

Communication

Highly Extensible Supramolecular Elastomers with Large Stress Generation Capability Originating from Multiple Hydrogen Bonds on the Long Soft Network Strands

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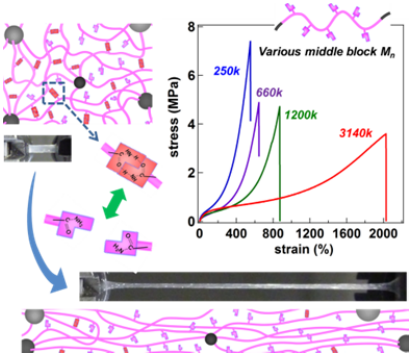
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Highly extensible supramolecular elastomers were prepared from ABA triblock-type copolymers bearing glassy end blocks and a long soft middle block with multiple hydrogen bonds. The copolymer used was polystyrene-*b*-[poly(butyl acrylate)-*co*-polyacrylamide]-*b*-polystyrene (S-Ba-S), which was synthesized via reversible addition-fragmentation chain transfer (RAFT) polymerization. Tensile tests revealed that the breaking elongation (ϵ_b) increased with an increase in the middle block molecular weight (M_{middle}). Especially, the largest S-Ba-S with M_{middle} of 3140k, which was synthesized via high-pressure RAFT polymerization, achieved ϵ_b of over 2000% with a maximum tensile stress of 3.6 MPa, while the control sample without any middle block hydrogen bonds, polystyrene-*b*-poly(butyl acrylate)-*b*-polystyrene with M_{middle} of 2780k, was merely a viscous material due to the large volume fraction of soft block. Thus, incorporation of hydrogen bonds into the large molecular weight soft middle block was found to be beneficial to prepare supramolecular elastomers attaining high extensibility and sufficiently large stress generation ability simultaneously. This outcome was probably due to concerted combination of entropic changes and internal potential energy changes originating from the dissociation of multiple hydrogen bonds by elongation.

FIGURE FOR ToC_ABSTRACT



1. Introduction

Elastomers are polymeric materials that exhibit stretchability accompanied with softness at ambient temperature,^[1-5] unlike stiff materials such as metals and ceramics. The unique mechanical properties of elastomers are attributed to molecular network structures composed of cross-linked melt polymers. Rubbers are conventional elastomers,^[6] which attain their good material strength due to chemical cross-linking via vulcanization. However, the irreversible nature of the chemical cross-links makes rubbers poor candidates for re-processing or recyclability. Thermoplastic elastomers (TPEs) are elastomeric materials at ambient temperature that have overcome the limitations of rubbers.^[7,8] ABA triblock copolymers, such as polystyrene-*b*-polybutadiene-*b*-polystyrene or polystyrene-*b*-polyisoprene-*b*-polystyrene,^[9,10] are typical TPEs, in which the A end block is a glassy polymer with a glass transition temperature (T_g) higher than room temperature and the B middle block being a melt polymer with a T_g lower than room temperature.^[11-14] In the self-assembled state, the glassy A end blocks form cross-link domains while the soft B middle blocks serve as bridging elastic strands to attain rubber elasticity. Since the cross-link domains are formed by self-assembly of the glassy blocks via van der Waals forces, TPEs can flow at higher temperatures than the T_g of the glassy blocks, providing re-processability and recyclability.

The physical property enhancement of ABA triblock copolymer-based elastomers, especially with the introduction of non-covalent cross-links, has drawn attention in recent years.^[15-21] Long and colleagues have prepared supramolecular elastomers by blending an ABA triblock copolymer bearing adenine groups on the A blocks with a comparable copolymer bearing thymine groups on the A blocks,^[22] which displayed higher softening temperature due to the complementary hydrogen bonding between adenine and thymine groups in the glassy A blocks. Feldman et al. prepared elastomeric materials composed of triblock-type copolymers bearing quadruple hydrogen bonding moieties, ureido-4-[1H]-pyrimidinone (UPy), on the end blocks, where the stiffness and relaxation time could be controlled by the average composition and distribution of UPy's along the polymer chain.^[23] We recently reported the synthesis of ABA triblock copolymer-based TPEs bearing hydrogen bonds on the

soft B middle block.^[24] Usually, incorporation of multiple weak hydrogen bonds (conventionally, with bond energy per associated bond $\Delta E_{\text{bond}} < 40$ kJ/mol) into soft polymer chains can only increase the T_g and induce retardation of the relaxation,^[25-28] but it cannot contribute to attainment of useful elastomeric soft materials bearing stable network structures with infinite relaxation time. On the other hand, our previous report demonstrated that incorporation of multiple weak amide-amide hydrogen bonds ($\Delta E_{\text{bond}} \sim 30$ kJ/mol)^[29] into the soft network strands bound by glassy cross-link domains can improve the mechanical properties of elastomers. However, our previous study used polymers with molecular weights lower than the critical molecular weight for entanglement (M_c) to simplify the rheological analysis, where toughness and breaking elongation (ϵ_b) of the prepared elastomer were just 2.8 MPa and 201%, respectively. These values are not so large as elastomers; therefore, the usefulness of the proposed concept has remained unclear.

Herein, we focus on a relationship between molecular weight (M) of polymers and the extensibility. Considering the ideal change of average end-to-end distance (r) from a random coil state ($r \sim M^{0.5}$)^[30,31] to a fully-stretched state ($r \sim M$), the maximum degree of extensibility, *i.e.*, ϵ_b should ideally depend on M as tentatively expressed by $\epsilon_b \sim M / M^{0.5} = M^{0.5}$ on the basis of the Kuhn model.^[32,33] Therefore, ABA triblock copolymer-based elastomers with larger molecular weight B blocks should provide higher extensibility. However, the stress during elongation of such elastomers would be very low because the volume fraction of the melt middle block chains is quite large whereas the volume fraction of the glassy end blocks that govern the stiffness is quite low, which prevents the materials from being useful as elastomers. On the other hand, ABA triblock copolymers bearing hydrogen bonds on the long soft B middle block could be greatly extended, simultaneously attaining sufficiently large stress as elastomers.

The above speculation is based on our hypothesis regarding the concerted combination of internal energy changes and entropy changes: As each active hydrogen bond on the long soft network strands is extended, the internal potential energy on the hydrogen bond is increased ($\Delta U > 0$), generating stress from energetic elasticity. After the hydrogen bond is broken/dissociated by the further elongation,

the soft strands are then extended with a decrease in the degrees of freedom of the chain conformation, generating stress from entropic elasticity until stress concentration begins to occur at another hydrogen bond. Successive generation of stress from the above energetic elasticity and entropic while avoiding stress concentration at permanent cross links can also take place continuously and concertedly for other hydrogen bonds during elongation because of the presence of multiple hydrogen bonds on the long soft network strands. Thus, high extensibility and ability to generate larger stress would be simultaneously attained.

To examine the above hypothesis, we prepare supramolecular elastomers composed of large molecular weight polystyrene-*b*-[poly(butyl acrylate)-*co*-polyacrylamide]-*b*-polystyrenes (S-Ba-S, **Figure 1**), which are ABA triblock-type copolymers bearing glassy end blocks and a soft middle block with multiple hydrogen bonds. Note that the S end block and the Ba middle block exhibit the T_g at approximately 100 °C^[34] and -25 °C^[24], respectively. We synthesize several types of S-Ba-S copolymers by varying the middle block molecular weights (M_{middle}), where the M_{middle} s of these copolymers are designed to be sufficiently larger than M_c of poly(butyl acrylate) (~ 55k).^[35] To attain high molecular weight copolymers with $M_{\text{middle}} \gg 1000k$, we utilize high pressure living radical polymerization methodology for our material design. We also investigate the mechanical properties by uniaxial dynamic mechanical measurements and tensile tests to examine effects of M_{middle} on the elongation properties.

2. Results and Discussion

Four examples of S-Ba-S were synthesized via reversible addition-fragmentation chain transfer (RAFT) polymerizations^[36] (details of the synthesis are described in SI). The mole fraction of acrylamide units in the middle block (f_{amide}) was kept at ~ 20 mol% (see Table 1). S-Ba-S with M_{middle} of 3140k was synthesized via high pressure RAFT polymerization methodology (at 300 MPa), where the propagation step of the radical polymerization proceeded much more efficiently.^[37,38] The dispersity

indices (\mathcal{D}) were determined by size exclusion chromatography (SEC) as shown in **Figure 2**, and average molecular weights were determined by $^1\text{H-NMR}$ spectroscopy (see SI). The S-Ba-S samples were coded as S-Ba-S(X), where X represents M_{middle} . The molecular characteristics are summarized in Table 1 (see also Table S1). As control samples, we prepared block copolymers without hydrogen bonding functional groups; the polystyrene-*b*-poly(butyl acrylate)-*b*-polystyrene (S-B-S) copolymers with $M_{\text{middle}} = 280\text{k}$ and 2780k were synthesized via RAFT polymerizations under ambient pressure and high pressure, respectively. These S-B-S control samples were coded as S-B-S(280k) and S-B-S(2780k), where the value in parentheses denotes M_{middle} . The molecular characteristics are also shown in Table 1 and Table S1.

To confirm hydrogen bond formation between the acrylamide groups, FT-IR spectroscopy was performed. Characteristic absorption peaks were observed at 3350 cm^{-1} and 3450 cm^{-1} (Figure S9), which originated from stretching vibrations of hydrogen-bonded and free N-H of amide groups, respectively.^[24] These results suggest that some fraction of acrylamide groups formed self-complementary hydrogen bonds at room temperature.^[39] We also performed DSC measurements for S-Ba-S samples and another control sample without the S end blocks, *i.e.*, poly(butyl acrylate)-*co*-polyacrylamide with $M_n \sim 320\text{k}$ and $f_{\text{amide}} \sim 20\%$. We observed no melting peaks in the thermograms on heating (see Figure S10). In addition, we conducted small angle X-ray scattering measurement for the poly(butyl acrylate)-*co*-polyacrylamide, but no peaks appeared in the scattering profile (Figure S11). These results suggest that the acrylamide hydrogen bonds did not induce crystallization of the melt middle block in S-Ba-S.

We performed linear rheological measurements with a dynamic temperature ramp mode to investigate mechanical properties of the samples as TPEs (see SI for detailed experimental conditions). All samples showed clear rubbery plateaus with plateau modulus (E_p) of $1.4 \sim 2\text{ MPa}$ and a decrease of storage modulus (E') as the temperature neared the T_g of the S glassy chains (the E' spectra are shown in Figure S13). Note that E_p of S-Ba-S should include the contributions from hydrogen bond formation

as well as entanglements (detailed estimation of the plain modulus from the soft network stands (E_{net}) and the theoretical network modulus based on the classic theory of rubber elasticity^[40] ($E_{\text{net,theo}}$) are shown in SI).

Tensile tests were performed to investigate the elongation properties at 2.5 mm/s by using specimens with a length of ~ 12 mm (see detailed sample preparation method and experimental conditions in SI). In **Figure 3a**, the stress-strain curves experimentally obtained by tensile tests (S-S_{exp}) are compared with the theoretical stress-strain curves based on the Affine network model (S-S_{Affine}). In this model, the molecular dimension of elongated polymer chains are approximated to follow a Gaussian distribution, where the stress (σ) can be expressed with a function of Young's modulus (E_Y) and the extension ratio (λ) as written by $\sigma = (E_Y \times (\lambda - 1/\lambda^2)) / 3$.^[30,41] Herein, we estimated the E_Y values from the slope of the S-S_{exp} within 10% strain (see the E_Y values in Table S2). In the small elongation region (strain < 30%, the inset of Figure 3a), the S-S_{exp} of each S-Ba-S sample was almost consistent with the corresponding S-S_{Affine}. Subsequently, the S-S_{Affine} exceeded the S-S_{exp} in the middle elongation region, which could reflect the dissociation of the hydrogen bonds and the gradual decrease of entanglements on the middle block. In the large elongation region, the stress increased sharply and the S-S_{exp} again exceeded the S-S_{Affine}, except in S-Ba-S(3140k). The degrees of freedom of the chain conformation were lowered by large elongation, which could induce a sharp stress increase due to contributions from the entropic change as well as the internal potential energy change caused by elongation of the soft Ba block bearing multiple hydrogen bonds. The maximum stress (σ_{max}) decreased as the M_{middle} increased because the volume fraction of the stiff glassy domains decreased with the increase in M_{middle} , which has also been observed in other reports.^[42,43]

In contrast to the tendency toward σ_{max} changes, the breaking elongation (ϵ_b) increased as the M_{middle} increased, and especially, S-Ba-S(3140k) achieved ϵ_b of over 2000% (Figure 3a). The toughness of S-Ba-S(3140k) estimated from the area under the S-S_{exp} curve was 28 MJ/m³ (all toughness values appear in Table 1). Note that such high values can be hardly achieved in gel materials due to the

presence of large amounts of solvents, which makes maintaining constant mechanical properties difficult because of evaporation of the solvents. Although the control sample S-B-S(280k) showed higher elongation ($\sim 1200\%$) than S-Ba-S(250k) having similar M_{middle} , S-B-S(280k) did not show sufficient stress (σ_{max} was 0.28 MPa and the toughness was merely 2.3 MJ/m^3) during the elongation (see Figure S14 and Table 1). In addition, the larger molecular weight control sample, S-B-S(2780k), was not self-standing but highly viscous at room temperature due to the significantly large volume fraction of the soft block (see the picture in SI). Thus, formation of hydrogen bonds in the melt middle block was essential for attaining supramolecular elastomers that simultaneously exhibit high extensibility and sufficient stress generating ability as elastomers (*e.g.*, $\sigma_{\text{max}} = 7.4 \text{ MPa}$ for S-Ba-S(250k) and $\sigma_{\text{max}} = 3.6 \text{ MPa}$ for S-Ba-S(3140k)). The lower ϵ_b of S-Ba-S(250k) than that of S-B-S(280k) reflects the larger stress generated during elongation of S-Ba-S(250k) due to formation of multiple hydrogen bonds. In other words, a portion of the large stress generated by elongation of S-Ba-S(250k) would inevitably be applied to the S glassy domains, causing the earlier collapse of the cross-link domains and inducing earlier fracture of the sample.

The integral of the stress-strain curve (*i.e.*, toughness) for elastomers is well known to be composed of the contributions from both the internal energetic changes (ΔU) and the entropic changes ($-T\Delta S$).^[30] In conventional ABA triblock copolymer-based elastomers, especially for the elastomers with long B middle block chains, the generating energy mainly originates from entropic changes of the B middle block chains. Notably, in such elastomers with long B middle block chains, the stress during elongation is relatively small as shown in the S-S_{exp} curve of S-B-S(280k) (Figure S14). On the other hand, S-Ba-S samples showed sufficient stress as elastomers. Presumably, the sufficient stress was derived from multiple hydrogen bonds in the middle block. Elongation of the soft middle block bearing multiple hydrogen bonds could induce a dramatic increase in the internal energetic changes (ΔU) due to extension of the hydrogen bonds, contributing to the large stress generation in S-Ba-S in concert with

the entropic changes. Therefore, incorporation of multiple hydrogen bonds into the long soft network strands could provide elastomers with high extensibility and large stress generation capability.

The effects of elongation rates on the elongation properties were also investigated with a higher elongation rate of 5.0 mm/s (**Figure 3b**), where it was also obvious that ϵ_b became longer with an increase in M_{middle} . Note that ϵ_b at 2.5 mm/s was longer (except S-Ba-S(250k)) than ϵ_b at 5.0 mm/s (compare ϵ_b values in Table 1), because hydrogen-bonded cross-links can be relaxed at a slower elongation rate and therefore can be dissociated more easily.^[44] This observation suggests that the stress dissipation ability^[45] (*i.e.*, suppression of stress concentration at the glassy cross-link domains) would be greater at a slower elongation rate. To confirm the above speculation, we performed tensile tests at a much slower elongation rate, 0.8 mm/s (**Figure 3c**). As expected, ϵ_b was longer than that obtained at 2.5 mm/s (compare ϵ_b values in Table 1), which was consistent with the above speculation. It should be clearly noted that the elongation behavior of S-Ba-S(3140k) at 0.8 mm/s was similar to that of S-B-S, *i.e.*, elongation without large stress generation, suggesting most of the middle hydrogen bonds are relaxed. The observed decrease of ϵ_b from the data at a rate of 2.5 mm/s compared to that at 5.0 mm/s became larger as the M_{middle} increased, as shown in Table 1. This result may be relevant to the fact that the increase in M_{middle} induces retardation of network strand relaxation due to an increase in the number of entanglements,^[46] which results in a loss of the stress dissipation ability at higher elongation rates. In addition, confirmation of residual strain was also made, and some residual strain was observed after quarter elongation of ϵ_b , as shown in Figure S15. Although this outcome means that the molecular network structure cannot be retained perfectly during elongation, the ratio of residual strain was not so large (15 ~ 25%), which suggests S-Ba-S are useful as elastomers. As observed in several reports for soft materials bearing dynamic cross-links,^[17,45] the presence of the large hysteresis during the loading-unloading S-S curves implies energy dissipation originating from relaxation of the middle block hydrogen bonds.

Figure 3d summarizes the relationship between ε_b and M_{middle} for the elongation data at 2.5 mm/s (red dots). Considering the Kuhn model, the relationship between ε_b and M should follow $\varepsilon_b \sim M / M^{0.5} = M^{0.5}$ in an ideal case.^[32,33] However, the slope in the double logarithmic $\varepsilon_b - M_{\text{middle}}$ expression (0.16) for $250\text{k} \leq M_{\text{middle}} \leq 660\text{k}$ was evidently lower than the slope (0.5) predicted by the Kuhn model, suggesting that the chains did not reach the fully-stretched state during elongation in this region. On the other hand, the slope at higher M_{middle} range ($1200\text{k} \leq M_{\text{middle}} \leq 3140\text{k}$) was much greater than 0.16. Similar behavior was also observed in the plots based on the elongation data at 5.0 mm/s and 0.8 mm/s (see blue and green dots in Figure 3d). From these results, most of the stress in the sample having larger M_{middle} was probably applied directly to the melt middle block due to the small volume fraction of the S end blocks, resulting in fracture suppression on the glassy domains.

3. Conclusions

In summary, we have successfully achieved preparation of highly extensible ABA triblock copolymer-based supramolecular elastomers (the largest $\varepsilon_b > 2000\%$) that simultaneously attained sufficiently large stress or toughness (*e.g.*, toughness of 28 MJ/m^3 for the largest molecular weight elastomer) by incorporating dynamic cross-links into the long melt middle block. The generation of sufficient stress was attributed to the large changes of internal potential energy induced by extension of the middle block hydrogen bonds, so-called “soft cross-links,” by elongation, where the dynamic nature of hydrogen bonds to prevent stress concentration at the glassy cross-link domains also plays an important role in attaining high extensibility. To our best knowledge, this is also the first report to utilize high pressure RAFT polymerization for material design on elongation property enhancement of elastomers. In the future, we will conduct nano-structural investigations to clarify the relationship between the nano-structures and the mechanical properties. We also expect that the present molecular design can be applied to conventional ABA triblock copolymer-based TPEs or other soft materials to afford further high performance elastomeric materials.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author

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[1] R. Pelrine, R. Kornbluh, Q. B. Pei, J. Joseph, *Science* **2000**, *287*, 836.

[2] J. Li, C. L. Lewis, D. L. Chen, M. Anthamatten, *Macromolecules* **2011**, *44*, 5336.

[3] S. Cai, D. Chen, Z. Suo, R. C. Hayward, *Soft Matter* **2012**, *8*, 1301.

[4] J. Araki, T. Kataoka, K. Ito, *Soft Matter* **2008**, *4*, 245.

- [5] A. Takahara, R. W. Hergenrother, A. J. Coury, S. L. Cooper, *J. Biomed. Mater. Res.* **1992**, *26*, 801.
- [6] M. Akiba, A. S. Hashim, *Prog. Polym. Sci.* **1997**, *22*, 475.
- [7] W. Shi, N. A. Lynd, D. Montarnal, Y. Luo, G. H. Fredrickson, E. J. Kramer, C. Ntaras, A. Avgeropoulos, A. Hexemer, *Macromolecules* **2014**, *47*, 2037.
- [8] J. Kylma, J. V. Seppala, *Macromolecules* **1997**, *30*, 2876.
- [9] H. Watanabe, *Macromolecules* **1995**, *28*, 5006.
- [10] T. Pakula, K. Saijo, H. Kawai, T. Hashimoto, *Macromolecules* **1985**, *18*, 1294.
- [11] K. Satoh, D.-H. Lee, K. Nagai, M. Kamigaito, *Macromol. Rapid Commun.* **2014**, *35*, 161.
- [12] A. Takano, I. Kamaya, Y. Takahashi, Y. Matsushita, *Macromolecules* **2005**, *38*, 9718.
- [13] Y. Matsumiya, H. Watanabe, A. Takano, Y. Takahashi, *Macromolecules* **2013**, *46*, 2681.
- [14] C. L. Wanamaker, L. E. O'Leary, N. A. Lynd, M. A. Hillmyer, W. B. Tolman, *Biomacromolecules* **2007**, *8*, 3634.
- [15] N. Hosono, L. M. Pitet, A. R. A. Palmans, E. W. Meijer, *Polym. Chem.* **2014**, *5*, 1463.
- [16] A. A. Kavitha, N. K. Singha, *Macromolecules* **2010**, *43*, 3193.
- [17] K. J. Henderson, T. C. Zhou, K. J. Otim, K. R. Shull, *Macromolecules* **2010**, *43*, 6193.
- [18] F. W. Speetjens, II, M. K. Mahanthappa, *Macromolecules* **2015**, *48*, 5412.
- [19] A. Noro, Y. Matsushita, T. P. Lodge, *Macromolecules* **2008**, *41*, 5839.
- [20] A. Noro, Y. Matsushita, T. P. Lodge, *Macromolecules* **2009**, *42*, 5802.
- [21] A. Noro, S. Matsushima, X. He, M. Hayashi, Y. Matsushita, *Macromolecules* **2013**, *46*, 8304.
- [22] B. D. Mather, M. B. Baker, F. L. Beyer, M. A. G. Berg, M. D. Green, T. E. Long, *Macromolecules* **2007**, *40*, 6834.
- [23] K. E. Feldman, M. J. Kade, E. W. Meijer, C. J. Hawker, E. J. Kramer, *Macromolecules* **2009**, *42*, 9072.
- [24] M. Hayashi, S. Matsushima, A. Noro, Y. Matsushita, *Macromolecules* **2015**, *48*, 421.

- [25] C. L. Lewis, K. Stewart, M. Anthamatten, *Macromolecules* **2014**, *47*, 729.
- [26] C. L. Elkins, T. Park, M. G. McKee, T. E. Long, *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43*, 4618.
- [27] M. Hayashi, A. Noro, Y. Matsushita, *J. Polym. Sci., Part B: Polym. Phys.* **2014**, *52*, 755.
- [28] A. Noro, M. Hayashi, Y. Matsushita, *Soft Matter* **2012**, *8*, 6416.
- [29] A. J. Doigt, D. H. Williams, *J. Am. Chem. Soc.* **1992**, *114*, 338
- [30] P. C. Himenz, T. P. Lodge, *Polymer Chemistry*, 2nd ed., CRC Press, Boca Raton, FL, **2007**.
- [31] P. G. de Gennes, *Scaling Concepts in Polymer Physics*, Cornell University Press, Ithaca, NY, **1979**.
- [32] W. Kuhn, *J. Polym. Sci.* **1946**, *1*, 380.
- [33] Y. Akagi, T. Katashima, H. Sakurai, U.-i. Chung, T. Sakai, *Rsc Adv.* **2013**, *3*, 13251.
- [34] T. G. Fox, P. J. Flory, *J. Polym. Sci.* **1954**, *14*, 315.
- [35] H. Yamazaki, M. Takeda, Y. Kohno, H. Ando, K. Urayama, T. Takigawa, *Macromolecules* **2011**, *44*, 8829.
- [36] J. T. Lai, D. Filla, R. Shea, *Macromolecules* **2002**, *35*, 6754.
- [37] J. Rzyayev, J. Penelle, *Angew. Chem., Int. Ed.* **2004**, *43*, 1691.
- [38] T. Arita, Y. Kayama, K. Ohno, Y. Tsujii, T. Fukuda, *Polymer* **2008**, *49*, 2426.
- [39] C. B. Aakeroy, A. M. Beatty, B. A. Helfrich, *J. Am. Chem. Soc.* **2002**, *124*, 14425.
- [40] D. Yamaguchi, M. Cloitre, P. Panine, L. Leibler, *Macromolecules* **2005**, *38*, 7798.
- [41] Y. Akagi, T. Katashima, Y. Katsumoto, K. Fujii, T. Matsunaga, U.-i. Chung, M. Shibayama, T. Sakai, *Macromolecules* **2011**, *44*, 5817.
- [42] X. Liu, R.-Y. Zhao, T.-P. Zhao, C.-Y. Liu, S. Yang, E.-Q. Chen, *Rsc Adv.* **2014**, *4*, 18431.
- [43] J. M. Yu, P. Dubois, P. Teyssie, R. Jerome, *Macromolecules* **1996**, *29*, 6090.
- [44] K. Mayumi, A. Marcellan, G. Ducouret, C. Creton, T. Narita, *ACS Macro Lett.* **2013**, *2*, 1065.

[45] T. L. Sun, T. Kurokawa, S. Kuroda, A. Bin Ihsan, T. Akasaki, K. Sato, M. A. Haque, T.

Nakajima, J. P. Gong, *Nature Mater.* **2013**, *12*, 932.

[46] H. Watanabe, *Prog. Polym. Sci.* **1999**, *24*, 1253.

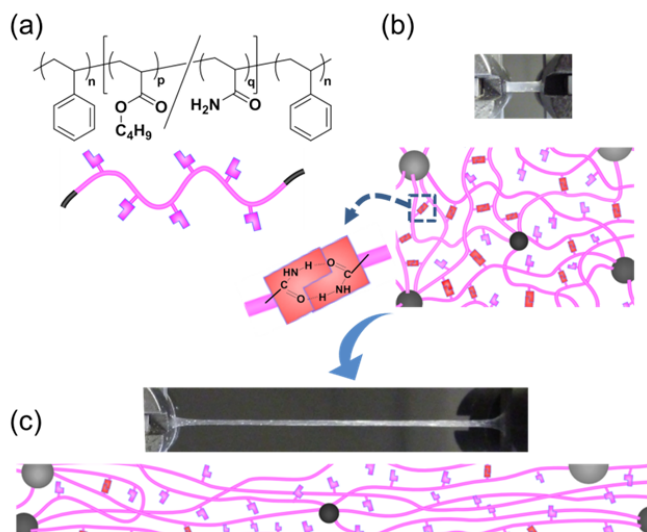


Figure 1. (a) Chemical structure and schematic representation of S-Ba-S. Photos and schematic networks of S-Ba-S elastomers before elongation (b) and after elongation (c) are also shown. In the schematics, black spheres represent S block assemblies while Ba middle blocks and acrylamide groups are illustrated with pink lines and “L-type” blocks. Illustration of acrylamide hydrogen bonds is also shown near the schematic of the network.

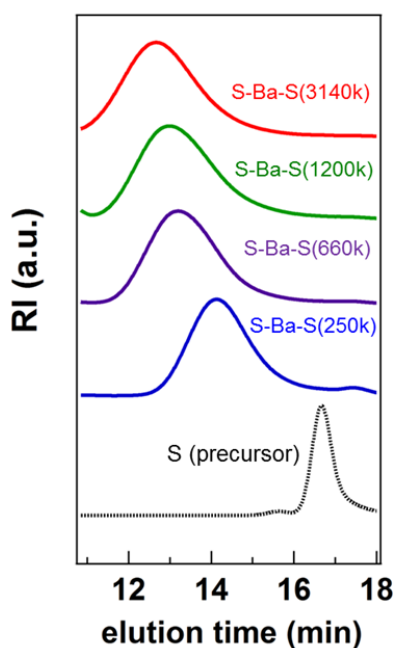


Figure 2. SEC chromatograms of the precursor polystyrene (S) and S-Ba-S.

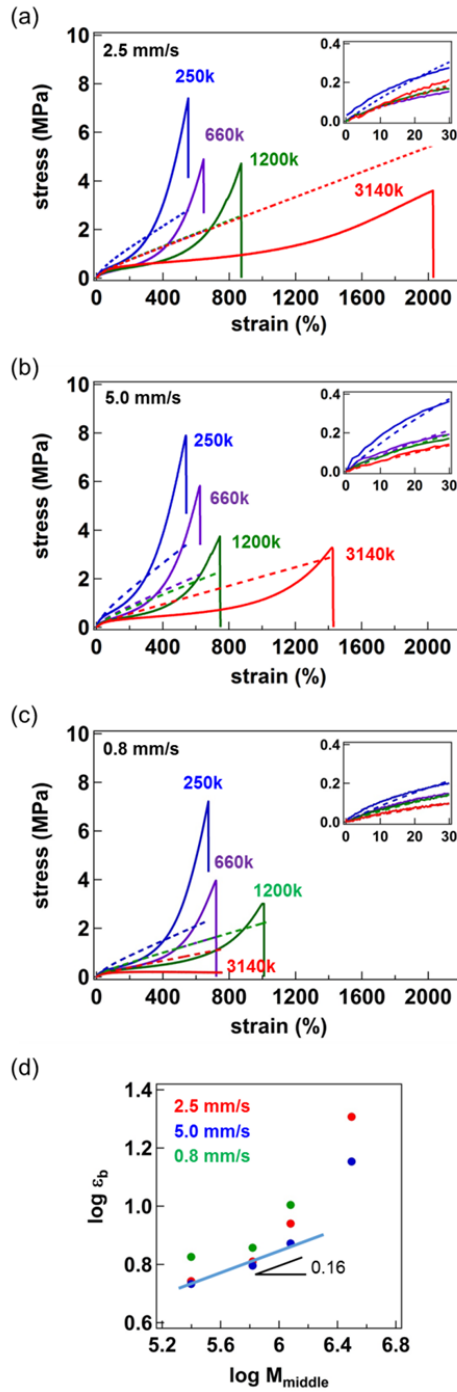


Figure 3. Stress-strain curves obtained by tensile tests (a) at 2.5 mm/s, (b) at 5.0 mm/s, and (c) at 0.8 mm/s, where the insets of (a), (b), and (c) show the expanded stress (Y-axis) -strain (X-axis) curves within 30% strain region. The colors of the curves correspond with the sample codes in the same color. The dashed line represents the theoretical stress-strain curves based on the Affine network model. (d) Double logarithmic plots of ϵ_b as a function of M_{middle} on the basis of the elongation data at 0.8mm/s (green), 2.5 mm/s (red), and 5.0 mm/s (blue), where the straight line was used to estimate the slope in the small M_{middle} region for the data at 2.5 mm/s. The test of S-Ba-S(3140k) at 0.8 mm/s was stopped in the course of the measurement because the stress was decreasing and almost zero stress was detected after the elongation of 700%, and therefore the plot of ϵ_b at 0.8 mm/s is not provided in (d).

Table 1. Molecular characteristics and mechanical properties of polymers

| Sample code | M_S^a | M_{middle}^a | f_{amide}^b (mol%) | \mathcal{D}^c | σ_{max}^d (MPa) | ε_b^e (10 ² %) | Toughness ^f (MJ/m ³) |
|---------------|---------|-----------------------|--------------------------------|-----------------|----------------------------------|------------------------------------------|------------------------------------------------|
| S-Ba-S(250k) | 38k | 250k | 19 | 1.3 | 7.4/7.9/7.2 | 5.5/5.5/6.7 | 12/14/12.6 |
| S-Ba-S(660k) | 38k | 660k | 17 | 1.5 | 4.9/5.8/4.0 | 6.5/6.3/7.2 | 8.5/10/8.0 |
| S-Ba-S(1200k) | 38k | 1200k | 16 | 1.6 | 4.7/3.7/3.0 | 8.7/7.5/10.1 | 11/8.3/9.1 |
| S-Ba-S(3140k) | 38k | 3140k | 23 | 1.5 | 3.6/3.3/0.2 | 20.3/14.3/NE ^g | 28/14/NE ^g |
| S-B-S(280k) | 38k | 280k | - | 1.3 | 0.28/0.36/NE ^g | 12.3/11.1/NE ^g | 2.3/2.8/NE ^g |
| S-B-S(2780k) | 38k | 2780k | - | 1.5 | NE ^g | NE ^g | NE ^h |

^a)Number average molecular weight of the S block (M_S) and the middle block (M_{middle}) determined by ¹H-NMR. Note that molecular weight of polystyrene in each end block is $M_S / 2 = 19\text{k}$; ^b)Mole fraction of acrylamide units in the soft block, which was calculated from $N_B / (N_B + N_{\text{amide}})$. N_B and N_{amide} represent average number of monomeric units of butyl acrylate (N_B), and acrylamide (N_{amide}) in a middle block determined by ¹H-NMR (see N values in Table S1); ^c)Dispersity indices measured by SEC; ^d)The maximum tensile stress; ^e)Breaking elongation; ^f)Mechanical toughness estimated from the area under S- S_{exp} curves. For σ_{max} , ε_b , and toughness, the values represent the data at the elongation rates of 2.5 mm/s, 5.0 mm/s, and 0.8 mm/s, arranged from left to right, respectively; ^g)Not evaluated.

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Highly extensible supramolecular elastomers are prepared from ABA triblock-type copolymers with glassy end blocks and a long soft middle block bearing multiple hydrogen bonds (polystyrene-*b*-[poly(butyl acrylate)-*co*-polyacrylamide]-*b*-polystyrene). The elastomer attained the breaking elongation > 2000% and maximum tensile stress of 3.6 MPa. The excellent elongation property is probably due to concerted contribution of entropic and internal potential energy changes during elongation.

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Highly Extensible Supramolecular Elastomers with Large Stress Generation Capability Originating from Multiple Hydrogen Bonds on the Long Soft Network Strands

ToC figure

