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REVIEW

Design and properties of supramolecular polymer gels

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Supramolecular polymer gels are precisely designed physical gels brought together by reversible secondary interactions to form three dimensional networks of melt macromolecules. Generally, they differ from supramolecular gels because they are comprised of polymers instead of low molecular weight compounds. Recently, much effort has focused on designing supramolecular polymer gels and related materials with excellent properties; indeed, improvements have been made in their supramolecular interactions, complementarity in the non-covalent bonding units, the nature of the macromolecular building blocks, and strand elasticity of supramolecular polymer networks. Owing to the precise molecular design, they represent nanophase separation and characteristic viscoelasticity. Here, we review supramolecular polymer gels in terms of molecular design, morphology, and rheology. We also discuss future directions in practical application of supramolecular polymer gels.

1. Introduction

"Polymer gels"[1] are among the most attractive and versatile soft materials. They are used in our daily lives for contact lenses, superabsorbent polymers, *etc.*, and more high-tech applications are in development.[2–11] Polymer gels typically contain a large amount of solvent,[12] which gives them a characteristic softness originated from a liquid nature. On the other hand, they can maintain shape like solid materials, unless excessive stress is applied. Consequently, the combination of softness and shape retention ability provides unique properties, particularly mechanical properties.[13–16]

To understand the interesting mechanical properties of polymer gels, they should be considered at the molecular level. Polymer gels are regarded as three dimensional networks of cross-linked, melt macromolecules, typically surrounded by a large number of solvent molecules. This polymer network

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consists of several elements, including bridging strands, cross-links (or junctions), dangling ends, and loops. The latter two elements can be regarded as defects in the network; the former two are indispensable for maintaining a network. Here, a bridging strand is defined as a polymer chain that connects one cross-link to another. Three or more strands[1,17–20] must be connected to one cross-link to form a network structure.

On the other hand, a "supramolecular polymer gel"[21] (also known as a supramacromolecular gel[22,23]), the subject of this review, can be regarded as three dimensional networks of non-covalently bound, melt macromolecules. Here, the term "supramolecular"[24,25] is defined as a state of self-assembling *via* non-covalent bonding or interactions. These precisely designed physical gels are different from polymer gels in that their bonding is reversible; thus they are semi-solid at room temperature and liquefy at high temperatures. Like polymer gels, a supramolecular polymer gel is composed of polymer components termed macromolecular building blocks (macro-building blocks); however, these macro-building blocks are generally designed to participate in attractive interactions to form the non-covalent cross-links of a supramolecular polymer network. At the same time, the macro-building blocks also include parts that are not involved in non-covalent bonding, which typically serve as bridging strands for network formation of supramolecular polymer gels. Note that a similar term "supramolecular gel"[26–28] typically refers to physical gels built of low molecular weight gelators; another similar term "supramolecular polymers"[29–31] refers to a polymeric array built of monomeric units that are brought together through reversible, highly directional secondary interactions. Thus, the term "supramolecular polymer gels" refers to a type of physical gel with a network structure, but built of "polymer" chains.

As for molecular design for supramolecular polymer gels, there are two main types of design. One design uses single polymer chains that include randomly arrayed, non-covalent bonding units.[32–35] The other design is more precise: the non-covalent bonding units are attached at specific locations on the chains, particularly on both ends.[36,37] In either case, when self-complementary non-covalent bonding units are used, a single polymer chain can serve as both a bridging strand and a cross-link to produce a supramolecular polymer gel.

When we look at the gels in terms of chemical nature, strands and cross-links are very different from each other. Thus they are apt to repel each other at the nanoscopic level. The distance between cross-links is easily defined in supramolecular polymer gels, because they are built according to precise molecular designs. Based on design, nanophase separation,[38] also conventionally called "microphase separation",[39–46] can be engineered into supramolecular polymer gels. In fact, recent studies have described supramolecular polymer gels that represented nanophase separation. However, because attractive interactions are considered a key to form supramolecular polymer networks, most researchers have focused on gel preparation and physical properties, particularly viscoelasticity. In contrast, few studies have focused on nanophase separation in supramolecular polymer gels.

In this review, we summarize the basic properties of supramolecular polymer gels. We focus on the molecular design, morphology, and viscoelasticity. We consider the molecular scale (preparation), nanoscopic scale (nanophase separation), and macroscopic scale (viscoelasticity) of supramolecular polymer gels. We also suggest some future directions in applications of the gels.

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2. Molecular design and preparation

There are many reports and reviews on supramolecular polymer gels and related materials.[47–50] However, they mainly focused on non-covalent bonding units themselves that connect macro-building blocks. Here, we first summarize the classifications of non-covalent bonding (or supramolecular interactions) for preparation. We also discuss the important features of the molecular design, including complementarity, macro-building blocks, and strand elasticity.

2.1 Supramolecular interactions between non-covalent bonding units

2.1.1 Hydrogen bonding. Hydrogen bonding is the most versatile interaction that can be used for preparing supramolecular materials.[34,36,51–56] Many functional groups can form hydrogen bonds. Stadler *et al.* used urazole and benzoic acid units for hydrogen bonding.[57–59] However, urazole and benzoic acid are not a well-matched complementary pair; therefore, hydrogen bonding was sometimes formed between two urazole units or between two benzoic acid units. Sijbesma and Meijer *et al.* developed a novel, self-complementary, hydrogen bonding array known as ureidopyrimidone; this molecule formed supramolecular polymers and gels with more precise designs than those formed by Stadler *et al.* (Fig. 1).[60,61] Although ureidopyrimidone is an excellent functional unit, it was only useful for self-complexation. Later, hetero-complementary pairs (*e.g.*, cyanuric acid and diaminopyrimidine-substituted isophthalamide) were synthesized for preparing supramolecular assemblies of small molecules.[62,63] Inspired by those works, Binder *et al.* incorporated heterocomplementary hydrogen bonding units into macro-building blocks for building supramolecular assemblies of polymers.[64–67] All the units described above were completely

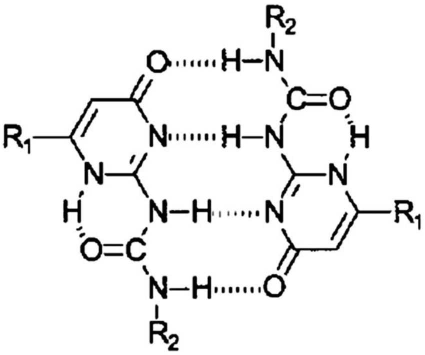

Fig. 1 Dimerization of 2-ureido-4[1*H*]-pyrimidone *via* self-complementary hydrogen bonding. Reprinted with permission from ref. 60. Copyright 1998 American Chemical Society.

synthetic; nevertheless, there are naturally occurring, unique, heterocomplementary hydrogen bonding motifs, for example, the nucleotides that form DNA. In fact, some studies have prepared supramolecular polymer materials based on nucleotide units.[68–72]

2.1.2 Metal-to-ligand coordination. Metal-to-ligand coordination is another popular interaction to bind building blocks.[73–75] Thanks to the development and improvement of polymer synthesis in recent years, this interaction has been used preferably to build up supramolecular assemblies of polymers.[76–81]

Although the assemblies were more like linear polymers, it is meaningful to note the work of Velten and Rehahn *et al.* They studied complexes of phenanthroline units and metal ions (Ag^+ or Cu^+).[82–84] Schubert *et al.* described supramolecular polymer assemblies made from terpyridine units and metal ions (*e.g.*, Ru^{2+} or Fe^{2+}).[85–94] Terpyridine units and these metal ions readily formed a 2 : 1 complex (Fig. 2); therefore, they described their polymer assemblies as linear polymers rather than a network. Rowan *et al.* showed that bis(benzimidazolyl) pyridine units and trivalent metal ions like La^{3+} and Eu^{3+} formed supramolecular polymer gels in solvents.[37,95–101] In addition, Craig *et al.* prepared supramolecular polymer gels from a complex of organopalladium and pyridine. They have been intensely studying viscoelasticity.[102–105]

2.1.3 Ionic interactions. The term "ionic interactions" typically refers to electrostatic or Coulombic interactions; here, we use this term specifically to describe interactions between organic cations and organic anions.[106–109] Organic cations and anions readily form pairs by mixing an acid and a base, a well-known neutralization reaction in classical and basic chemistry. Recently, this concept was applied to macromolecular systems.[110–123] Supramolecular complexation with an acid and a base in solution produces separated cation–anion pairs; in bulk, this complexation occurs within confined nanospaces and ion pairing occurs through hydrogen bonding. This is termed ionic hydrogen bonding.[124–128] Ionic interactions are not so directional, but they can be used to generate branches at cross-links, which facilitates use of the interactions within macromolecular systems. Therefore, ionic interactions hold promise for building up supramolecular polymer gels. Our recent study described simple preparation for these types of gels; a carboxy-terminated telechelic polymer was mixed with a polymer that had many amino groups in a bulk state (Fig. 3).[21]

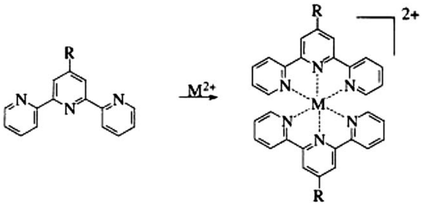

Fig. 2 Complex formation of terpyridine units and metal ions *via* metal-to-ligand coordination. Reprinted with permission from ref. 85. Copyright 2002 John Wiley & Sons, Inc.

Organic cation and anion pairs are also formed by mixing anion salts (*cf.* sulfonate and carboxylate) and cation salts (*cf.* pyridinium and ammonium).[129,130] In fact, well-defined supramolecular polymer gels were formed recently in water by mixing ionic ABA triblock copolymers (Fig. 4).[131] Due to the ionic charges, very clear nanophase separated structures were observed. In another study, hybrid supramolecular polymer gels were successfully prepared by mixing sodium polyacrylate-coated clay nanosheets and dendritic molecules with multiple guanidium ions in water.[132] This fascinating interaction will be studied in more detail in the future.

2.1.4 Inclusion complexation. Because non-covalent interactions are sometimes (or often) essential for inclusion complexation, we consider inclusion complexation in the class of supramolecular

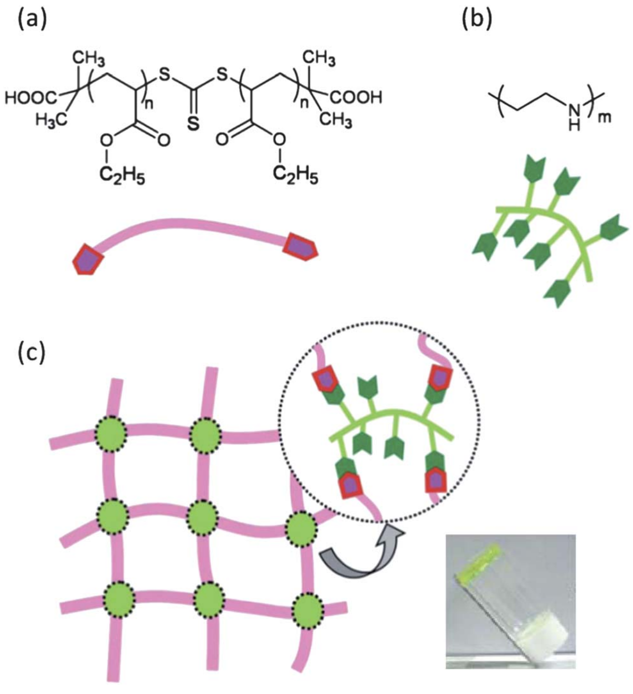

Fig. 3 Schematic illustrations show macro-building blocks and the chemical structures of supramolecular polymer gels. Carboxylic acids on one macro-building block (a) and many amines on the other building block (b) form acid–base complexes (c). These complexes serve as cross-links in polymer networks (c, inset). The blend of macro-building blocks in bulk forms a gel at room temperature (photograph). Reprinted with permission from ref. 21. Copyright 2011 RSC Publishing.

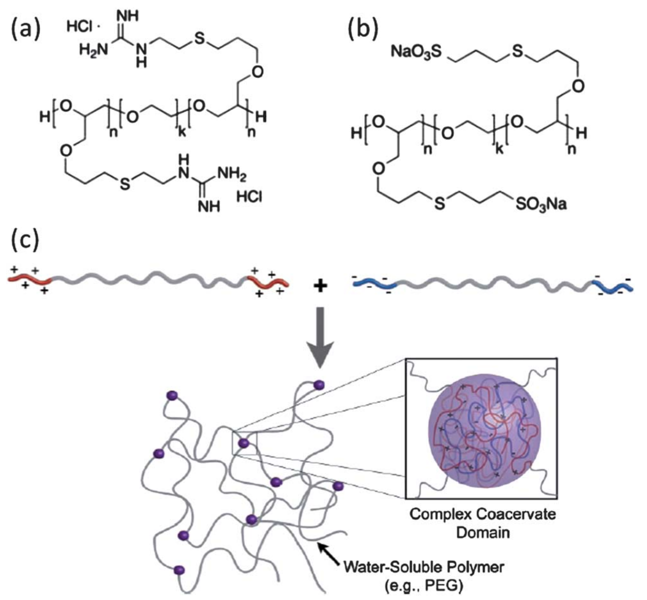

Fig. 4 Formation of supramolecular polymer gels in water by mixing ionic ABA triblock copolymers. (a) Chemical structure of a cationic ABA triblock copolymer with guanidinium units. (b) Chemical structure of an anionic ABA triblock copolymer with sulfonate units. (c) Schematic illustration of gelation in water formed *via* ionic interactions. Reprinted with permission from ref. 131. Copyright 2011 John Wiley & Sons, Inc.

interactions. In fact, inclusion complexation is a powerful tool for preparation of supramolecular polymer materials.[133–139] Takata *et al.* described the preparation of supramolecular polymer gels *via* inclusion complexation between crown ether units and ammonium salts (Fig. 5).[140–144] More recently, Huang and Liu *et al.* produced more defined gels with the same pair.[145] Although this molecular design is chemically elegant,[146–160] it is complicated, because functional units must be attached to the polymer side chains or ends to synthesize macro-building blocks for supramolecular gelation. The simplified synthetic procedures will make this complexation useful for the preparation.

2.2 Complementarity

There are two types of complementarity: self-complementarity (homocomplementarity) and heterocomplementarity.[161–165] Self-complementary units contain both key and keyhole motifs, and they connect by aligning appropriately.[166–175] Heterocomplementary units are used in more definite molecular designs, as shown by Lehn *et al.* In this design (Fig. 6), one unit serves as a key and the other as a keyhole for molecular recognition.[63] Metal-to-ligand coordination and inclusion complexation always represent heterocomplementary designs;[176] they require two different functional units to build supramolecular assemblies. Hydrogen bonding and ionic interactions are sometimes self-complementary; thus, they require only one type of macro-building block for non-covalent bonding formation. In any case, heterocomplementary systems are more reliable for defined molecular designs.

2.3 Macro-building blocks

Supramolecular polymer gels as well as covalent-bonded polymer gels comprise three dimensional networks, where each cross-link has more than two degrees of functionality. Therefore, the simplest molecular design is to synthesize a macro-building block with three or more branches with self-complementary non-covalent bonding units attached to the branch ends. On the other hand, a heterocomplementary molecular design typically requires two kinds of building blocks. One building block must have more than two non-covalent bonding units attached that can form branches when it is mixed with the other building block. This requirement can be satisfied with a mixture of a bifunctional small molecule and a multifunctional linear polymer (Fig. 7).[177] A supramolecular polymer gel can also be formed from a mixture of a linear polymer functionalized at both ends and a multi-functional polymer (Fig. 3).[21]

2.4 Elasticity of bridging strands

Supramolecular polymer gels require some molecular flexibility in the network, *i.e.*, chain elasticity. To achieve this, solvents can

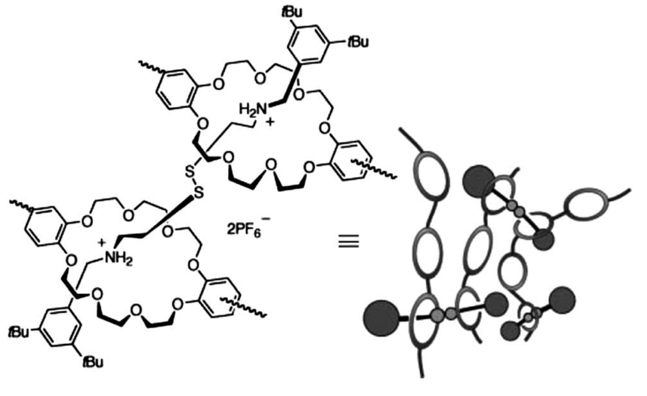

Fig. 5 Supramolecular polymer networks *via* inclusion complexation between crown ether units and ammonium salts. Reprinted with permission from ref. 140. Copyright 2004 John Wiley & Sons, Inc.

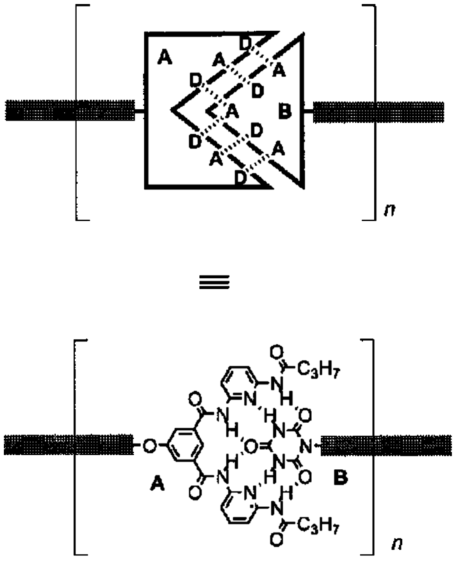

Fig. 6 Two heterocomplementary hydrogen bonding units (A = keyhole unit, and B = key unit) form a functional pair. Reprinted with permission from ref. 63. Copyright 2002 John Wiley & Sons, Inc.

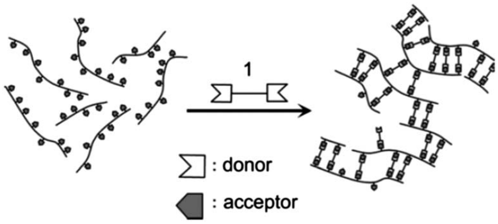

Fig. 7 Schematic illustration of the formation of a supramolecular polymer network. (Left) Multifunctional linear polymers with acceptor units are mixed with (1) bifunctional small molecules with donor units. Reprinted with permission from ref. 177. Copyright 2006 John Wiley & Sons, Inc.

be added to make the network strands elastic. Solvents can lower the glass transition temperature of network strands; the quantitative effect can be approximated with the Fox equation or other equations.[178] Adding solvents is the simplest way to render strands elastic, but the drawback of this approach is that solvents can evaporate, and this can cause supramolecular polymer gels to lose viscoelastic reversibility.

Recently, we developed use of an ionic liquid[179–185] as a nonvolatile solvent for preparing supramolecular polymer gels.[22,23] This molecular design (Fig. 8) enabled an exploration of the temperature dependence of viscoelasticity over a wide range of temperatures to nearly 200 °C. Another novel molecular design that precludes solvent evaporation is to use melt macro-building blocks[186–188] that have low glass transition temperatures below room temperature (Fig. 3).[21] The simplicity of this molecular design will facilitate future investigations. It should be noted that supramolecular polymer gels do not always require solvents.

3. Nanophase separation and density fluctuation

As mentioned in Section 1 (Introduction), few reports have focused on nanophase separation in supramolecular polymer gels. One potential reason is that the phenomenon is difficult to observe directly. However, knowledge of phase separation provides better understanding of their viscoelastic properties. There are more reports on phase separation in supramolecular assemblies without networks than on phase separation in supramolecular polymer gels, but the phenomena are expected to be similar. Therefore, we first review phase separation behaviour in supramolecular assemblies without networks.

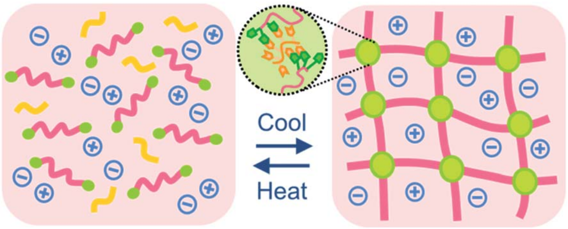

Fig. 8 Schematic representation of a supramolecular polymer network connected *via* hydrogen bonding in an ionic liquid. One macro-building block is a telechelic-type polymer (pink) with ends of hydrogen bonding units (green), and the other is a homopolymer (yellow) with many hydrogen bonding units. Because the hydrogen bonded cross-links (magnified in the circle) have a finite lifetime, the gel state (right) and the liquid state (left) are reversible.

3.1 Morphologies of supramolecular assemblies of polymers without network structures

3.1.1 Nanophase separation in block supramacromolecules. One of the most studied supramolecular assemblies of polymers representing nanophase separation is a “block-type supramacromolecule”[189–191] (or block supramacromolecule; Fig. 9b). This term actually refers to a “block-type supramolecular assembly of polymers”; in fact, some researchers favour the term “supramolecular block copolymer.”[192,193] The latter is easy to remember and use, but it does not clearly express how supramolecular it is.[194] Furthermore, the latter term can be misleading, because block copolymers themselves are sometimes used as macro-building blocks for preparing[195] “supramolecular block copolymers.” To avoid confusion, we used the term “block supramacromolecule” throughout this paper.

From the 1960’s, it has been well established that block copolymers represent nanophase separated structures when the constituent blocks are immiscible.[196–201] Here, nanophase separated structures are defined as ordered structures of several tens of nanometres (sometimes smaller, sometimes larger), that are expected to become highly functional materials. In recent years, many researchers in this field have investigated the morphology of block supramacromolecules.[202–207] In a pioneering work performed by Russell *et al.*, block supramacromolecules were prepared with ionic interactions.[208] The design included macro-building blocks of two different kinds of polymers with non-covalent bonding end-groups. The nanophase separated structures were detected by small angle X-ray scattering (SAXS). Similar molecular designs were employed in other studies, where two different kinds of polymers with non-covalent bonding end-group(s) were mixed to build block supramacromolecules with ionic interactions.[209–216]

Recently, more precise molecular designs for supramacromolecules were employed with metal-to-ligand coordination,[217–224] inclusion complexation,[225–230] and hydrogen bonding.[231–236] Some studies, including ours,[189,190] have reported the formation of nanophase separated structures from block supramacromolecules. SAXS and transmission electron microscopy (TEM) are the preferred methods for detecting periodic structures.

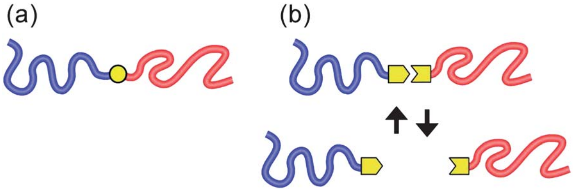

Fig. 9 Schematic of different types of block-type assemblies. (a) A block copolymer molecule has a junction with a covalent bond. (b) A block supramacromolecule has a junction with a non-covalent interaction; the block supramacromolecule will dissociate into a polymer blend of macro-building blocks in response to external stimuli, like heat or applied stress. The polymer blend will reform into a block supramacromolecule when the external stimuli are removed.

3.1.2 Thermoresponsive morphology of block supramacromolecules. For the past decade, a central interest for researchers in this field has been whether block supramacromolecules represent nanophase separated structures. This question was addressed in several studies mentioned above. The next issue was the thermo-responsiveness of block supramacromolecule morphology. The morphology of block supramacromolecules was expected to be thermally responsive, because they are built of non-covalent bonding units, which provide a temporary connection between macro-building blocks; thus, high temperatures can weaken the interaction strength. Conversely, at low temperatures, block supramacromolecules *via* non-covalent bonding should behave as block copolymers representing nanophase separated structures. On the other hand, block supramacromolecules may not maintain an ordered structure at high temperatures; they may behave as an immiscible polymer blend, known as a macrophase separated mixture of macro-building blocks (Fig. 10). This thermo-responsiveness is not typical in inorganic materials; therefore, this functionality of block supramacromolecules is expected to be developed for creating novel thermoresponsive nanostructured materials.

Several studies have described the temperature dependence of nanophase separated structures in block supramacromolecules.[231,232,237] A pioneering study by Russell *et al.* used SAXS to follow structural changes in block supramacromolecules. Increasing the temperature to around 300 °C typically caused the polymer samples to degrade.[208] Therefore, they could not clearly determine the mechanism underlying morphological transitions in block supramacromolecules. To elucidate this issue, several recent studies have used different molecular designs to investigate the temperature dependence of nanophase separated morphology. For example, Noro *et al.* added an ionic liquid as a non-volatile solvent to remove the effects of glass transition temperatures of macro-building blocks. The solvents also serve as a filler for the dissolved phase. Then, the temperature was changed from 30 to 110 °C and the structural changes were followed by SAXS to determine the thermo-responsiveness of the morphology.[191] At the lower temperatures (*e.g.*, 30 °C), there were several sharp peaks with relative scattering vector values of 1, 2, 3, and 4; this clearly indicated a lamellar nanophase separated structure. In contrast, no peaks appeared at temperatures above 90 °C; this might have indicated macrophase separation due to weakened interactions between macro-building blocks (Fig. 11). This system was interesting because the morphological behaviour was completely thermoreversible. The design should be simplified to facilitate its application to preparation of thermoresponsive nanostructured materials.

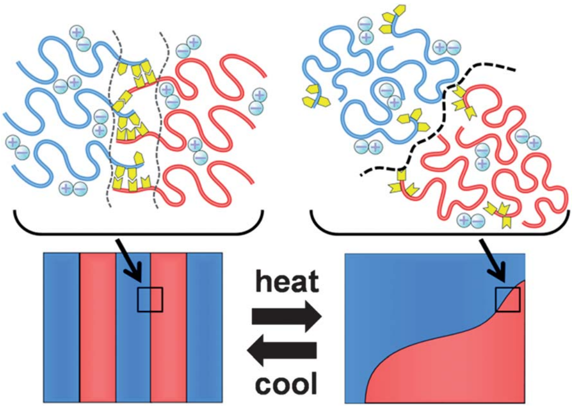

Fig. 10 Schematic illustration of thermoreversible morphology. The block supramacromolecule structure is represented on the molecular scale (upper section) and macromolecular scale (lower section). Changes in temperature induce the transition between a nanophase separated structure (left) and a macrophase separated mixture (right). Reprinted with permission from ref. 191. Copyright 2009 American Chemical Society.

3.1.3 Phase of non-covalent bonding units. To approach the "ideal" block supramacromolecule, which, in the extreme case, includes only "one" non-covalent bonding unit, a small number of non-covalent bonding units is desirable. On the other hand, a large number of non-covalent bonding units provides greater interaction strength, which favours stable macro-building block connections. For instance, in the case of hydrogen bonding, multiple hydrogen bonds are typically utilized to ensure tightly bound building blocks; in turn, these bonds occupy relatively large volume fractions, and therefore, they may form a new phase.[238–241]

In fact, some reports on the nanophase separation of block supramacromolecules have demonstrated the formation of a new phase. Jiang *et al.* described nanophase separation in block supramacromolecules formed by mixing a polystyrene-*b*-poly(1,2-butadiene)-*b*-poly(methacrylic acid) triblock copolymer

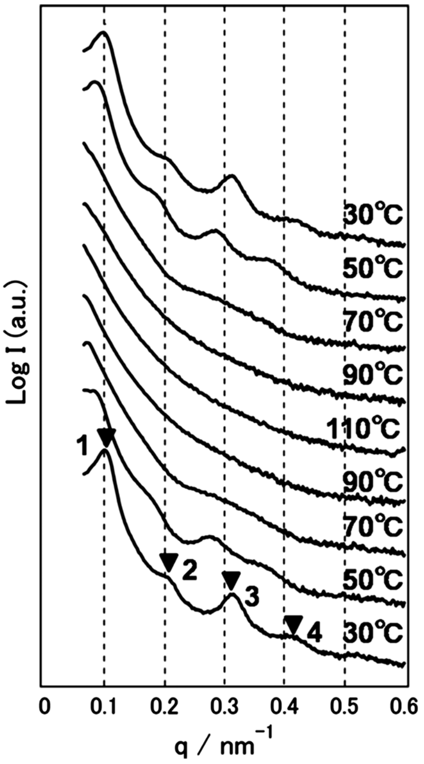

Fig. 11 SAXS profiles of a block supramacromolecule in an ionic liquid at various temperatures. The temperature was increased from 30 °C to 110 °C, and then, decreased again to 30 °C. Reprinted with permission from ref. 191. Copyright 2009 American Chemical Society.

with a polystyrene-*b*-poly(2-vinylpyridine) diblock copolymer. There, the poly(methacrylic acid) and poly(2-vinylpyridine) formed a hydrogen-bonded complex phase.[242] Similar, but more precise molecular designs have also resulted in block supramacromolecules with a clear nanophase separated structure and a complex new phase. Moreover, three-phase nanophase separated structures have been clearly observed in diblock–diblock[243–245] and even diblock–triblock[246] copolymer mixtures, when the parent block copolymers carried hydrogen bonding moieties (Fig. 12). Our recent work also demonstrated that a mixture of end-functionalized homopolymers and multifunctional homopolymers resulted in nanophase separated structures made of grafted supramacromolecules *via* ionic hydrogen bonding (Fig. 13).[247]

3.2 Morphologies of supramolecular polymer gels

3.2.1 Nanophase separation in supramolecular polymer gels. As described above, supramolecular assemblies represent nanophase separated structures that often have a phase of non-covalent bonding units, when the volume fraction of non-covalent bonding units is large. Accordingly, supramolecular polymer gels should also exhibit nanophase separation with phases of cross-links and strands. Although some works have implied that nanophase separation plays an important role in gelation, definitive experimental results were not available until recently. In fact, our recent work is one of the most detailed reports to demonstrate clear experimental results on the occurrence of nanophase separation. We prepared supramolecular polymer gels by mixing a poly(2-vinylpyridine)-*b*-poly(ethyl acrylate)-*b*-poly(2-vinylpyridine) (VEAV) triblock copolymer and a poly(4-hydroxystyrene) (H) in an ionic liquid (Fig. 8). The poly(2-vinylpyridine) (V) and H formed a hydrogen-bonded cross-link phase, which was excluded from the ionic liquid. On the other hand, a strand fraction of poly(ethyl acrylate) was soluble in the ionic liquid. Therefore, with SAXS, we detected nanophase separation between the matrix of poly(ethyl acrylate) and the spherical (or cylindrical) cores of a hydrogen-bonded, cross-linked phase (Fig. 14).[23] It should be noted that, in the ionic liquid, VEAV itself did not show a scattering peak. However, when VEAV was mixed even with a small amount of H in an ionic liquid, it showed very broad peaks; this suggested that the addition of H definitely induced nanophase separation.

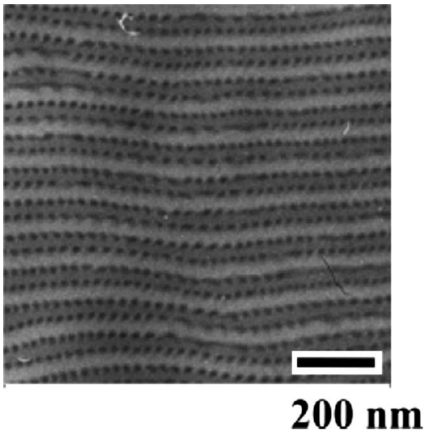

Fig. 12 TEM image of a block supramacromolecule with hydrogen bonding created by mixing polystyrene-*b*-poly(4-hydroxystyrene) (M_n = 86k and $\phi_{polystyrene}$ = 0.86) and polyisoprene-*b*-poly(2-vinylpyridine) (M_n = 80k and $\phi_{polyisoprene}$ = 0.91). The sample was stained with osmium tetroxide. The lightest phase is polystyrene, the next darkest phase is polyisoprene, and the darkest phase (spherical shapes) is a hydrogen-bonded complex of poly(4-hydroxystyrene)–poly(2-vinylpyridine). Reprinted with permission from ref. 243. Copyright 2005 American Chemical Society.

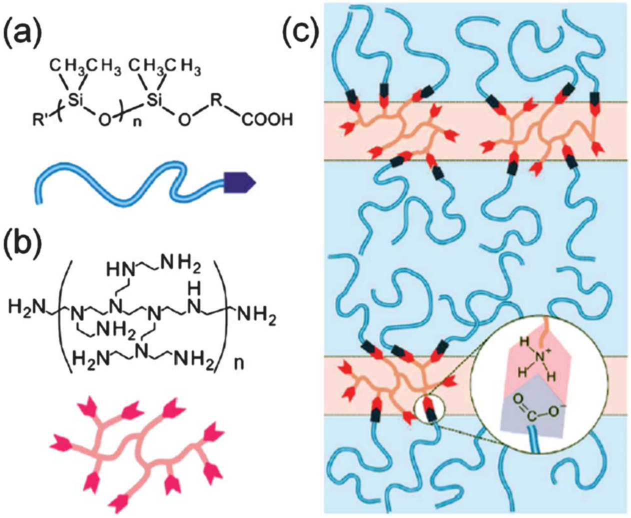

Fig. 13 Schematics of the chemical structures and macro-building blocks that formed nanophase-separated supramolecular assemblies. (a) Carboxy-terminated poly(dimethylsiloxane). (b) Polyethyleneimine. (c) Supramolecular assemblies of these macro-building blocks. Reprinted with permission from ref. 247. Copyright 2011 American Chemical Society.

A hydrogen-bonded, cross-link phase can be disassembled into individual polymers at high temperatures or with high energy stress. Therefore, we investigated the thermoresponsive nature of the morphology of the supramolecular polymer gel in an ionic liquid (also called supramacromolecular ion gels or supramolecular ion gels).[22,23] An ionic liquid is a non-volatile solvent; thus, we could investigate morphologies at comparatively high temperatures (*e.g.*, 180 °C). At lower temperatures (*e.g.*, 30 °C), the SAXS profile showed a peak at around 0.2 nm^{-1} and a bump at 0.35 nm^{-1}, which indicated the presence of an ordered nanophase separated structure. In contrast, a single and comparatively broad peak appeared at higher temperatures (*e.g.*, 180 °C), which suggested a disordered state. The analysed data are shown in Fig. 15. As the temperature increased, the intensity of the first peak decreased and the peak width became broader. This phenomenon indicated an order-to-disorder transition, but the transition occurred over a wide range of temperatures. As described below, this order-to-disorder transition corresponds to the gel-to-liquid transition that could be detected with oscillatory shear measurements; it indicated the transition between assembled and disassembled supramolecular polymer networks.

3.2.2 Density fluctuation in supramolecular polymer gels. Although the nanophase separation phenomenon appears to be important for gelation,[248–254] Feldman *et al.* reported that no

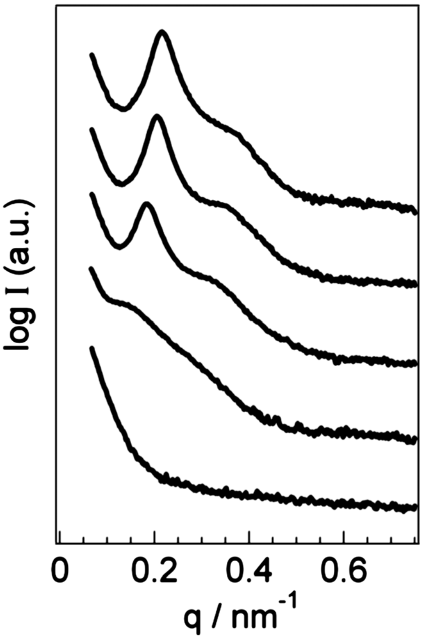

Fig. 14 Comparison of SAXS profiles for supramacromolecular ion gels prepared with different concentrations of a triblock copolymer (VEAV), poly(4-hydroxystyrene) (H), and an ionic liquid (IL). The weight ratio of VEAV : H : IL in the gels was systematically varied from 10 : 0 : 90 to 10 : 4 : 90 (bottom to top traces, respectively). See also ref. 23.

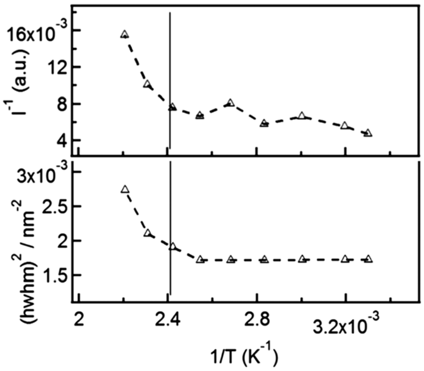

Fig. 15 The reciprocal of the maximum of scattering intensity (I^{-1}) and the square of half-width of half-maximum ($hwhm$)^2 as a function of inverse absolute temperature. The sample is a supramacromolecular ion gel with a weight ratio of VEAV : H : IL of 10 : 4 : 90 (see Fig. 14). The vertical line represents the temperature that induces a gel-to-liquid transition (T_{gel}; 141 °C). See also ref. 23.

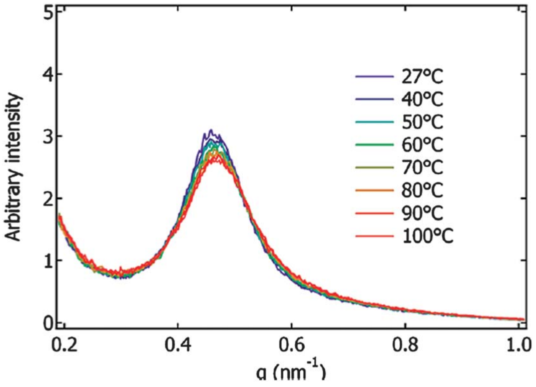

Fig. 16 SAXS profiles at various temperatures of supramolecular polymer gels formed from telechelic-type triblock copolymers connected by self-complementary hydrogen bonding. Reprinted with permission from ref. 35. Copyright 2009 American Chemical Society.

nanophase separation occurred in their supramolecular polymer gels, despite the gelation detected with a rheometer.[35] They observed correlation hole peaks[255] on SAXS profiles of their materials (Fig. 16), which suggested an electron density fluctuation between the non-covalent bonding units and the strands. Therefore, it should be noted that nanophase separation is not always induced at the time of gelation; its occurrence depends on the product of the effective interaction parameter (χ) and the degree of polymerization (N) between cross-links and strands, similar to the interaction observed in block copolymers. However, the nanophase separation phenomenon remains a fairly reliable indicator for this gelation, because the product is typically large in supramolecular polymer gel systems.

4. Viscoelasticity

A recent review on viscoelasticity of supramolecular polymer networks was presented by Seiffert and Sprakel that focused on dynamics.[256] Here, we summarize viscoelastic properties of stiffness, temperature dependence, damping performance, and robustness that are required to attain better supramolecular polymer gels.

4.1 Stiffness

It can be difficult to carry out tensile measurements on supramolecular polymer gels, because they tend to have little stiffness or toughness and they may not maintain their shape for a long time. The viscoelastic properties of these soft materials are best evaluated with shear measurements.

Several groups have carried out dynamic shear measurements in linear viscoelastic regimes.[257–263] In fact, we have performed studies on supramolecular polymer gels composed of well-defined macro-building blocks in an ionic liquid to determine the relationship between stiffness and molecular weight.[22,23] As mentioned in Section 3.2.1, we mixed macro-building blocks of VEAV triblock copolymers and H homopolymers in an ionic liquid, and networks were formed *via* hydrogen bonding. SAXS results strongly suggested that these networks comprised cross-links of a hydrogen-bonded V–H complex phase and strands of polyethyl acrylate (EA) that were soluble in the ionic liquid. We could roughly estimate stiffness (G_{x}), based on the assumption of an ideal (or Gaussian) network formation from the blend of H and bridging VEAV in an ionic liquid. In this ideal network, G_{x} is expressed as

$$G_{\mathrm{x}} = \nu k_{\mathrm{B}} T$$

here, ν denotes the number of elastically effective strands per unit volume, k_{B} is the Boltzmann constant, and T is the absolute temperature. At the appropriate stoichiometric ratio of V blocks and H homopolymers, a clear plateau was evident on curves of the storage modulus (G') and the loss modulus (G'').

The number of elastically effective strands per unit volume, ν, was derived as follows:

$$\nu = cN_A/M_x$$

where c is the concentration of elastically effective strands (*i.e.*, the concentration of bridging VEAV),[264,265] N_A is Avogadro's number, and M_x is the molecular weight of the molecules between cross-links. Note that experimental value of the plateau modulus (G_x) was around 3000 Pa (Fig. 17) and the calculated value is almost the same, approximately 2500 Pa. The applicability of this expression indicated that the supramolecular polymer gel was analogous to an ideal network at the molecular level. This is because the formation of supramolecular polymer networks proceeds slowly and homogeneously at the time of preparation. Note that the preparation procedure of the conventional covalently bonded polymer network produced with chemical reactions is quite different from that of supramolecular polymer networks. In any case, when the macro-building blocks are designed and synthesized precisely, then the desired stiffness of the gels can be available.

4.2 Temperature dependence

Supramolecular polymer networks can be formed homogeneously during the preparation procedure. The key to homogeneous network formation is the cross-linking, which depends on temporary and weak non-covalent bonding. In other words, by controlling the non-covalent bonding units, we can design the temperature dependence of the gel.

4.2.1 Gel–liquid transition temperature. The interaction strength of non-covalent bonding, particularly hydrogen bonding, is relatively high at low temperatures, and network cross-links are able to maintain shape. However, as the temperature increases, the non-covalent bonding strength weakens to the point that supramolecular cross-links will begin to fall apart; thus, the networks can collapse, and the macroscopic appearance will become a liquid. However, the gel–liquid transition temperature (T_{gel}) is difficult to determine from appearance alone. A rheometer is needed for a quantitative measure of the T_{gel}. Here, we define the T_{gel} of a supramolecular polymer gel as the temperature where the storage modulus G' (elasticity) and loss modulus G'' (viscosity) have the same value on dynamic temperature ramp tests. The moduli values depend on the amplitude of angular frequency; thus, the T_{gel}s from different samples should be acquired at the same angular frequency for comparison among samples. Although a T_{gel} does not represent all the properties related to the temperature dependency, it is easily understandable, and hence, it is a useful indicator for preparing gels.

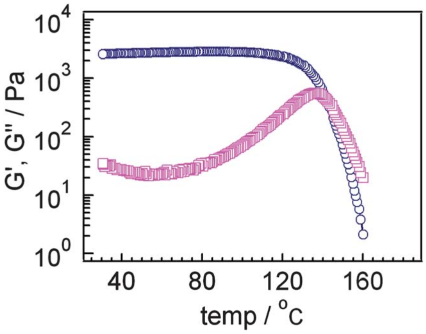

Fig. 17 Dynamic moduli of shear storage, G' (○), and loss, G'' (□), of a supramacromolecular ion gel as a function of temperature. The supramacromolecular ion gel was prepared by mixing a triblock copolymer (VEAV), poly(4-hydroxystyrene) (H), and an ionic liquid (IL). The weight ratio of VEAV : H : IL in the sample was 10 : 4 : 90. See also ref. 22 and 23.

To date, few studies have systematically run dynamic temperature ramp tests, because the tests are typically thought to provide only qualitative assessments by experts in the field of rheology. However, recent studies on supramolecular polymer gels composed of VEAV and H in an ionic liquid clearly showed the usefulness of the T_{gel} indicator. The T_{gel}s of supramolecular polymer gels could be increased systematically with increasing amounts of H cross-linker molecules; this indicated that, with larger amounts of H, higher energies were required to weaken the cross-link bonds. This suggested that the addition of more H induced a larger fraction of hydrogen bonding between V blocks and H homopolymers. Recently, it was shown that the T_{gel} also increased with the degree of hydrogen bonding units per cross-linker molecule (H), although an equal mass of H was added for gel preparation.[266,267] Those results indicated that the T_{gel} can be adjusted by designing the gel preparation conditions to achieve an appropriate degree of non-covalent bonding units per cross-linker molecule.

4.2.2 Time–temperature superposition (TTS). Compared to the few studies that used dynamic temperature ramp tests, more studies have used systematic dynamic frequency sweeps. The dynamic frequency sweep determines whether the time–temperature superposition (TTS) principle holds. The TTS master curve shows the change in a sample state at a given temperature over a given time. TTS master curves of supramolecular polymer gels were analysed to investigate their molecular motion, or gel dynamics. The results showed that supramolecular polymer gel systems exhibited TTS over a wide temperature range and the relaxation time varied over a wide time range. This result assumed that the networks were formed with cross-links of finite lifetimes. Clearly, this property arose from the non-covalent bonding features based on the number of non-covalent bonding units per cross-link.

4.3 Damping performance

Gel materials with high damping performance are attractive, because most other materials do not exhibit damping. Here, damping is defined as the suppression of vibration and noise by dissipating deformation energy. Damping performance can be estimated rheologically with the loss tangent, tan δ ($= G''/G'$). A nice study by Urayama *et al.*[268] showed improvement in damping performance with the use of a silicon elastomer; *i.e.*, a chemical gel in bulk solution. They prepared chemically bonded polymer networks by simultaneously reacting mono- and bifunctional precursors with trifunctional cross-linking agents. When mono-functional precursors reacted with the cross-linking agents, they could not extend the growth of the polymer networks; instead, they became dangling ends in the networks. This feature contributed to improving the damping performance of the material.

This concept was successfully applied to supramolecular polymer gels. In Fig. 18, the loss tangent changed as a function of temperature for gels composed of VEAV triblocks (or VEA diblocks) and H in an ionic liquid.[23] Here, the loss tangent depended on the stoichiometry of non-covalent bonding units and also on the amount of non-telechelic VEA. An appropriate stoichiometric balance could attain the most elastic state at temperatures lower than the T_{gel}, but inappropriate stoichiometric ratios produced dangling ends in the networks, leading to improved damping performance at $T < T_{gel}$. Homogeneous polymer networks are readily prepared with the preparation procedure described above; thus, supramolecular polymer gels are good candidates for materials with tuned damping performance.

4.4 Robustness

For practical applications, it is also important to note the robustness of supramolecular polymer gels. Estimation of the linear viscoelastic regime is one of the best ways to evaluate robustness. Unfortunately, in the gel state, supramolecular polymer gels have a very narrow linear viscoelastic regime, typically below approximately 10% strain. Fig. 19 shows dynamic amplitude sweeps of the gels in an ionic liquid (a)[23] and in water (b).[132] The drops in the G' modulus above a 10% strain may be due to loss of cross-linking or dissociation of non-covalent bonding induced by a large strain. In recent studies, the robustness of the gel state (at $G' > G''$) of supramolecular polymer gels was associated with non-Newtonian behaviour in the liquid state (at $G'' > G'$): shear-thickening and shear thinning phenomena.[269,270] These properties will be investigated in more detail with future studies.

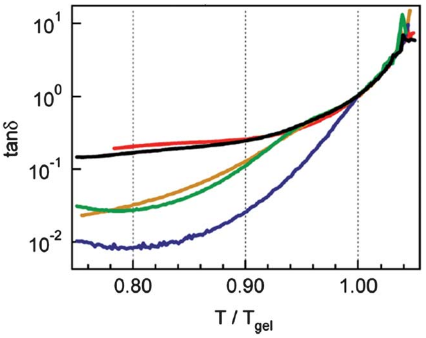

Fig. 18 Loss tangent (tan δ) of supramacromolecular ion gels as a function of normalized absolute temperature (T/T_{gel}). The supramacromolecular ion gels were prepared by mixing a triblock copolymer (VEAV), poly(4-hydroxystyrene) (H), and an ionic liquid (IL). Red, yellow, blue, and green curves represent supramacromolecular ion gels with VEAV : H : IL weight ratios of 10 : 1 : 90, 10 : 2 : 90, 10 : 4 : 90, and 10 : 8 : 90, respectively. The black curve represents a supramacromolecular ion gel made of VEA diblocks and H, where the concentration of VEA : H : IL was 10 : 4 : 90. Reprinted with permission from ref. 23. Copyright 2009 American Chemical Society.

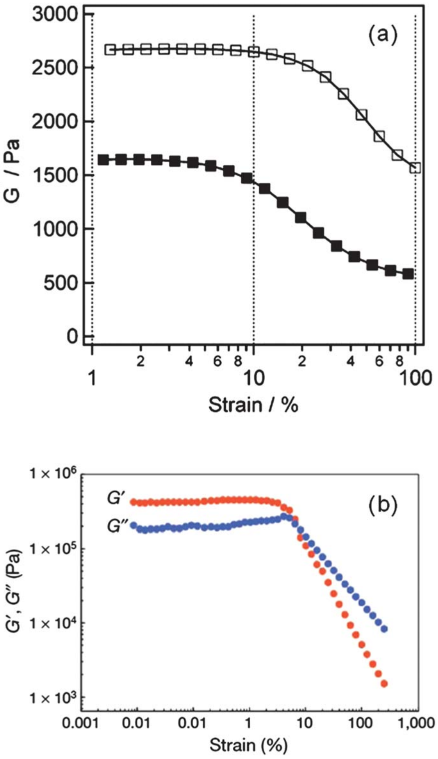

Fig. 19 Strain amplitude sweeps for testing gel robustness. Supramacromolecular ion gels were prepared by mixing triblock or diblock copolymers (VEAV or VEA, respectively) and poly(4-hydroxystyrene) (H) in an ionic liquid (IL). (a) The complex modulus of supramacromolecular ion gels of VEAV and H (□), and VEA and H (■) in an IL was tested; (b) storage (red) and loss (blue) moduli of supramolecular polymer gels in water were tested. Reprinted with permission from ref. 23 and 132. Copyright 2009 American Chemical Society and Copyright 2010 Nature Publishing Group.

5. Conclusions and future outlook

In this review, we discussed supramolecular polymer gels in terms of design, morphology, and rheology. The studies on morphology and rheology depended on the preparation; therefore, much effort has been devoted to determining simple, efficient procedures for preparing homogeneous supramolecular polymer gels. Thanks to that effort, many groups have produced supramolecular polymer gels and applied many different measurements. In particular, many basic rheological properties have been revealed. Although this review also summarized the data available on the basic features of gel viscoelasticity, many issues remain to be addressed for practical applications. Further fundamental studies are needed in the future to reveal more about these basic properties.

Although supramolecular polymer gels are interesting and should be useful materials for some applications, in themselves, they cannot be considered perfect materials. As mentioned in Section 4, these gels do not have sufficient robustness in the gel state. Furthermore, their physical properties lack outstanding optics, magnetism, electrical properties, *etc.*, because they are typically composed solely of organic materials, except in the case of supramolecular polymer gels with metal-to-ligand coordination. On the other hand, they do have novel properties, including a characteristic temperature dependence (self-healing and thermoresponsive properties), high damping performance, and controllable stiffness; these properties are lacking in other materials. Therefore, we propose three goals for improving the properties of supramolecular polymer gels. One is to incorporate covalently bonded cross-links into the supramolecular polymer networks.[34,271–276] The second is to hybridize the materials with inorganic components,[277–279] particularly metal or semiconductor nanoparticles.[280–284] The third is to use supramolecular polymer gels as thin films. Several groups are currently working on some improvements. We expect that changes which compensate for the deficits in supramolecular polymer gels will produce unprecedented materials with novel properties and functions in the future.

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Addition and correction

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