of phase sizes gives rise to very broad glass transitions (with respect to both the temperature and frequency), a property exploited in acoustic damping and vibration isolation applications [5]. Figure 2 shows the peak in the mechanical loss tangent, which occurs at a temperature near the glass transition, for IPNs of polydimethylsiloxane and cellulose [2]. The transition is broader than for neat polymers and occurs at temperatures intermediate to  $T_g$  of the pure components.

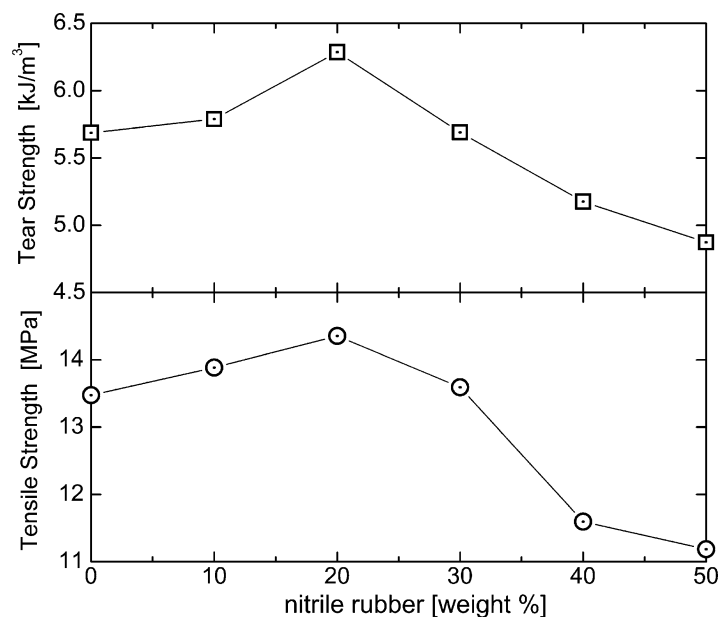
The improvements in mechanical properties of full IPNs are illustrated in Fig. 3, showing maxima in strength properties of an IPN based on nitrile rubber (a random copolymer of polyacrylonitrile and 1,4-polybutadiene) and a fluoroelastomer.

Solid polymer electrolytes for use in fuel cells, batteries, and capacitors can benefit from cross-linking, which increases their mechanical strength and stability; however, networks are less conductive, which is a major drawback in such applications. IPNs offer a means to circumvent this limitation: one component enhances the mechanical properties, and the other confers high ionic conductivity. By tailoring the chemistry of the IPN, a synergy can be obtained whereby the performance exceeds that of either neat material [8].

A variation on the conventional method of forming an IPN that has potential for mechanical actuators such as artificial muscles is the polymerization and cross-linking of monomers absorbed into a stretched network [9]. The second network is compressed at mechanical equilibrium, with the physical dimensions and properties reflecting a balance between the two components. Such a structure has features in common with rubber double networks [10].



**Fig. 2** Ratio of loss to storage modulus for polydimethylsiloxane, acetate butyrate cellulose, and three IPNs. The transitions for the blends are broader and intermediate in temperature to the pure components (Data from Ref. [6])



**Fig. 3** Strength properties of IPNs based on networks of nitrile rubber and a fluoropolymer (Data from Ref. [7])

**Table 1** Properties of IPN membrane based on polydimethylsiloxane and polystyrene networks [11]

	Flux ( $\text{g m}^{-2}/\text{h}$ )	Selectivity <sup>a</sup>	Strength (MPa)	Elongation (%)
Neat PDMS	160	2.2	2.5	200
50 % PS	210	7.6	3.7	450

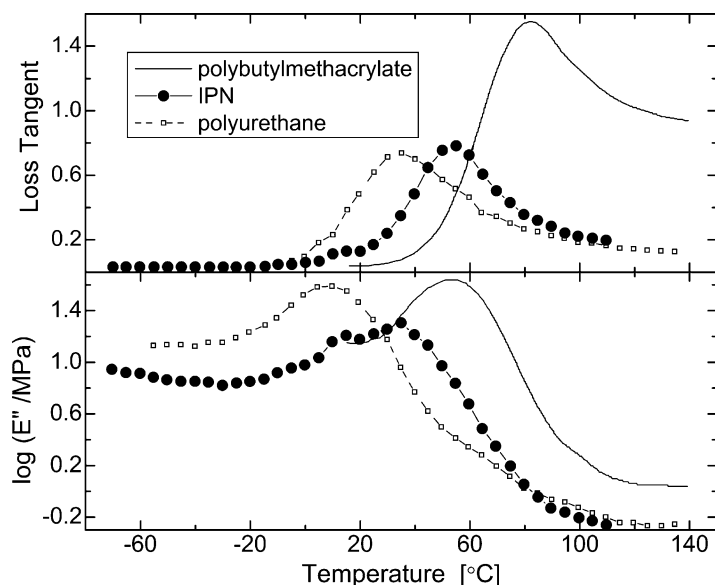
<sup>a</sup>Arbitrary units

Another technology area for IPNs is separation membranes for fluid mixtures and for the recovery of liquids. The use of two polymer networks affords the ability to control the morphology to enhance selectivity and throughput while improving the mechanical properties. Obtaining a more homogeneous phase structure is an important design criterion. Table 1 illustrates the improvements in both the performance and mechanical properties of a silicone membrane through blending with cross-linked polystyrene [11]. A related application of IPNs is for anion exchange membranes [12].

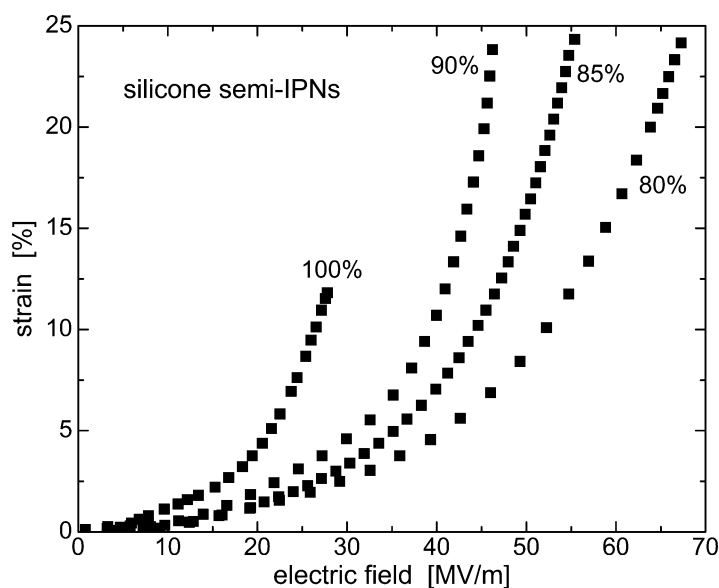
## Semi-IPNs

In a semi-IPN, only one polymer is present as a network. This enhances the miscibility in comparison to a full IPN, although the mobility of the uncross-linked component increases the potential for phase segregation if the components are not thermodynamically compatible. Similar to full IPNs, the glass transition of a semi-IPN is intermediate between that of the neat constituent polymers (Fig. 4).

Potential applications for semi-IPNs that have received much attention are as solid polymer electrolytes [14, 15] for fuel cells and as soft mechanical actuators. Figure 5 compares the electro-mechanical strains obtained in a silicone elastomer known to have high actuator performance with a semi-IPN based on the same polymer incorporated into a network of a room-temperature



**Fig. 4** Comparison of the damping peaks associated with the glass transition dynamics in a linear polymer, and polyurethane network, and their semi-IPN (Data from Ref. [13])



**Fig. 5** Electromechanical strain in semi-IPNs having different amounts of the uncross-linked component (as indicated in weight percent) (Data from Ref. [16])

vulcanizing (RTC) silicone [16]. The semi-IPN morphology improves actuation strains and the breakdown strength.

An intriguing application for semi-IPN is self-healing polymers. Cracks formed by mechanical or thermal stress can be bridged by diffusion of the linear chains, with the network component providing structural integrity. Healing efficiencies, for example, the rate and duration of strength recovery, have been shown to be optimized for semi-IPNs having a minor, but significant amount of uncross-linked polymer [17].

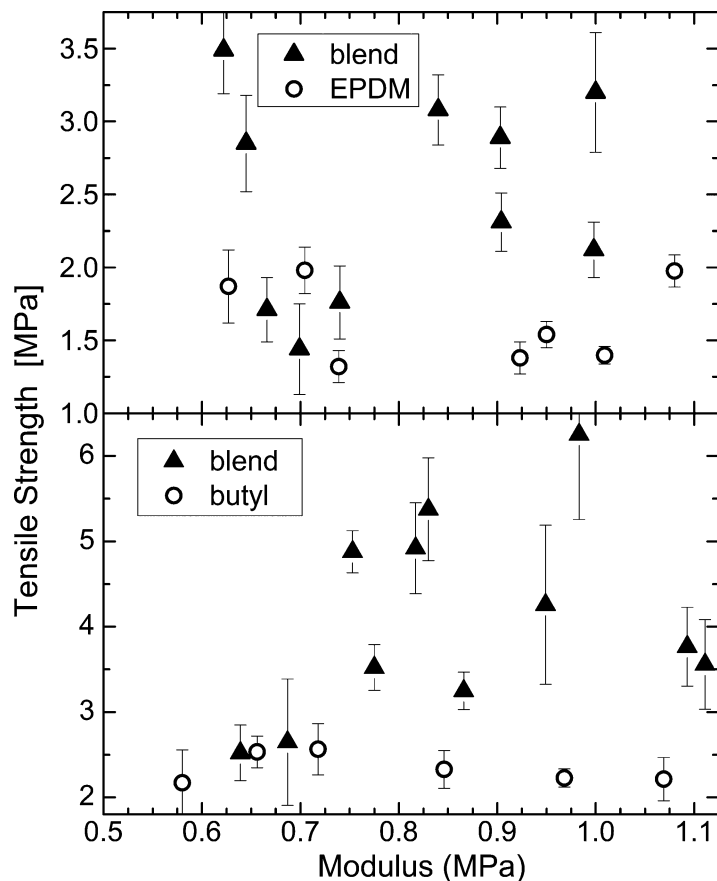
## Miscible Blends

Since the polymers comprising an IPN are rarely thermodynamically miscible, reliance is made on cross-linking to suppress phase segregation. The enhanced properties derive from the co-continuity of component networks that are different mechanically or otherwise. An example is bimodal networks, in which the chains between cross-links are either very short (few 100 g/mol molecular weight) or very long (typically  $\sim$  hundredfold longer than the short strands); such materials have higher elongation and strength than conventional elastomers [18]. However, since they are prepared by end-linking a mixture of low and high molecular weight precursor chains, the practical opportunities for bimodal networks are limited. Another example is double network hydrogels (see ► [Double Network Hydrogels: Soft and Tough IPN](#)), in which two networks having very different cross-link density are compatibilized using water as a solvent. A related approach described here is an elastomeric blend having miscible components that can be cross-linked to very different extents.

A homogeneous morphology per se does not yield better properties; rubber toughened plastics, for example, require a certain dispersed particle size for optimal performance. Usually miscible blends exhibit behavior intermediate between that of the components [19]. However, when a large disparity in cross-linking of the constituent networks exists, a new mechanism becomes possible: The chains of the more cross-linked component stiffen the material during deformation, while the more weakly cross-linked stands are better able to rearrange and stretch. The latter reduces local overstressing of the network, which arises due to the irregular structure of randomly cross-linked polymer chains. Disparity of cross-linking in a homogenous blend results in better failure properties for a given modulus; thus, the usual compromise between the stiffness and strength of elastomers can be overcome.

The two requirements for this method are that the polymers are miscible and have very different cross-linking reactivities. Miscibility can be achieved with components that are chemically identical except for a small fraction of repeat units that serve as the site of the cross-links. This approach is exemplified in blends of polyisobutylene (PIB) with butyl rubber (which is PIB with a few percent of randomly distributed isoprenyl units) and ethylene-propylene copolymer with EPDM, a random terpolymer of ethylene, propylene, and a few percent of a diene (e.g., ethylidene norbornene, vinyl norbornene, or dicyclopentadiene). The saturated components of these blends cannot be sulfur vulcanized and thus remain uncross-linked during formation of a network of the other polymer. Provided no phase separation is induced by the cross-linking (as may be driven by the chemical modification of the reactive component), superior mechanical properties can be achieved. This is illustrated in Fig. 6, showing tensile strength versus modulus data for EPDM and its blend with ethylene-propylene copolymer [20] and butyl rubber and its blend with polyisobutylene [21]. Sulfur vulcanization is used for curing, and the saturated components of these miscible blends are unreactive to sulfur. The cured material consists of linear chains dispersed in a network. Continuity of the uncross-linked component is due to physical entanglements (topological constraints).

An alternative to using components with similar chemical structures in their backbones is to employ polymers that are thermodynamically miscible because of specific interactions; that is, some chemical attraction. This gives rise to a negative heat of mixing (negative excess enthalpy) and a stronger driving force for homogeneity than just the entropy of mixing of the blends in Fig. 6. In principle this is advantageous by facilitating retention of a homogeneous morphology during processing. Examples of candidate blends include natural rubber (*cis*-1,4-polyisoprene) and 1,2-polybutadiene [22, 23] and blends of 1,4-polychloroprene and epoxidized 1,4-polydienes. Although the components in these systems have different cross-linking reactivities, efforts to date have failed to achieve sufficient disparity of the degree of cross-linking to achieve significant



**Fig. 6** Strength of elastomers based on a single polymer (*open circles*) and its blend with an uncross-linked component (*filled triangles*) (Data from Refs. [20, 21])

property improvements. Nevertheless, it is an attractive technology because new or better materials can be obtained without the need to synthesize new polymers.

**Related Entries**

- ▶ [Double Network Hydrogels: Soft and Tough IPN](#)
- ▶ [Polymer Blends](#)

Q2

**Acknowledgments**

This work was supported by the Office of Naval Research.

**References**

Q3, Q4 1. Kim SC, Sperling LH (eds) (1997) IPNs around the world: science and engineering. Wiley, Chichester/New York



- Q5**
2. Roland CM (2011) Viscoelastic behavior of rubbery materials. Oxford University Press, Oxford
  3. Sangermano M, Cook WD, Papagna S, Grassini S (2012) Hybrid UV-cured organic–inorganic IPNs. *Eur Polym J* 48:1796–1804
  4. Bird SA, Clary D, Jajam KC, Tippur HV, Auad ML (2013) Synthesis and characterization of high performance, transparent interpenetrating polymer networks with polyurethane and poly (methyl methacrylate). *Polym Eng Sci* 53:716–723
  5. Corsaro RD, Sperling LH (eds) (1990) Sound and vibration damping with polymers. American Chemical Society, Washington, DC
  6. Vidal F, Fichet O, Laskar J, Teyssie D (2006) Polysiloxane-cellulose acetate butyrate cellulose interpenetrating polymer networks close to true IPNs on a large composition range. *Polymer* 47:3747–3753
  7. Chunming C, Chuanxi X, Jian Y, Lijie D (2008) Microstructure and properties of fluoroelastomer/butadiene-acrylonitrile rubber interpenetrating polymer networks. *J Wuhan Univ Technol Mater Sci Ed* 23:50–53
  8. Goujon LJ, Khaldi A, Maziz A, Plesse C, Nguyen GTM, Aubert PH, Vidal F, Chevrot C, Teyssie D (2011) Flexible solid polymer electrolytes based on nitrile butadiene rubber/poly (ethylene oxide) interpenetrating polymer networks containing either LiTFSI or EMITFSI. *Macromolecules* 44:9683–9691
  9. Ha SM, Yuan W, Pei QB, Pelrine R, Stanford S (2006) Interpenetrating polymer networks for high-performance electroelastomer artificial muscles. *Adv Mater* 18:887–891
  10. Mott PH, Roland CM (2000) Mechanical and optical behavior of double network rubbers. *Macromolecules* 33:4132–4137
  11. Pa NFC, Ahmed I, Nawawi MGM, Rahman WA (2012) Influence of polystyrene on PDMS IPNs blend membrane performance. *Sep Sci Technol* 47:562–576
  12. Ghamouss F, Mallouki M, Bertolotti B, Chikh L, Vancaeyzeele C, Alfonsi S, Fichet O (2012) Long lifetime in concentrated LiOH aqueous solution of air electrode protected with interpenetrating polymer network membrane. *J Power Sources* 197:267–275
  13. Babkina NV, Lipatov YS, Alekseeva TT, Sorochinskaya LA, Datsyuk YI (2008) Effect of spatial constraints on phase separation during polymerization in sequential semi-interpenetrating polymer networks. *Polym Sci Ser A* 50:798–807
  14. Lee MJ, Choi YS, Kang YS, Choi JH, Kang MS (2012) All-solid-state proton conductive membranes prepared by a semi-interpenetrating polymer network (semi-IPN). *J Mater Chem* 22:18522–18527
  15. Zhou B, Pu H, Pan H, Wan D (2011) Proton exchange membranes based on semi-interpenetrating polymer networks of Nafion and poly(vinylidene fluoride) via radiation crosslinking. *Int J Hydrog Ener* 36:6809–6816
  16. Brochu P, Stoyanov H, Niu X, Pei Q (2013) All-silicone prestrain-locked interpenetrating polymer network elastomers: free-standing silicone artificial muscles with improved performance and robustness. *Smart Mater Struct* 22:055022
  17. Peterson AM, Kotthapalli H, Rahmathullah MAM, Palmese GR (2012) Investigation of interpenetrating polymer networks for self-healing applications. *Compos Sci Technol* 72:330–336
  18. Mark JE (2003) Elastomers with multimodal distributions of network chain lengths. *Macromol Symp* 191:121–130
  - Q6** 19. Roland CM (2013) Immiscible rubber blends. In: *Advances in elastomers I, advanced structured materials*, Springer, pp 167–181



20. Buckley GS, Fragiadakis DM, Roland CM (2011) Strength enhancement from heterogeneous networks of ethylene-propylene/ethylene-propylene-diene. *Rubber Chem Technol* 84:520–526
21. Giller CB, Roland CM (2013) Strength enhancement in miscible blends of butyl rubber and polyisobutylene. *Macromolecules* 46:2818–2822
22. Tomlin DW, Roland CM (1992) Negative excess enthalpy in a van der Waals polymer mixture. *Macromolecules* 25:2994–2996
23. Wang J, Roland CM (2005) Heterogeneous networks of polyisoprene/polyvinylethylene. *Polymer* 46:4160–4165