

Design and Properties of Supramolecular Elastomers

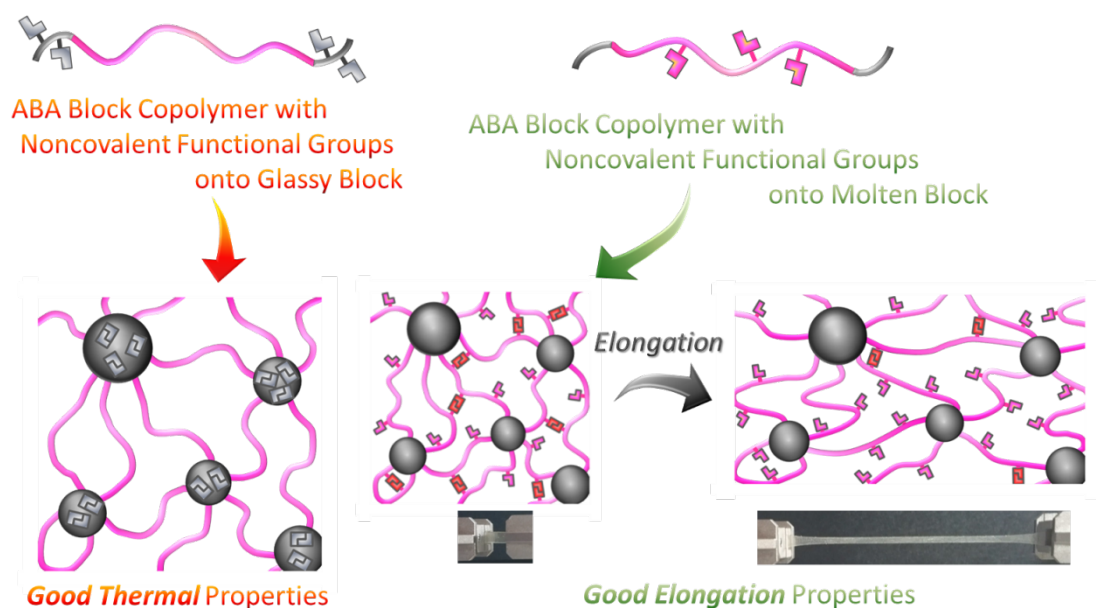
Takato Kajita, Atsushi Noro*, Yushu Matsushita

Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan *noro@nagoya-u.jp

Abstract

Supramolecular elastomers are supramolecular soft polymeric materials with both transient cross-links and (semi)permanent cross-links, where transient cross-links have a finite relaxation time and are typically composed of noncovalent bonds such as hydrogen bonds, metal–ligand coordination bonds, etc., whereas (semi)permanent cross-links such as covalent bonds, crystalline segments and glassy hard domains have an infinite relaxation time. Excellent elastomeric properties were induced by all the above molecular features. However, if soft polymeric materials have only supramolecular/transient cross-links with a finite relaxation time, the materials eventually flow within a finite time and cannot behave as elastomers; in other words, they are merely supramolecular polymers that have only transient cross-links or bonds. Therefore, the key to preparing higher-performance supramolecular elastomers is their molecular design. Here, we firstly review the fundamental design of supramolecular polymers to make the differences between supramolecular polymers and supramolecular elastomers clear. Second, we discuss the simultaneous incorporation of (semi)permanent cross-links and supramolecular cross-links into polymeric materials to prepare supramolecular elastomers. Finally we summarized their properties and potential applications.

Graphical Abstract



Keywords

Supramolecular Polymer, Supramolecular Cross-link, Supramolecular Elastomer.

1. Introduction

Cross-linked melt polymers at ambient temperature do not flow even in an infinite time because of network structures but show softness and stretchability; such materials are called elastomers [1-4]. These properties cannot be observed in stiff materials such as metals and ceramics; therefore, elastomers are used in various applications, such as in films [5-8], dampers [9-11], and adhesives [12,13]. The most familiar elastomers are rubber bands, pen grips [14], and vehicle tires [15]. Natural rubber is one of the most typical elastomers prepared via chemical cross-linking [16,17]. However, the elastomers with chemical cross-links of covalent bonds usually cannot be reprocessed, unfortunately [18]. Conversely, cross-links formed by intermolecular interactions such as hydrogen bonding [19-26], ionic bonding [27-35], metal–ligand coordination [36-45], and so on are reversible, and these can be called physical cross-links, which have been attracting researchers' attention in recent years.

Elastomeric materials with hard polymeric components (hard segments) and soft ones (soft segments) at ambient temperature exhibit good processability because they can flow when the hard segments become molten at high temperatures; such elastomeric materials are called thermoplastic elastomers (TPEs). Polyurethane [46,47] and ABA triblock copolymers are the most famous TPEs. In polyurethane, some urethane groups crystallize and behave as hard segments, whereas other groups, e.g., polyether parts, behave as soft segments. An ABA triblock copolymer composed of a glassy polymer component A and a molten polymer component B at ambient temperature is self-assembled into regularly periodic structures at a nanometer scale, i.e., nanophase separated structures [48-50] (conventionally-called microphase-separated structures [51,52] because they are microscopic), where glassy end block A becomes hard domains and melt middle block B becomes soft matrices that bridge the hard domains. Such block copolymer-based materials also exhibit elastomeric properties because A hard domains have an almost infinite relaxation time and B matrices are molten. Polystyrene-*b*-polybutadiene-*b*-polystyrene (SBS) [53,54] and polystyrene-*b*-polyisoprene-*b*-polystyrene (SIS) [55-57] are well-known ABA triblock copolymer TPEs, and they have been widely used in our daily lives and researched actively since they were first industrially produced in the 1960s.

Since around 2000, many studies on preparation of high-performance soft polymer materials using noncovalent interactions such as hydrogen bonding, ionic bonding, and metal–ligand coordination have been conducted. Supramolecular polymers are one of the hot topics in the research area of soft polymer materials. They are defined as a polymeric array built of monomeric units that are brought together through reversible secondary interactions (supramolecular interactions) [58-60]. Even if the monomeric unit is a polymer, a self-assembled polymeric array through supramolecular interactions can also be regarded as a supramolecular polymer. The interaction in

supramolecular polymers is sometimes highly directional but there are also less directional interactions in supramolecular polymers, and such interactions behave as supramolecular/transient cross-links that form transient polymer network. However, transient polymer network formed by only supramolecular cross-links or bonds does not enable the substances to exhibit sufficient elastomeric properties, because substances bearing only supramolecular cross-links flow within a finite time and cannot behave as conventional elastomers [61,62]; i.e., they cannot be regarded as “supramolecular elastomers”. Therefore, to prepare supramolecular elastomers, it is also necessary to incorporate (semi)permanent cross-links, such as crystalline segments, glassy hard domains, and covalent bonds, which have an almost infinite relaxation time. In other words, to attain supramolecular elastomers with good mechanical properties, molecular design is crucial. It should be noted that supramolecular polymers or supramolecular elastomers with some solvents can be regarded as supramolecular polymer gels [63]; the former have a finite relaxation time and finally flow like supramolecular polymers in bulk, but the latter have an infinite relaxation time and never flow, so they exhibit elastomeric properties like supramolecular elastomers. In this review, to make the differences between supramolecular polymers and supramolecular elastomers clear, we firstly focus on the fundamental design of supramolecular polymers composed of end-functionalized molecules or random copolymers with noncovalent bonding units. Then, we review the studies on supramolecular elastomers that have (semi)permanent cross-links as well as supramolecular cross-links. Finally, we discuss the properties and potential applications of supramolecular elastomers by comparing them with conventional elastomers.

2. Supramolecular Polymers

2.1 Supramolecular Polymers Composed of End-functionalized Low-molecular-weight Molecules or

Polymers

Melt low-molecular-weight compounds or polymers at room temperature, which have noncovalent bonding units at both chain ends, form noncovalent bonds among them. Molecular assemblies via noncovalent bonding behave as high-molecular-weight polymers; therefore, they are called supramolecular polymers, and there are a lot of studies about supramolecular polymers [64-73]. However, in some studies the materials studied were called supramolecular elastomers even without (semi)permanent cross-links, but they should be called supramolecular polymers because they flow within a finite relaxation time.

One famous study on supramolecular polymers was reported by Meijer and coworkers in 1997. They synthesized polydimethylsiloxane ($M_n = 6,000$) both-end terminated with 2-ureido-pyrimidone as a hydrogen bonding group and investigated its intrinsic viscosity and dynamic viscoelasticity [74]. In 2000, they also carried out dynamic mechanical analysis (DMA) of poly(ethylene-butylene) ($M_n = 3,500$) both-end terminated with 2-ureido-4[*IH*]-pyrimidinone [75]. In both cases, they found that incorporating hydrogen bonding groups increased the materials' intrinsic viscosity and rubbery plateaus was observed in the dynamic mechanical spectra; in other words, these materials behave as high-molecular-weight polymer melt. However, their properties are clearly different from those of typical elastomers, and they flow easily at relatively low temperatures such as 30–40 °C due to not having any permanent cross-links.

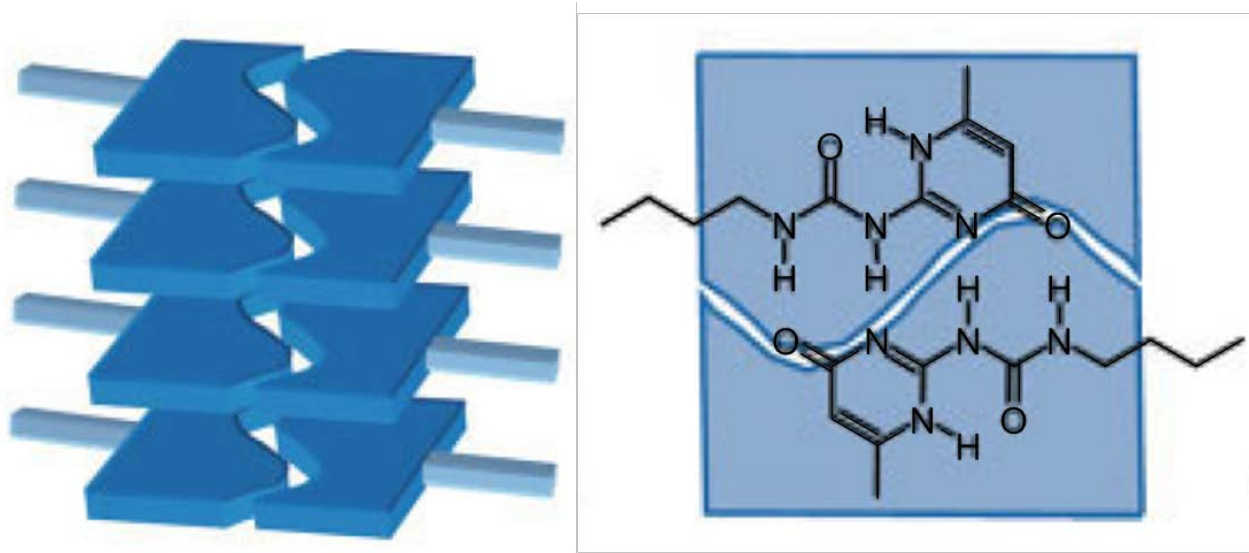


Figure 1. Illustration of hydrogen bonds between 2-ureido-4[1H]-pyrimidinone groups. Reprinted with permission from Ref. [67]. Copyright 2008 John Wiley & Sons, Inc.

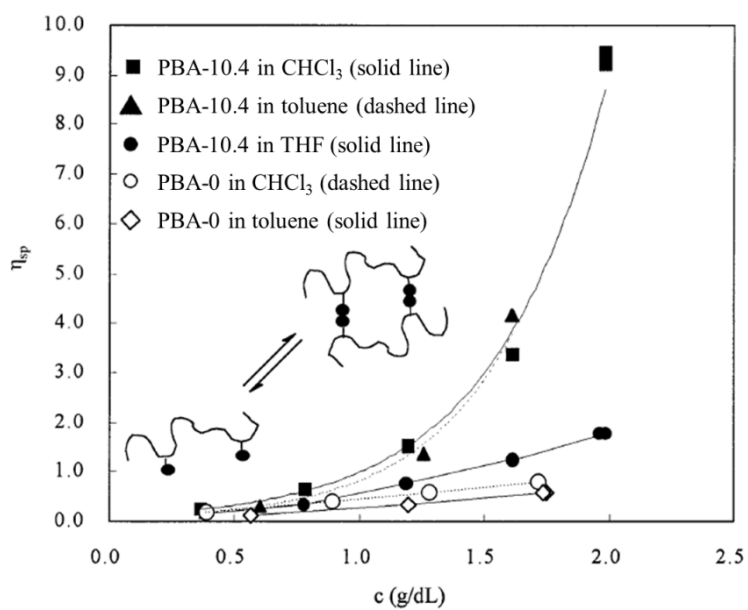
2.2 Supramolecular Polymers Composed of Randomly-functionalized Copolymers

Elastomers are necessarily composed of melt polymers to attain softness and stretchability. If noncovalent bonding functional groups are incorporated into a melt polymer at room temperature, such supramolecular soft polymer materials seem to be supramolecular elastomers [76-86]. However, such materials are not supramolecular elastomers exactly but should be regarded as supramolecular polymers because the materials do not have permanent cross-links or hard domains with an infinite relaxation time. It should be noted that such materials without permanent cross-links can flow within a finite time.

As an example of such materials, Long and coworkers synthesized supramolecular melt substances composed of random copolymer ($M_n = 38,000\text{--}55,000$) with self-complementary multiple hydrogen bonding (SCMHB) groups (0–10.4 mol%) by free radical copolymerization of *n*-butyl acrylate and methacrylate monomers that can form SCMHB [87]. For PBA-0 (fraction of SCMHB is 0 mol%, $T_g = -50\text{ }^\circ\text{C}$) and PBA-10.4 (fraction of SCMHB

is 10.4 mol%, $T_g = -23\text{ }^{\circ}\text{C}$), PBA-10.4 with hydrogen bonding groups in a poorly polar solvent (e.g., chloroform and toluene) exhibit higher viscosity than PBA-0 when the concentration of polymers is the same. Conversely, in a polar solvent (THF), both of them exhibit almost the same viscosity at any concentrations. Melt rheological measurements were also carried out for PBA-0, PBA-2.5 (fraction of SCMHB is 2.5 mol%, $T_g = -46\text{ }^{\circ}\text{C}$), and PBA-3.3 (fraction of SCMHB is 3.3 mol%, $T_g = -43\text{ }^{\circ}\text{C}$). The measurements revealed that the samples' viscosity decreased as temperature increased from -10 to $10\text{ }^{\circ}\text{C}$, but it remained constant in the temperature range from 10 to $70\text{ }^{\circ}\text{C}$. It should be noted that the absolute value of viscosity of PBA-2.5 was tenfold of viscosity of PBA-0 in the temperature range from 10 to $70\text{ }^{\circ}\text{C}$, and the viscosity of PBA-3.3 was a hundred times of that of PBA-0 in the same temperature range. In a higher temperature range, the viscosity of PBA-2.5 and that of PBA-3.3 became smaller, and approached that of PBA-0. Thus, these results indicate that hydrogen bonds formed by SCMHB units begin to dissociate at $70\text{ }^{\circ}\text{C}$ or above. Although, the materials composed of random copolymers exhibited high viscosity, they were still fluid because they did not form permanent polymer networks with an infinite relaxation time; hence, they could not be regarded as elastomers.

Scheme 1. Synthesis scheme of poly(*n*-butyl acrylate)-*co*-poly(SCMHB MA). Reprinted with permission from Ref. [87]. Copyright 2003 American Chemical Society.



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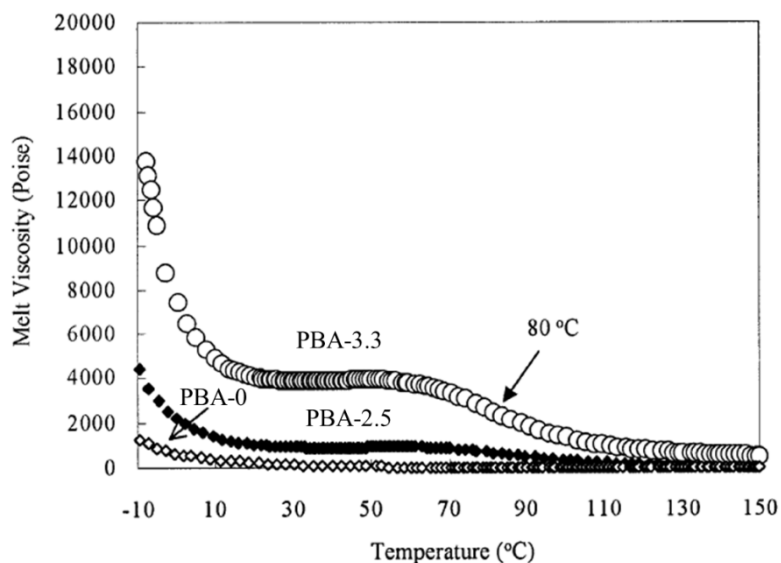


Figure 3. The melt viscosity of PBA-0, PBA-2.5, and PBA-3.3 in the temperature range from -10 to 150 $^{\circ}\text{C}$.

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Long and coworkers also studied similar systems [88]. They synthesized poly(2-ethylhexyl methacrylate-*co*-2-ureido-4[*IH*]-pyrimidone methacrylate) (PEHMA-*co*-UPyMA) with a number-average molecular weight of about 100 k using free radical copolymerization. 2-Ureido-4[*IH*]-pyrimidone (UPy) was incorporated into the side chain of copolymers as a hydrogen bonding functional group, and the mole fraction of UPy in the copolymers was varied from 0 mol% to 10 mol%. According to differential scanning calorimetry (DSC) analysis, T_g increased with the UPy fraction due to the formation of self-complementary hydrogen bonds of UPy, and the copolymers with a high UPy fraction finally became glassy polymers. Thus, these results suggest that only incorporation of many hydrogen bonding groups into molten polymers cannot make materials elastomeric.

Scheme 2. Synthesis scheme of PEHMA-*co*-UPyMA. Reprinted with permission from Ref. [88]. Copyright 2005

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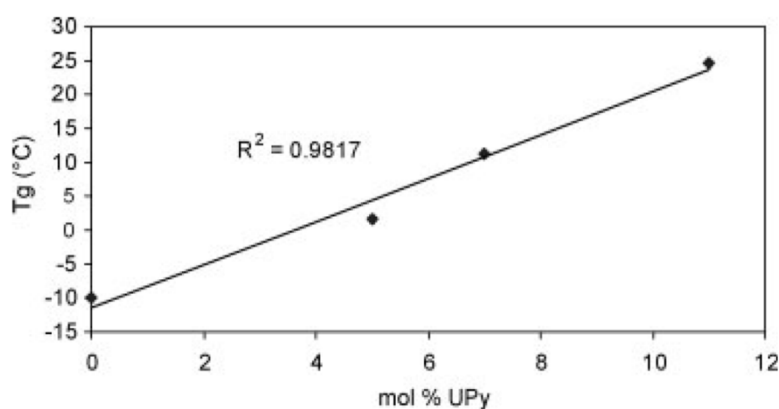
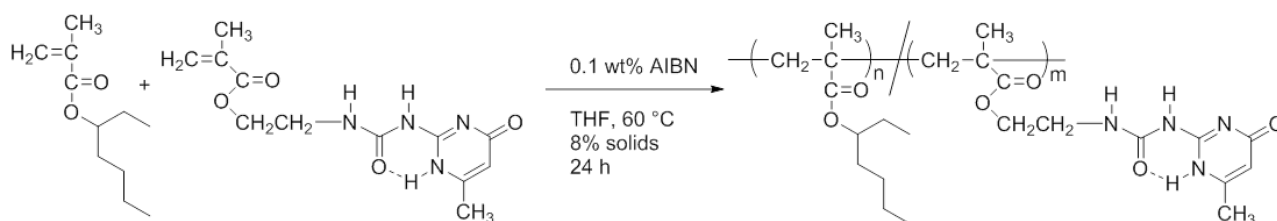


Figure 4. Relationship between T_g and the UPy mol% in copolymers. Reprinted with permission from Ref. [88].

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3. Supramolecular Elastomers

3.1 Supramolecular Elastomers with Crystalline Hard Segments

Although a lot of studies on supramolecular polymers and related materials have been conducted since approximately 2000, studies on supramolecular elastomers had already been reported in the 1990s [89,90]. In 1996, Stadler and coworkers synthesized melt polyisobutylene ($M_n = 4,800$) terminated with 4-urazoylbenzoic acid (U4A) as a hydrogen bonding functional group, and they investigated its mechanical properties [91]. In this

system, the melting point was around 400 K (127 °C), because the amide group and the carboxylic acid formed hydrogen bonds, producing crystalline clusters of U4A groups due to their high crystallizability. The crystalline clusters have an infinite relaxation time, which is one important feature of supramolecular elastomers. The results of DMA exhibited the rubbery plateau, where the storage modulus was constant, 6 MPa, from 250 K (−23 °C) to 350 K (77 °C). Similarly, as another study on supramolecular elastomers with crystalline segments, Chino and Ashiura introduced acid anhydride into polyisoprene ($M_w = 390,000$), and then the product was reacted with 3-amino-1,2,4-triazole [92]. In this way, they incorporated carboxylic acid, amide groups, and amine groups into polyisoprene, which formed hydrogen bonding. The melting point of the materials was at 185 °C after introducing functional groups by DSC measurements; in other words, crystallization was confirmed. These materials behaved as elastomers because they had semipermanent cross-links of crystalline segments formed by hydrogen bonding. Unfortunately, the materials studied merely showed similar mechanical properties to those of TPU [93-99]. However, these results suggest that incorporation of not only supramolecular cross-links, but also semipermanent cross-links such as crystalline segments, is very important and useful for preparing supramolecular elastomers with good mechanical properties.

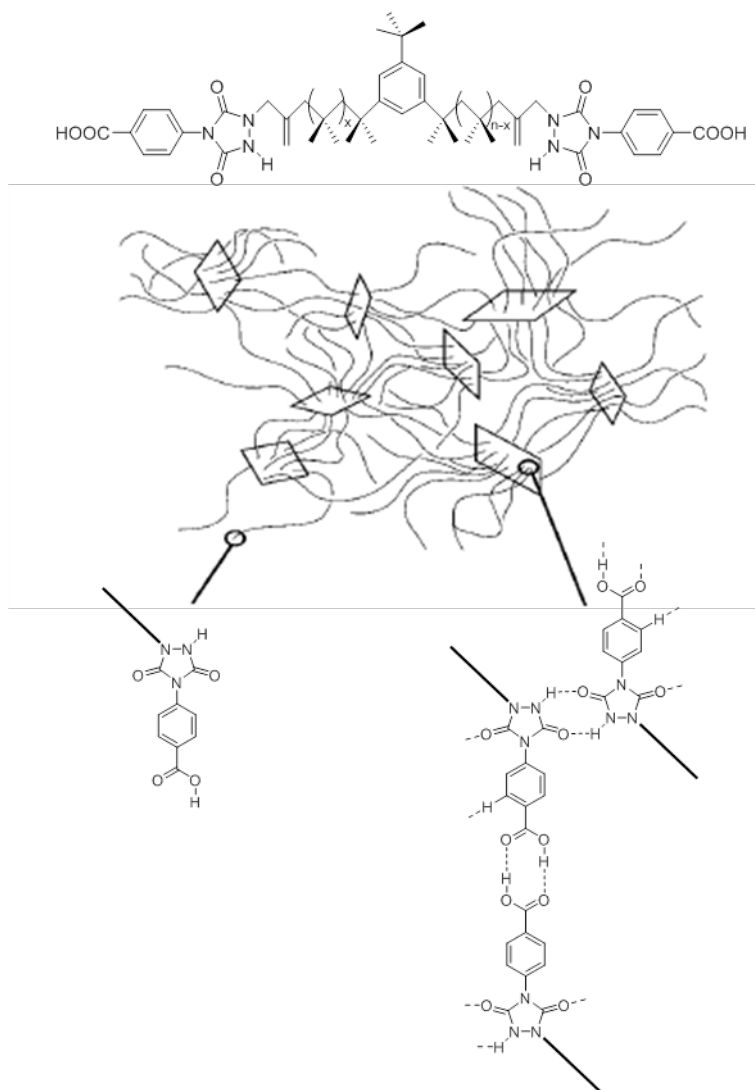


Figure 5. Illustration of polyisobutylene network with 4-urazoylbenzoic acid as a functional group. Crystalline clusters are formed by hydrogen bonding. Reprinted with permission from Ref. [91]. Copyright 1995 American Chemical Society.

3.2 Supramolecular Elastomers Bearing Both Covalent Cross-links and Supramolecular Cross-links

As described above, semipermanent cross-links are essential for the preparation of supramolecular elastomers.

There are also some studies using both supramolecular cross-links and permanent cross-links of covalent bonds

[100-109]. The soft polymer materials with only permanent cross-links are regarded as conventional elastomers

such as rubbers, which do not flow in an infinite time because all the cross-links in the elastomers are covalent bonds that have an infinite relaxation time. Taking account of the definition of conventional elastomers, the soft polymer materials with both permanent cross-links and supramolecular/transient cross-links can be called supramolecular elastomers.

Leibler and coworkers prepared an amorphous mixture composed of diacid and triacid derived from natural renewable resources (vegetable oils), and the mixture was condensed with diethylene triamine and further reacted with urea. In this way, they synthesized a mixture composed of low-molecular-weight molecules incorporating amidoethyl imidazolidone (UDETA), which could form hydrogen bonding between end groups of the molecules. Thus, this material had branches serving as chemical cross-links with an infinite relaxation time [110,111]. The reacted mixture was glassy with $T_g = 28\text{ }^{\circ}\text{C}$, and the T_g was decreased to $8\text{ }^{\circ}\text{C}$ by mixing with dodecane. The mixture's mechanical properties were investigated by DMA and tensile tests. According to DMA, its relaxation time was $3 \times 10^6\text{ s}$, i.e., a few weeks, at $50\text{ }^{\circ}\text{C}$, and a rubbery plateau region with a storage modulus of $3 \times 10^4\text{ Pa}$ was observed. Thus, the mixture was substantially elastomeric due to presence of permanent cross-links, and therefore different from the above-described supramolecular polymers. In addition, the tensile tests revealed that the mixture's maximum stress was 3.5 MPa , and its elongation at break was about $600\text{ }\%$. Moreover, the mixture showed good stretchability, that is, its residue strain was below $5\text{ }\%$ after a constant strain of $300\text{ }\%$ was released. Furthermore, when a broken sample was placed into contact with fractured surfaces and left for 180 min , it showed self-healing, i.e., its mechanical properties were almost the same as those of an unbroken sample. The mixture exhibited good elastomeric performance in these points; therefore, the mixture can be called supramolecular elastomers. Nevertheless, in terms of mechanical properties, the performance of the mixture was

not better than that of conventional elastomers, and it did not have thermoplasticity because of its covalent bonded cross-links and network.

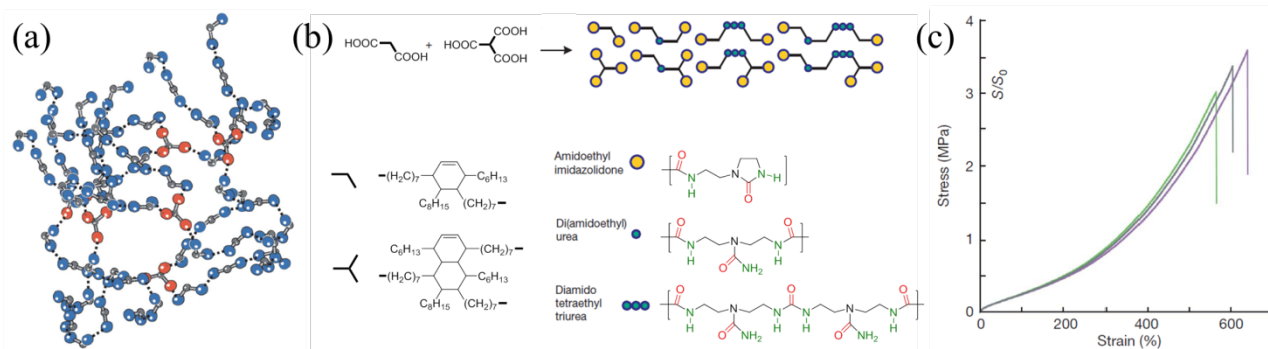


Figure 6. Illustration of supramolecular elastomers bearing both covalent cross-links and supramolecular cross-links. (a) Schematic view of network of both covalent cross-links and supramolecular cross-links. (b) Chemical structures of the reacted mixture. (c) Stress-strain curves of the supramolecular elastomer. Data for three samples are shown. Reprinted by permission from Macmillan Publishers Ltd: Nature Ref. [110], copyright 2008.

Additionally, Leibler and coworkers synthesized similar mixtures with carboxylic acids and amide groups, and then the mixtures were reacted with diglycidyl ether of bisphenol A (DGEBA) that is used to produce an epoxy resin [112]. In this way, they prepared supramolecular polymeric materials with a hybrid network composed of both chemical cross-links with an infinite relaxation time, and physical cross-links of hydrogen bonding, i.e., supramolecular cross-links with a finite relaxation time. The dynamic mechanical analysis of all the samples showed a glassy region with the storage modulus of 2 GPa below 30 °C and a sudden drop of the storage modulus derived from a glass transition at around 30–50 °C. The sample with 10 mol% amide group per carboxylic acid group (HN-10) had a rubbery plateau in the temperature range from 50 to 130 °C or higher. On the other hand, the sample with 50 mol% amide group per carboxylic acid group (HN-50) reached a flow region at 50 °C or higher

because of incomplete network formation by chemical cross-links. Although the storage modulus was about 10^5 to 10^6 Pa in the rubbery plateau of HN-10, tensile tests for HN-10 revealed its maximum stress of 1.3 MPa and breaking elongation of only 100 %; therefore, the mechanical properties were not superior to those of conventional elastomers, either. In short, incorporating covalent bond cross-links with an infinite relaxation time into supramolecular polymer materials can make them supramolecular elastomers, and in some cases supramolecular elastomers had a self-healing ability. However, in terms of mechanical properties, the supramolecular elastomers of the above materials do not surpass those of conventional covalent bonded elastomers or TPEs, and they do not have thermoplasticity, either.

3.3 ABA Triblock Copolymers-based Supramolecular Elastomers

We already reviewed supramolecular elastomers with crystalline parts or covalent bonds as (semi)permanent cross-links that have an almost infinite relaxation time. It should be noted that glassy hard domains formed by van der Waals forces can also be used as semipermanent cross-links. Therefore, if noncovalent bonds are incorporated into ABA triblock copolymers serving as TPEs, the block copolymer-based TPEs become supramolecular elastomers, and are expected to show improved mechanical properties by reinforcement of polymer network via noncovalent bonding. There are two parts where noncovalent bonds can be introduced: one is the glassy end block A and the other is the molten middle block B. Here, we review above two cases, i.e., supramolecular TPEs with noncovalent bonds onto the glassy end block A and the molten middle block B.

3.3.1 Supramolecular Elastomers with Noncovalent bonds onto Glassy Hard Domains

In an ABA triblock copolymer-based TPE composed of incompatible two polymers, the glassy end block A is

self-assembled into the glassy domain via van der Waals forces, and the domains serve as the cross-links with an almost infinite relaxation time. Fracture of ABA triblock copolymer-based TPEs is supposed to be breaking of the glassy domains formed by van der Waals forces at the molecular level. Thus, the mechanical properties can be enhanced if the hard domains are reinforced by introducing hydrogen bonds or coordination bonds [113-115].

Long and coworkers prepared supramolecular thermoplastic elastomers (supramolecular TPEs) bearing supramolecular cross-links of hetero-complementary hydrogen bonds onto their glassy blocks with an almost infinite relaxation time [116]. Specifically, they synthesized two ABA triblock copolymers, where the glassy end blocks were poly(9-vinylbenzyladenine) or poly(1-vinylbenzylthymine), and the melt middle block was poly(*n*-butyl acrylate). Here, the triblock copolymer with adenine units is called Ad-B-Ad, whereas the triblock copolymer with thymine units is called Thy-B-Thy. The total number average molecular weights of Ad-B-Ad and Thy-B-Thy were 66,900 and 72,700, respectively, and the number average molecular weights of their melt middle blocks were 62,300 and 69,900, respectively. DMA was performed for Ad-B-Ad, Thy-B-Thy, and the supramolecular thermoplastic elastomer composed of Ad-B-Ad/Thy-B-Thy, where the ratio of adenine and thymine was 1:1. Ad-B-Ad generated weak self-complementary hydrogen bonding between adenine units, exhibiting the glassy region below $-40\text{ }^{\circ}\text{C}$. The glass transition region, where the modulus decreased suddenly from -40 to $-10\text{ }^{\circ}\text{C}$, was also observed, and the rubbery plateau was attained until $130\text{ }^{\circ}\text{C}$. As the temperature increased above $130\text{ }^{\circ}\text{C}$, the modulus decreased again because of the T_g of the end blocks, i.e., appearance of the flow region. Similarly, Thy-B-Thy also showed the glassy region below $-40\text{ }^{\circ}\text{C}$, the glass transition region from -40 to $-10\text{ }^{\circ}\text{C}$, the rubbery plateau up to $100\text{ }^{\circ}\text{C}$, and the flow region above $130\text{ }^{\circ}\text{C}$. The Ad-B-Ad/Thy-B-Thy mixture with the adenine:thymine ratio of 1:1 after annealing exhibited almost the same behavior as neat Ad-B-Ad

or neat Thy-B-Thy for the glassy region and the glass transition region; on the other hands, the mixture of Ad-B-Ad/Thy-B-Thy had a rubbery plateau up to 150 °C. This means that the mixture flew only at higher temperatures. The results suggested that the mixture of Ad-B-Ad/Thy-B-Thy generated strong hetero-complementary hydrogen bonding between adenine and thymine, which resulted in a T_g increase in the glassy domain. Thus, formation of supramolecular cross-links of hydrogen bonds in the hard domain gave more thermally stable TPEs that did not flow easily. However, Ad-B-Ad, Thy-B-Thy, and Ad-B-Ad/Thy-B-Thy showed almost the same storage modulus, around 0.1 MPa in rubbery plateau region. Therefore, mechanical property enhancement at ambient temperature could hardly be seen.

Scheme 3. (a) Synthesis scheme of Ad-B-Ad or Thy-B-Thy. (b) Schematic representation of hydrogen bonding between Ad-B-Ad and Thy-B-Thy. Reprinted with permission from Ref. [116]. Copyright 2007 American Chemical Society.

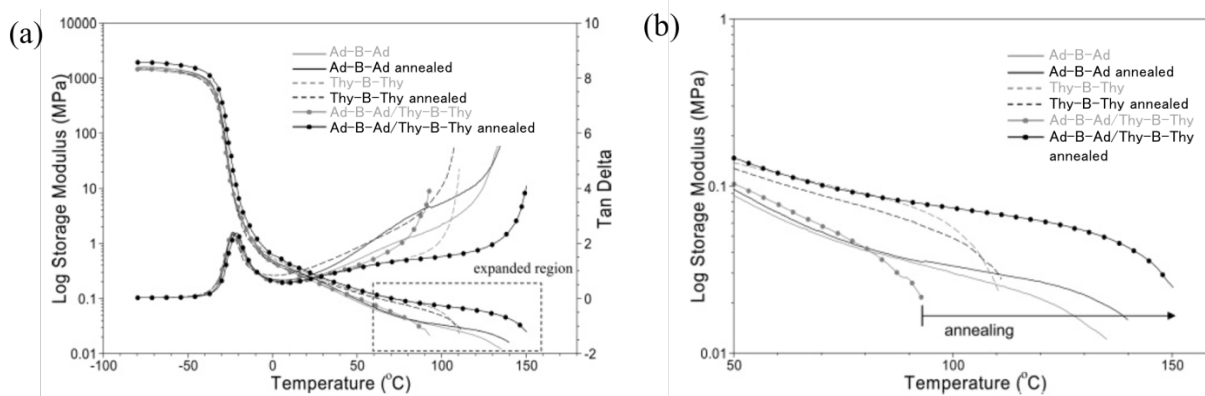
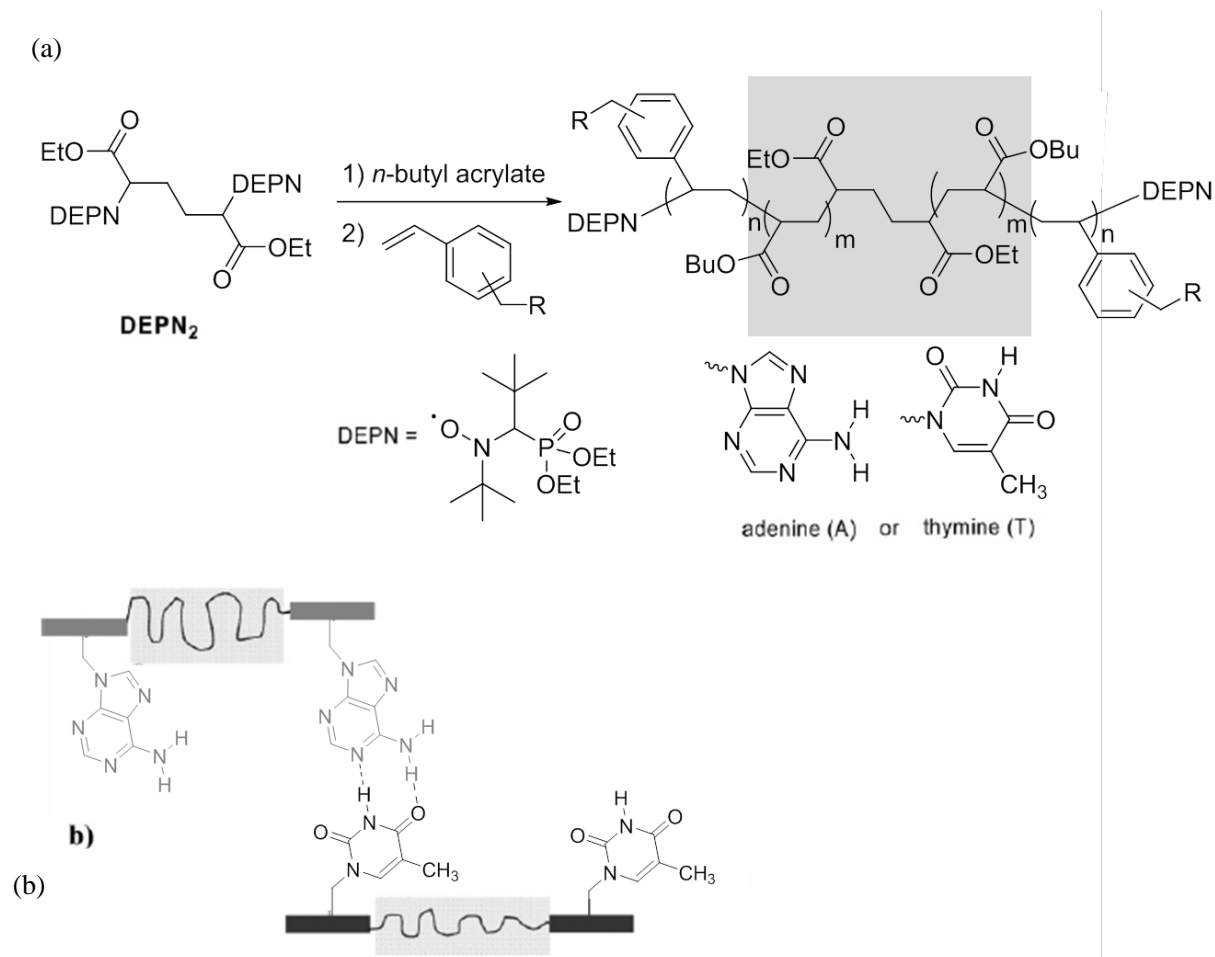


Figure 7. Dynamic mechanical analysis of Ad-B-Ad, Thy-B-Thy, and the mixture of Ad-B-Ad/Thy-B-Thy. (a)

Storage modulus and $\tan \delta$ against temperature. (b) Expansion of the graph of storage modulus at high

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Hawker, Kramer, and coworkers synthesized ABA triblock copolymers composed of molten hydrogen-bonded block A and molten nonhydrogen-bonded block B. Block A was a random copolymer with 2-ureido-4[*IH*]-pyrimidinone groups that form self-complementary hydrogen bonding, and block B was a poly(*n*-butyl acrylate) homopolymer [117]. In this case, both the end block A and the middle block B were in the molten state. As expected, the triblock copolymer-based materials showed fluidity, and could not be regarded as elastomers. Taking account of the results mentioned above, it is suggested that presence of the glassy block serving as semipermanent cross-links with an almost infinite relaxation time is essential for preparing supramolecular elastomers using triblock copolymers.

Scheme 4. Synthesis scheme of ABA triblock copolymers composed of molten, hydrogen-bonded block A and molten, nonhydrogen-bonded block B. Reprinted with permission from Ref. [117]. Copyright 2009 American Chemical Society.



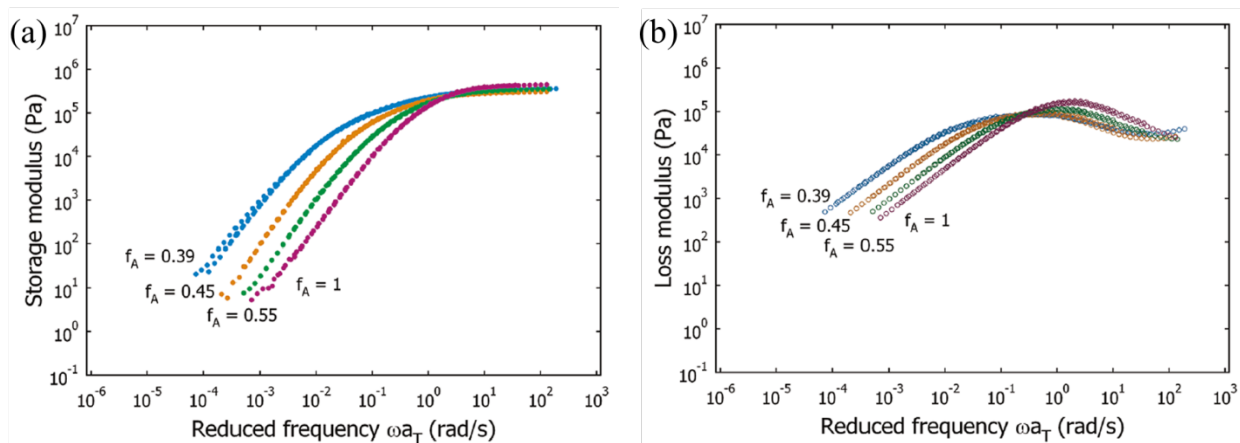


Figure 8. Master curves of dynamic mechanical analysis of ABA triblock copolymers composed of a molten hydrogen-bonded block A and a molten nonhydrogen-bonded block B. (a) Storage modulus vs. reduced frequency. (b) Loss modulus vs. reduced frequency. f_A represents the weight fraction of the end block A.

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To prepare higher performance supramolecular TPEs, our research group synthesized an ABA triblock copolymer of poly(4-vinylpyridine)-*b*-poly(*n*-butyl acrylate)-*b*-poly(4-vinylpyridine) (P-B-P), where the total number-average molecular weight was 30,000, and the number-average molecular weight of the middle block was 25,000. Then, a supramolecular thermoplastic elastomer of P-B-P/ ZnCl_2 was prepared by introducing zinc chloride (II) (ZnCl_2) selectively into the glassy P blocks via metal–ligand coordination [118]. Neat P-B-P before incorporating ZnCl_2 showed the glass transition region at around T_g of the middle block, between -40 and -20 °C, and the rubbery plateau region with constant storage modulus of 1 MPa was observed up to 90 °C. Above 90 °C, the flow region appeared due to reaching the T_g of the P end blocks. On the other hand, P-B-P/ ZnCl_2 after incorporating ZnCl_2 indicated that the rubbery plateau region continued over 130 °C, which suggested an increase in the T_g of the hard domain due to generation of metal–ligand coordination in the domain. However, similar to

the system by Long and coworkers, the storage modulus in the rubbery plateau region was almost unchanged before the introduction of ZnCl_2 , and there was no significant change in mechanical properties such as the Young's modulus, the breaking elongation, etc. at room temperature between before and after incorporating ZnCl_2 (the results are not shown here).

As mentioned above, for the ABA triblock copolymer-based TPEs, the supramolecular elastomers bearing noncovalent bonds in the hard domains with an almost infinite relaxation time did not show enhanced elongation properties at room temperature. This was probably because segments of the glassy end blocks were originally frozen. In other words, hard domains with only van der Waals forces were sufficient to attain effective semipermanent cross-links, and the hydrogen bonding or metal–ligand coordination, generated into the glassy domains had little influence on the elongation properties at room temperature, and could not be effectively utilized for enhancing the elongation properties. However, it should be noted that the thermostability can be improved by incorporating noncovalent bonds into the hard domains.

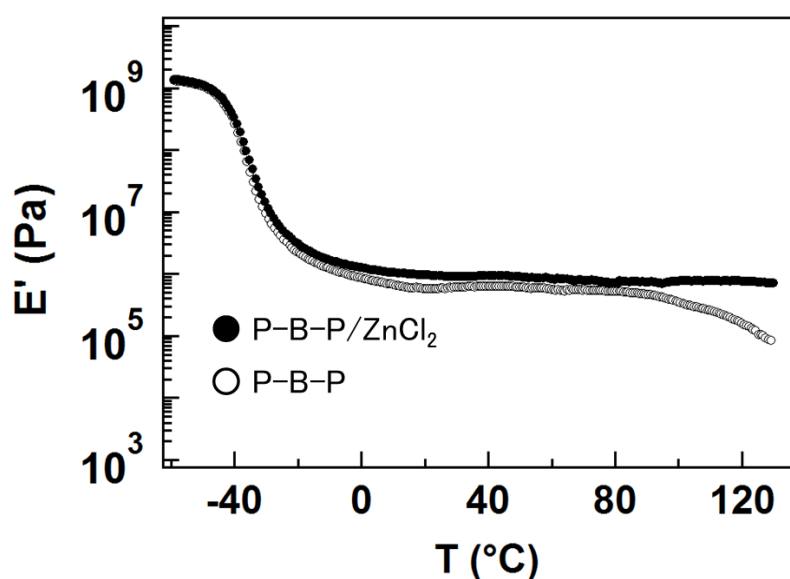


Figure 9. Storage modulus spectra of P-B-P/ZnCl₂ and P-B-P obtained by dynamic temperature ramp tests.

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3.3.2. Block Copolymer-based Supramolecular Elastomers with Noncovalent-bonded Soft Block Chains

3.3.2.1 Comparison between Block Copolymer-Based Supramolecular Thermoplastic Elastomer and Conventional ABA Triblock Copolymers-Based TPE

Even though the noncovalent bonds were incorporated into the glassy end blocks of the ABA triblock copolymers, their elongation properties were not significantly enhanced at room temperature, because the hard domains with an almost infinite relaxation time were originally frozen. Therefore, noncovalent bonds such as hydrogen bonds with a finite relaxation time onto the melt middle block might have greatly affected the elongation properties. Thus, ABA triblock copolymers with hydrogen-bonded amide groups into molten middle block B were synthesized, and the effect of the hydrogen bonds in the soft middle block on the elongation properties was investigated [118]. Specifically, poly(4-vinylpyridine)-*b*-poly(*n*-butyl acrylate-*co*-acrylamide)-*b*-poly(4-vinylpyridine) triblock copolymer (P-Ba-P) was synthesized with reversible addition–fragmentation chain transfer (RAFT) polymerization. As a control sample, poly(4-vinylpyridine)-*b*-poly(*n*-butyl acrylate)-*b*-poly(4-vinylpyridine) (P-B-P) having the molecular weight and composition similar to that of P-Ba-P was also synthesized. The total number-average molecular weight of both P-Ba-P and P-B-P was about 30,000, and the number-average molecular weight of their middle block was about 25,000. The composition of the glassy end block and the nanophase separated structures were also nearly the same for both P-Ba-P and P-B-P. The molar ratio of acrylamide units in the Ba middle block of P-Ba-P was 15 mol%.

As for P-B-P without amide groups, the glassy region was observed below $-40\text{ }^{\circ}\text{C}$, then the storage modulus sharply decreased from -40 to $-20\text{ }^{\circ}\text{C}$, and the rubbery plateau region with the constant modulus appeared until $90\text{ }^{\circ}\text{C}$. Then, the storage modulus decreased again from $90\text{ }^{\circ}\text{C}$, because the T_g of the P end blocks was reached. Thus, the P-B-P showed almost the same mechanical properties as those of the conventional block copolymer-based TPEs. On the other hand, P-Ba-P showed the glassy region up to $-20\text{ }^{\circ}\text{C}$. Above $-20\text{ }^{\circ}\text{C}$, the glass transition region of the Ba middle block began, but the storage modulus decreased more gently compared to that of P-B-P, i.e., the glass transition region was from -20 to $20\text{ }^{\circ}\text{C}$. Above $20\text{ }^{\circ}\text{C}$, the rubbery plateau region was seen, but it was different from that of P-B-P; the storage modulus was not constant but gradually decreased from 10^7 to 10^6 Pa . Above $90\text{ }^{\circ}\text{C}$, the modulus dropped sharply again, because the temperature reached the T_g of the P end block. One important feature of P-Ba-P is that the glass transition region was wider than that of P-B-P due to the formation of hydrogen bonds in the Ba middle block. In addition, the modulus of the rubbery plateau depended on temperature. This is also explained by hydrogen bonds of amide groups introduced into the Ba soft middle block, which serve as thermoresponsible dynamic cross-links (i.e., supramolecular cross-links). To investigate mechanical properties further, tensile tests with an initial strain rate of 0.014 s^{-1} (elongation rate of 0.167 mm/s for a sample length of approx. 12 mm) were carried out at room temperature for both P-Ba-P and P-B-P. The results of the tensile tests for P-B-P showed that the Young's modulus, the elongation at break, the maximum stress, and the toughness estimated from the area under the stress-strain curve were 0.60 MPa , 25% , 0.11 MPa , 0.020 MJ/m^3 , respectively, and all these values were not adequate for elastomers. This is probably because of the small total molecular weight. On the other hand, P-Ba-P had much better elongation properties compared to P-B-P, i.e., the Young's modulus, the elongation at break, the maximum stress, and toughness were

1.9 MPa, 201 %, 2.6 MPa, 2.8 MJ/m³, respectively. The molecular weight and the nanophase-separated structure of P-Ba-P were almost the same as those of P-B-P; hence, the difference of mechanical properties probably resulted from the incorporation of the amide groups into the melt middle block. Namely, hydrogen bonds formed by introduction of the amide groups resulted in an increase in the apparent cross-linking density, which induced an increase in the generated stress. The stretchability was also enhanced because the hydrogen bonds that can be broken/dissociated preferentially prevented the stress concentration to the P glassy domains during elongation. Overall, enhancement of all the elongation properties was attained. Recently, other block copolymer-based supramolecular elastomers were investigated by using different kind of block copolymers [119].

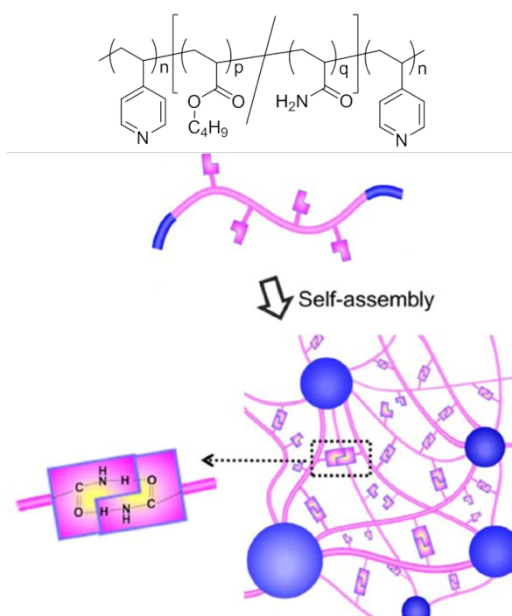


Figure 10. Chemical structure and schematic illustration of a P-Ba-P. The P glassy domains are illustrated as blue spheres while the Ba middle block and acrylamide units are drawn as pink lines and pink “L-type” blocks, respectively. Reprinted with permission from Ref. [118]. Copyright 2015 American Chemical Society.

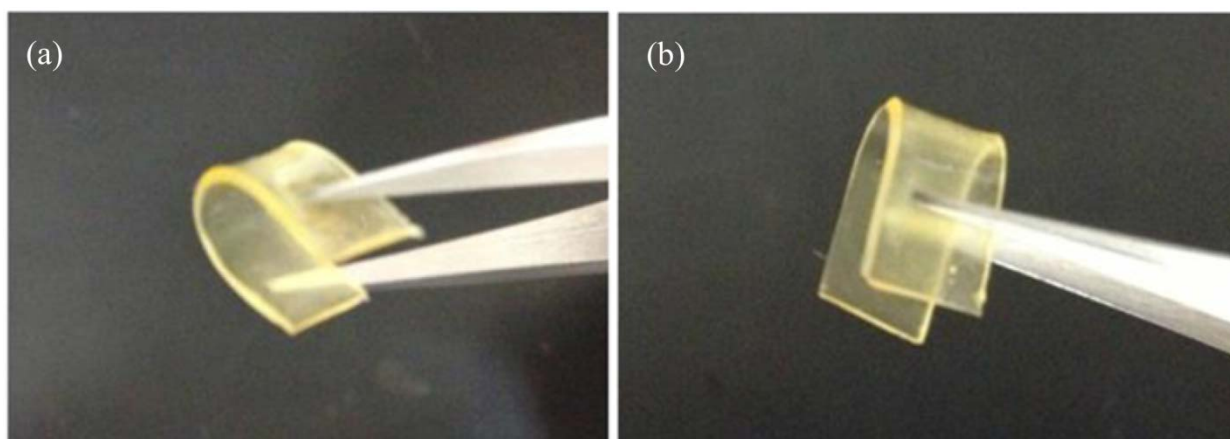


Figure 11. Macroscopic photographs of (a) P-B-P, and (b) P-Ba-P. Reprinted with permission from Ref. [118].

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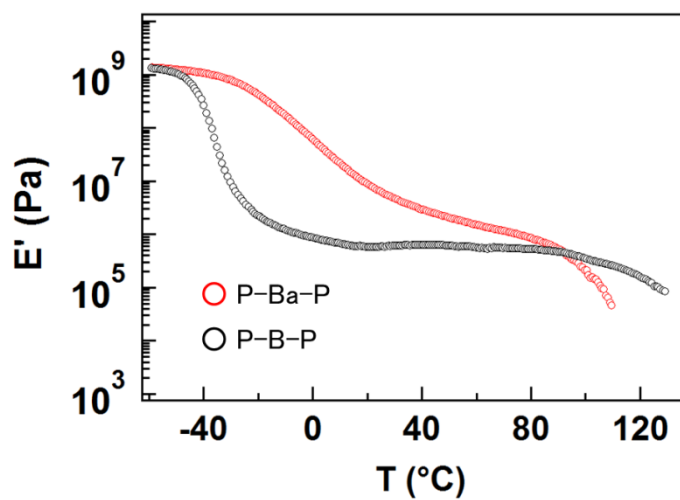


Figure 12. Storage moduli of P-B-P and P-Ba-P obtained by dynamic temperature ramp tests. Reprinted with

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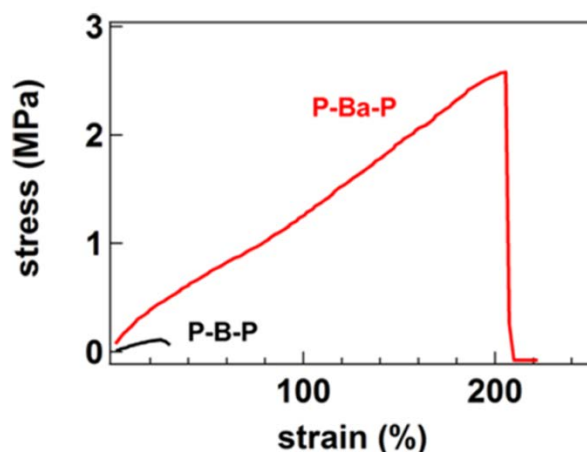


Figure 13. Stress-strain curves at room temperature of P-B-P and P-Ba-P. Reprinted with permission from Ref.

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3.3.2.2 Effect of Molten Middle Block Molecular Weight

As described above, incorporation of hydrogen bonding units into the soft middle block B of the ABA triblock copolymer obviously enhanced its elongation properties. However, in the above-mentioned study, the middle block molecular weight of 25,000 was small for practical applications of polymeric materials, so that the elongation properties were not so excellent. Based on the idea that increase in the molecular weight of polymers to be extended enhances their breaking elongation, we synthesized larger ABA triblock copolymers [120]. Specifically, polystyrene (S, $M_n = 38,000$) was firstly synthesized with RAFT polymerization by bifunctional RAFT reagent. Then, four kinds of polystyrene-*b*-(poly(*n*-butyl acrylate)-*co*-polyacrylamide)-*b*-polystyrene (S-Ba-S) with different molecular weights of the Ba middle block were synthesized via RAFT polymerization. Four samples of S-Ba-S had almost the same molar ratio of acrylamide units around 20 mol%, and their Ba middle block molecular weights were 250k, 660k, 1200k, and 3140k. These four samples were coded as S-Ba-S(X), where X represented the Ba middle block molecular weight. Tensile tests were performed for these

samples at an initial strain rate of approximately 0.21 s^{-1} (elongation rate of 2.5 mm/s for sample length of approx. 12 mm). For S-Ba-S (250k), the Young's modulus, the maximum stress, the breaking elongation, and the toughness were 13 MPa, 7.4 MPa, 550 %, and 12 MJ/m^3 , respectively. All these values were larger than those of the P-Ba-P with a molecular weight of 30,000. For S-Ba-S(3140k) with the largest middle block molecular weight, the Young's modulus, the elongation at break, the maximum stress, and the toughness were 0.77 MPa, 2030 %, 3.6 MPa, and 28 MJ/m^3 , respectively. The maximum stress was half of that of S-Ba-S (250k), whereas the breaking elongation was about four times larger than that of S-Ba-S (250k), so that the toughness was more than twice of that of S-Ba-S (250k). Introduction of hydrogen bonding groups into the melt middle block produces dynamic hydrogen bonds that increase the Young's modulus and simultaneously prevent the stress concentration to the sample (especially, the S glassy domains) by dissociating during elongation. Also, increasing the melt middle block molecular weight enabled the sample to be extended more. Overall, enhancement of the toughness could also be attained.

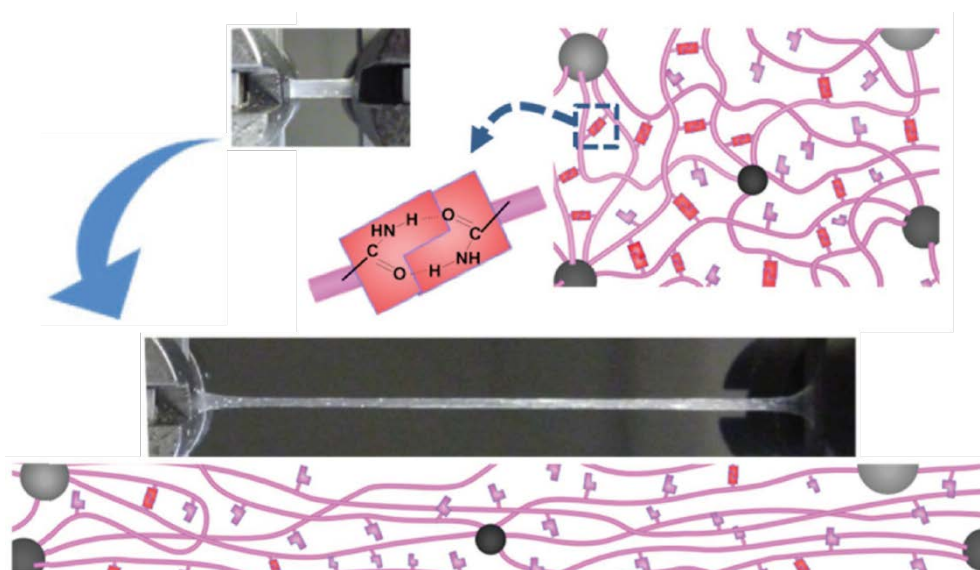


Figure 14. Photos and schematic networks of S-Ba-S elastomers before and after elongation. In the schematics,

black spheres represent S glassy domains, and Ba middle blocks and acrylamide groups are illustrated with pink lines and “L-type” blocks. Reprinted with permission from Ref. [120]. Copyright 2016 John Wiley & Sons, Inc.

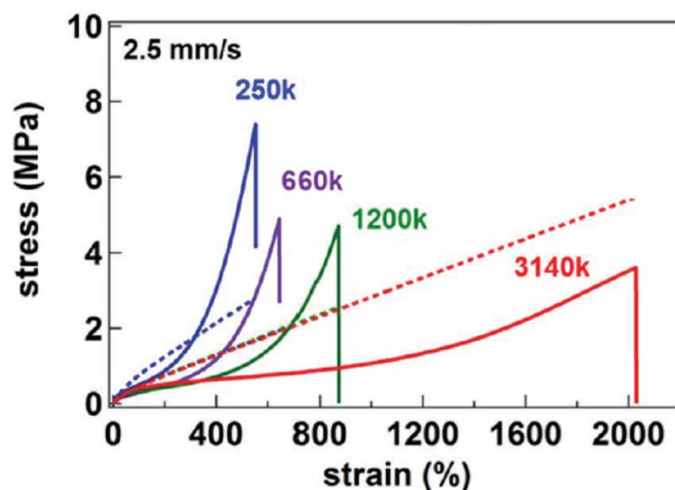


Figure 15. Stress-strain curves of S-Ba-S (250k), S-Ba-S (660k), S-Ba-S (1200k), and S-Ba-S (3140k). Reprinted with permission from Ref. [120]. Copyright 2016 John Wiley & Sons, Inc.

3.3.2.3 Effect of the Fraction of Hydrogen Bonding Groups

Not only introduction of hydrogen bonding groups into the melt middle block of an ABA triblock copolymer but also increase in the molecular weight is important for attaining supramolecular thermoplastic elastomers with better mechanical properties at ambient temperature. However, the details of the influence of the incorporation ratio of hydrogen bonding groups have not been revealed. To observe the effects clearly, three S-Ba-S were synthesized by varying the ratio between the *n*-butyl acrylate monomer and the acrylamide monomer by RAFT polymerization, where the total number-average molecular weight and the composition of S were almost the same, 110k and 0.25, respectively, but fraction of the amide group was different. The amide fraction of the Ba middle

block in three S-Ba-S was 11 mol%, 16 mol%, and 28 mol%; hence, the sample names were coded as S-Ba-S (11%), S-Ba-S (16%), and S-Ba-S (28%), respectively. Polystyrene-*b*-poly(*n*-butyl acrylate)-*b*-polystyrene (S-B-S) as a control sample was also synthesized, where the total number-average molecular weight and the composition of S were almost the same as the molecular weight and the composition of S-Ba-S (110k and 0.25, respectively), but amide groups were not incorporated, i.e., the amide fraction was 0 %. The elongation properties of these samples were also evaluated by tensile tests (initial strain rate: 0.20 s⁻¹; elongation rate of approximately 1.7 mm/s for a sample length of approx. 8.5 mm). S-B-S without any amide groups was able to be extended by more than 16 times, but the maximum stress (0.2 MPa) and the Young's modulus (0.1 MPa) were very low. On the other hand, S-Ba-S (11%) was extended up to 12 times, and its Young's modulus and the maximum stress increased to 3.0 MPa and 3.0 MPa, respectively, so that the toughness was also increased to 19 MJ/m³. For S-Ba-S (16%) having a larger amide fraction, the mechanical properties were more enhanced, i.e., the Young's modulus and the maximum stress increased again to 6.9 MPa and 13 MPa, respectively, and the breaking elongation was 11 times larger; therefore, the toughness was 65 MJ/m³. On the other hand, the Young's modulus and maximum stress of S-Ba-S (28%) with the largest amide group fraction were 26 MPa and 17 MPa, respectively, whereas the sample was only elongated up to six times, so that the toughness was also decreased to 57 MJ/m³ compared to S-Ba-S(16%). Thus, it was found that the Young's modulus and the maximum stress increased with increase in the amide fraction on the Ba middle block, because increase in apparent cross-linking density resulted from increase in transient cross-links of self-complementary hydrogen bonding, i.e., dynamic cross-links. On the other hand, the breaking elongation of S-Ba-S (16%) became slightly smaller than that of S-Ba-S (11%). Moreover, the breaking elongation of S-Ba-S (28%) became significantly smaller. If the amide fraction was small, the Ba middle block

was sufficiently elongated, since break/dissociation of amide's hydrogen bonds occurred easily in the Ba middle block before stress concentration occurs at the glassy S domains. However, if the amide group fraction was too high, stress concentration at the glassy S domains could not be avoided due to the large number of active hydrogen bonds during elongation, so that the glassy S domains were broken easily and the breaking elongation was decreased notably. It was suggested that the appropriate fraction (up to about 20 mol%) of the hydrogen bonding groups into the melt middle block enabled preparation of supramolecular elastomers with the best mechanical properties.

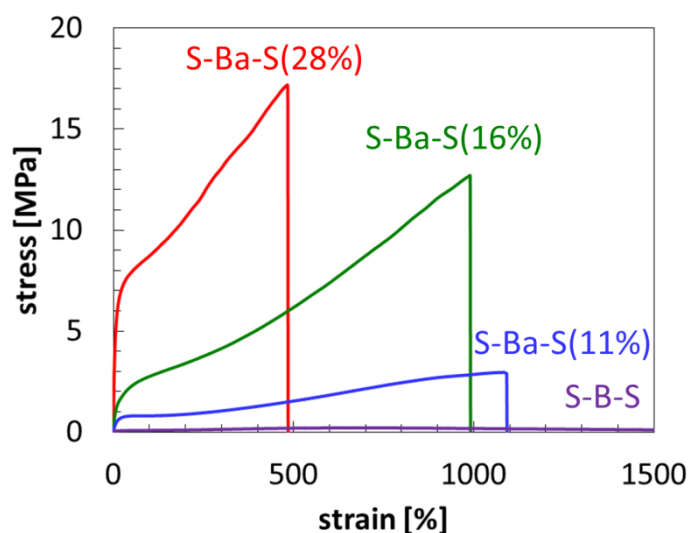


Figure 16. Stress-strain curves of S-B-S, S-Ba-S (11%), S-Ba-S (16%), and S-Ba-S (28%).

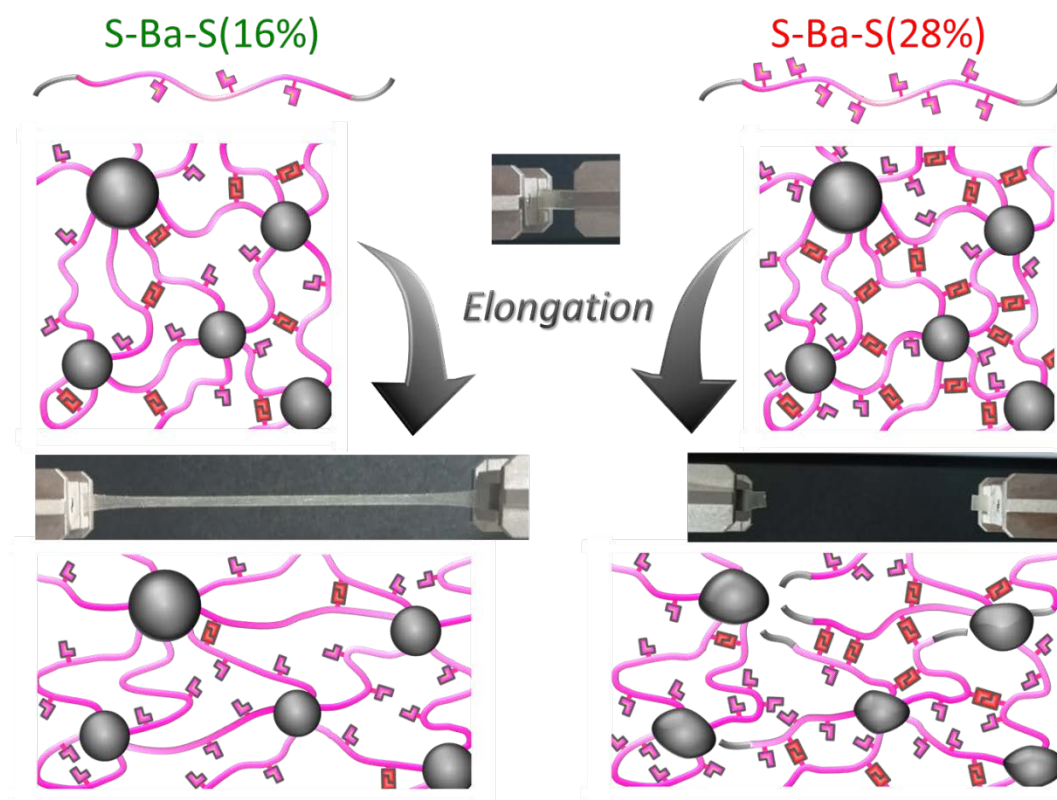


Figure 17. Photos and schematic networks of S-Ba-S elastomers with different ratio of amide groups before and after elongation. The left picture represents S-Ba-S with the appropriate number of hydrogen bonding groups and the right one represents S-Ba-S with the excess number of hydrogen bonding groups.

4. Conclusions and Future Outlook

In this paper, studies on supramolecular elastomers were reviewed, especially design and mechanical properties. Supramolecular soft polymer materials with only cross-links of noncovalent bonds with a finite relaxation time flow within a finite time and behave as polymer melts, so they cannot be elastomers. On the other hand, supramolecular soft polymer materials with crystalline segments serving as semipermanent cross-links show elastomeric properties. Therefore, semipermanent cross-links such as crystalline parts in polymers are very important for preparing supramolecular elastomers. Supramolecular soft polymer materials with both chemical

cross-links and physical cross-links express also elastomeric properties, but they do not show thermoplasticity. On the other hand, higher performance supramolecular thermoplastic elastomers can be obtained by incorporating noncovalent bonds into conventional ABA triblock copolymer TPEs. Introducing noncovalent bonds into hard block (glassy domains) cannot enhance the elongation properties of TPEs at room temperature, though the TPEs are highly thermally stable because the glass transition temperature of the hard segments can be increased. Most importantly, incorporation of the appropriate number of noncovalent bonds into the melt blocks enhances the elongation properties compared to conventional, noncovalent bonded TPEs. In this way, to attain supramolecular elastomers, presence of (semi)permanent cross-links is essential, and in order to prepare supramolecular elastomers having better physical properties, the molecular design is crucial.

Although effects of type of supramolecular cross-links, such as hydrogen bonding, ionic bonding, and metal-ligand coordination, in supramolecular elastomers have not been studied in detail, the bond strength and the corresponding relaxation time are very different, which probably affect the mechanical and thermal properties of supramolecular elastomers. Influence of the incorporation ratio of supramolecular cross-links in hard domains has not been also investigated in detail, but the detailed studies are probably helpful to attain the better thermal/mechanical properties for supramolecular elastomers. We expect that more useful supramolecular elastomers will be developed using the above knowledge acquired, which will help to enrich the quality of our lives.

Acknowledgement

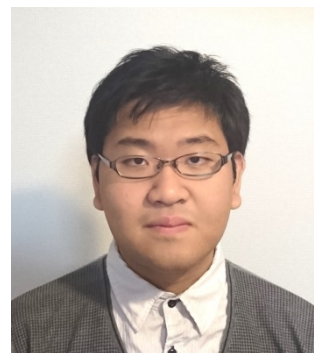
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Biography:

Takato Kajita earned B. Eng. in Applied Chemistry in 2016 at Nagoya University.

He is currently a graduate student in the Department of Applied Chemistry at Nagoya University under the direction of Prof. Yushu Matsushita and Prof. Atsushi Noro. His research interest is in the properties and applications of supramolecular elastomers and polymer gels.



Atsushi Noro is a Junior Associate Professor in the Department of Applied Chemistry at Nagoya University. He received his PhD degree in Applied Chemistry in 2006 at Nagoya University under the direction of Prof. Yushu Matsushita. After that, he joined Prof. Timothy P. Lodge's Group at the Department of Chemistry, University of Minnesota, as a JSPS postdoctoral fellow. He rejoined Nagoya



University in 2007. In 2011, he was a Visiting Scientist in Prof. Edwin L. Thomas's Group, Department of Materials Science and Engineering, Massachusetts Institute of Technology. He received the Award for

Encouragement of Research in Polymer Science from the Society of Polymer Science, Japan (SPSJ) in 2013 and the Award for Encouragement from the Society of Rheology, Japan (SRJ) in 2015. The main focuses of his research is on the design and properties of high functional supramolecular/noncovalent bonded soft materials and nano-hybrid materials.

Yushu Matsushita is currently a Trustee and a Vice President of Nagoya University since 2015. He is also a Professor of Applied Chemistry at Nagoya University. He received his Dr Eng in Synthetic Chemistry, School of Engineering at Nagoya University under the supervision of Prof. Mitsuru Nagasawa. Dr Matsushita joined Nagoya University in 1982; in 1994, he moved to the Institute



for Solid State Physics, University of Tokyo. He rejoined Nagoya University in 1999. He served as a Vice-President of the University from 2007 to 2013, a Dean, Graduate School of Pharmaceutical Sciences of the University from 2012 to 2013, and a Dean, Graduate School of Engineering of the University from 2013 to 2015. He received the Wiley Polymer Science Award in 1999 and the Award of Polymer Science in 2007, from the Society of Polymer Science, Japan (SPSJ). His research focus is the molecular design of complex polymeric systems and control of their morphology.

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