Enhanced Heat Resistance and Adhesive Strength of Styrene–Acrylic Triblock Copolymer Elastomers by Incorporating Acrylic Acid

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ABSTRACT: Herein, we present an industrially applicable strategy to enhance the heat resistance and adhesive properties of ABA triblock copolymer-based elastomers composed of styrene (St) and n-butyl acrylate (nBA) by incorporating acrylic acid (AA) at different segments. Three types of triblock copolymers, namely, poly(St-r-AA)-b-poly(nBA)-b-poly(St-r-AA), poly(St)-b-poly(nBA-r-AA)-b-poly(St), and poly(St)-b-poly(nBA)-b-poly(St), were synthesized by reversible addition–fragmentation chain-transfer (RAFT) polymerization. Large-scale RAFT polymerization afforded industrially applicable AA-containing ABA-containing triblock copolymers with moderate molecular weights and predetermined comonomer compositions (St/nBA/AA = 15/83/2–24/73/3, number-average molecular weight ($M_n$) = 30,000–110,000, and resulting product > 200 g). The heat resistance and pressure-sensitive adhesive properties of the triblock copolymers were evaluated. Among them, poly(St-r-AA)-b-poly(nBA)-b-poly(St-r-AA), having poly(nBA) as the middle soft segment and poly(St-r-AA) as hard segments at both ends, exhibited excellent heat creep resistance and increased adhesiveness to stainless steel. The feasibility to manipulate the heat resistance and adhesive properties by incorporating AA units into hard and soft segments, in addition to the ease of operation, high block efficiency, and metal-free nature owing to the RAFT process, is highly beneficial for practical applications of these copolymers.

INTRODUCTION

Thermoplastic elastomers, which are typically ABA-type triblock copolymers composed of glassy A end blocks and a rubbery B midblock, have attracted significant attention owing to their processability and recyclability.1–7 In industry, styrene (St)-based triblock copolymers, such as poly(St)-b-polybutadiene-b-poly(St) and poly(St)-b-polyisoprene-b-poly(St), have been widely used as thermoplastic elastomers.7,8 ABA triblock copolymers based on poly(alkyl acrylate) as the central soft block have been investigated extensively as substitutes of traditional St-based triblock copolymers because they exhibit better resistance to oxidation and ultraviolet (UV) light.9 All acrylic block copolymers composed of acrylates having a long-chain pendant alkyl group, such as poly(methyl methacrylate)-b-poly(alkyl acrylate)-b-poly(methyl methacrylate), have been the focus of another recent study.2–14 Their interesting properties and functions, for example, as modifiers of acrylic resins to improve their elongation and impact resistance, can be tuned by using different acrylate monomers and by manipulating their block lengths.

Over the past few decades, there has been continuous interest in pressure-sensitive adhesives (PSAs) because of their extensive utilization in everyday life (e.g., Scotch tape and Post-it notes) as well as in modern technologies.15–17 The rational design of the chemical structure and the architecture of the blocks as well as the incorporation of specific functional units in the block copolymers are promising approaches to develop high-performance PSAs.18–25 Acrylic-based PSAs are one of the most common classes of PSAs, which are generally composed of n-butyl acrylate (nBA), 2-ethylhexyl acrylate (2-EHA), acrylic acid (AA), and 2-hydroxyethyl acrylate as the main components.26–29 An industrial adhesive must display durability over a wide range of conditions depending on the application as well as cost-effective manufacturing at low cost. For example, an optical adhesive for bonding an optical film (typified by a polarizing plate or a phase difference film) to a display such as a liquid-crystal panels needs to maintain its performance even under severe environmental conditions, such as in-car and outdoor displays, and requires excellent durability under the usage environment.30,31 It has been proposed that to exhibit creep properties under a high-temperature environment (heat creep resistance), the acrylic adhesive composition should be in such a way that the weight-average molecular weight ($M_w$) of the acrylic copolymer is 1,000,000 or more and that it is used in combination with a cross-linking agent. However, the extremely high molecular weights increase the...
solution viscosity and necessitate the use of a large amount of organic solvent to adjust the viscosity and achieve desired coating properties. As the acrylic adhesive composition includes a cross-linking agent, the adhesive must be cured; unfortunately, curing occasionally reduces the reliability of the adhesive performance owing to uneven cross-linkage.

Instead of the typical cross-linked acrylic adhesives, another adhesive composition has been proposed with an acrylic triblock copolymer. This adhesive is classified as non-cross-linked because the lower solution viscosity resulting from the use of a triblock copolymer instead of an acrylic copolymer leads to improved coating properties. However, because the adhesive composition has heat resistance up to approximately 90 °C, a blend of a large number of adhesives is required to achieve higher heat creep resistance. It has been proposed that creep resistance can be improved with an additive composition where a silane coupling agent or an isocyanate has been added to the acrylic triblock copolymer.

In addition to traditional living anionic polymerization, controlled radical polymerization is frequently employed for the synthesis of acrylic triblock polymers, which can be used as thermoplastic elastomers. Among the various controlled radical polymerizations, reversible addition−fragmentation chain-transfer (RAFT) polymerization enables precise polymerization using a conventional radical initiator (e.g., 2,2′-azobis(isobutyronitrile), AIBN), while maintaining the wide applicability and reactivity of the monomers, and introduction of polar functional groups, which has been considered difficult to achieve by conventional ionic polymerization. Furthermore, RAFT polymerizations offer industry-oriented syntheses, involving easy scale-up from a laboratory setting to a commercial application. This motivated us to synthesize a novel adhesive having both excellent adhesion to various adherends and heat resistance by the RAFT process.

In this study, we proposed an industrially applicable molecular design of ABA triblock copolymer-based elastomers composed of St and nBA by incorporating AA at different segments for the enhancement of heat resistance and adhesive properties. For the synthesis of the triblock copolymers with AA units in different segments, RAFT polymerization was performed, as it allowed us to introduce the functional AA unit and manipulate the composition and
Results and Discussion


table 1. Synthesis of ABA Triblock Poly(St)-b-poly(nBA)-b-poly(St) and Poly(St)-b-poly(nBA-r-AA)-b-poly(St) Copolymers by RAFT (Co)polymerization Using Poly(St) Macro-CTAs

| code | macro-CTA | [nBA]₀/[AA]₀ | [macro-CTA]₀/[I]₀ | conv. (%) | BA AA | Mₙ (theory) | Mₙ(SEC) | Mₘ/Mₑ(SEC) | composition⁴ | St/nBA/AA |
|------|-----------|--------------|-------------------|-----------|-------|--------------|---------|------------|-------------|-----------|
| BP1  | poly(St) macro-CTA1 | 1,600/0/4/1 | 62 | 41,900 | 32,300 | 1.90 | 28:72:0 |
| BP2  | poly(St) macro-CTA2 | 3,400/0/4/1 | 67 | 88,300 | 55,800 | 2.19 | 18:81:1 |
| BP3  | poly(St) macro-CTA3 | 1,800/0/4/1 | 75 | 58,500 | 43,100 | 1.79 | 27:73:0 |
| BP4  | poly(St) macro-CTA4 | 3,364/268/4/1 | 71 | 93,000 | 55,500 | 1.99 | 16:81:2 |
| BP5  | poly(St) macro-CTA5 | 1,800/0/4/1 | 71 | 58,700 | 46,000 | 1.76 | 24:76:0 |

⁴Polymerization in ethyl acetate ([M] = 4.0 mol/L) at 85 °C for 10 h, macro-CTA 1: Mₙ = 10,000, Mₘ/Mₑ = 1.28, macro-CTA 2: Mₙ = 15,900, Mₘ/Mₑ = 1.25. Calculated by GC. Calculated by SEC using polystyrene standards in THF.

chain lengths. As illustrated in Scheme 1, three ABA-type triblock copolymers, namely, poly(St-r-AA)-b-poly(nBA)-b-poly(St-r-AA), poly(St)-b-poly(nBA-r-AA)-b-poly(St), and poly(St)-b-poly(nBA)-b-poly(St), were synthesized by RAFT polymerization. In these triblock copolymers, the poly(St) end blocks with a much higher glass-transition temperature (T_g) than room temperature should segregate periodically from the middle block, which act as pseudo-cross-linking domains. The incorporation of the AA unit in the hard domains may lead to an increase in the pseudo-cross-linking derived from self-complementary hydrogen bonding between the AA units. For achieving elastomeric properties, nBA was chosen as a major component of the middle block owing to its lower T_g. The randomly incorporated AA units were a minor component on the soft middle block and also contributed to the change in the T_g of the middle segment by hydrogen bonding. The effect of the incorporation of AA units in the hard domains had a demonstrable effect on the thermal properties, as compared to their inclusion in the middle domain, owing to more efficient pseudo-cross-linking.

Herein, we have described our strategies for the RAFT synthesis of AA-containing styrene–acrylic triblock copolymer elastomers under industrially applicable conditions, which are crucial for large-scale production. The advantage of the triblock polymer is the feasibility of optimization as a hot-melt PSA, as it can impart heat resistance via pseudo-cross-linking by forming microphase separation structures without using a cross-linking agent and aging. As cross-linking is not necessary, the total number of the reaction steps can be reduced. Additionally, the cohesive force of the triblock copolymers is higher, and the molecular weight can be lowered as compared with general PSAs, resulting in more solidification. A simpler process and high solid contents are attractive for cost-effective industrial applications. In this study, the heat resistance was controlled by introducing a polar AA functional group into poly(St) end segments or poly(nBA) middle chain in the pristine triblock copolymers, poly(St)-b-poly(nBA)-b-poly(St). The location of the polar AA unit, composition, and chain lengths of the segments were changed arbitrarily to evaluate the effects of these parameters on the heat resistance and adhesive strength. In addition to the inherent mechanical properties originating from the low T_g of poly(nBA) and glassy poly(St), the incorporation of the AA unit endowed these materials with increased heat resistance and adhesive properties.

Results and Discussion

Synthesis of Triblock Copolymers. In this study, seven block copolymers with arbitrarily changed positions of the polar functional group and hard/soft blocks were prepared by introducing the AA unit into the middle or end segments in poly(St)-b-poly(nBA)-b-poly(St) to control their heat resistance and adhesive strength. The synthetic procedure is shown in Scheme 1. The choice of AA was primarily related to the presence of the carboxylic acid group in the triblock copolymers, which provided high T_g and expanded the applicability of the copolymers as adhesives owing to its high hydrophilicity. The advantage of the ABA-type triblock polymer is the feasibility to optimize various properties; as a hot-melt PSA, the heat resistance can be improved by pseudo-cross-linking of microphase separation structures. Eliminating the need for a cross-linking agent is preferred in the industry as it decreases the number of steps in production, for example, the aging process is no longer required. The higher cohesive force enables the usage of lower molecular weight polymers compared to general PSAs, which lead to an increase in the solid content.

A bifunctional trithiocarbonate, dibenzyl trithiocarbonate, was selected as a RAFT agent, which enabled the synthesis of ABA triblock copolymers by simple two-stage polymerization. From the industrial point of view, 2,2'-azobis(2-methylbutyronitrile) (ABN-E) was used as a radical initiator instead of a conventional AIBN, in order to avoid the formation of potentially toxic tetramethylsuccinonitrile derived from AIBN as a byproduct. Ethyl acetate was chosen as the solvent because of its intermediate polarity and good solubility of all ingredients (three monomers, resulting copolymers, ABN-E, and RAFT agent). For the first series of triblock copolymers, poly(St) macro-CTA prepared using the bifunctional trithiocarbonate RAFT agent was employed for the copolymerization of nBA with AA, which allowed the incorporation of poly(nBA-ran-AA) as a middle block with poly(St) as hard segments at both ends (Scheme 1b). As a comparison, poly(St)-b-poly(nBA)-b-poly(St) was prepared using the same poly(St) macro-CTA (Scheme 1a). The polymerization results are summarized in Table 1. In all cases, polymerization conditions were adjusted to afford the triblock copolymers with moderate polydispersity index (PDIs) (Mₘ/Mₑ = 1.7–2.2), in order to provide excellent wettability to a material to bebonded by increasing the adhesive area, and to reduce the cost of manufacturing by improved productivity at elevated polymerization temperatures. The polymerization at lower temperatures using a relatively high [CTA]/[I] ratio can afford well-defined triblock copolymers with lower PDIs, whereas a longer
polymerization time is required to achieve high monomer conversion, which is undesirable for industrial production. When the RAFT copolymerization of nBA and AA was conducted using the poly(St) macro-CTA with \([\text{nBA}]_0/[\text{AA}]_0/[\text{macro-CTA}]_0/[\text{AIBN}]_0 = 1885/150/4/1\) in ethyl acetate at 85 °C for 10 h, the block copolymers were obtained with moderate monomer conversions (67% and 71% for nBA and AA, respectively, BP4 in Table 1). The triblock copolymer was obtained by reprecipitation into methanol, followed by filtration. The size exclusion chromatography (SEC) chromatograms of the starting poly(St) macro-CTA and triblock copolymers showed unimodal SEC peaks with clear shift to higher molecular weight for the triblock copolymer (Figure 2a), suggesting successful preparation of the targeted block copolymers without the unfavorable unreacted homopolymer.

The formation of the AA-containing triblock copolymer was further confirmed by \(^{1}H\) NMR spectroscopy by comparison of the peaks corresponding to each comonomer. To evaluate the AA unit, the poly(AA) unit in the block copolymer was modified by methylation of the carboxylic acid groups using trimethylsilyldiazomethane according to a slightly modified literature method.\(^\text{[34,35]}\) \(^{1}H\) NMR of the triblock copolymer in CDCl₃ clearly showed peaks corresponding to methyl acrylate, which was derived from AA, in addition to St and nBA units (Figure S1b, Supporting Information). The comonomer composition of the copolymers was calculated from the conversion and feed ratios of both monomers, and the molecular weight of macro-CTA was in reasonable agreement with the values calculated from \(^{1}H\) NMR. Similarly, the formation of poly(St)-b-poly(nBA)-b-poly(St) was confirmed by SEC and \(^{1}H\) NMR analyses (Table 1, Figures 2b, and S1a, Supporting Information).

For the second series of the triblock copolymers, poly(St-r-AA) macro-CTA was initially prepared by the copolymerization of St and AA using the bifunctional trithiocarbonate RAFT agent, followed by RAFT polymerization of nBA (Scheme 1c). The poly(St-r-AA) macro-CTA (\(M_n = 22,800, M_w/M_n = 1.36\)) was obtained by RAFT copolymerization of St and AA at the feed ratio \([\text{St}]_0/[\text{AA}]_0/[\text{CTA}]_0/[\text{AIBN}]_0 = 334/66/1/1\) in ethyl acetate at 80 °C for 12 h. It has been previously reported that in the radical copolymerization of polar and nonpolar monomers, the solvent polarity affects the relative monomer reactivity and copolymerization kinetics owing to the formation of complexes between the monomer and/or the propagating radical and the solvent, that is, the solvation of the transition state.\(^\text{[46]}\) In the case of St–AA copolymerization, for example, the higher polarity of the solvent led to a greater difference between the monomer reactivities, for example, \(r_{\text{AA}} = 0.15\) and \(r_{\text{St}} = 0.25\) for the copolymerization in bulk, \(r_{\text{AA}} = 0.05–0.08\) and \(r_{\text{St}} = 1.03–1.60\) in \(N,N\)-dimethyl formamide, and \(r_{\text{AA}} = 0.13\) and \(r_{\text{St}} = 0.25\) in 1,4-dioxane. Because nonpolar ethyl acetate was used as a solvent in our case, the St/AA comonomer composition should be comparable to that in the feed. Subsequent RAFT polymerization of nBA using the poly(St-r-AA) macro-CTA afforded triblock copolymers with poly(nBA) and poly(St-r-AA) as the middle soft and hard segments, respectively. The comparison of the SEC chromatograms of the starting macro-CTA and triblock copolymer in Figure 2c shows a clear shift to higher molecular weights for the block copolymer. These results indicate the formation of the targeted ABA triblock copolymers with predetermined chain lengths of the middle and end blocks, composition, and location and amount of the carboxylic acid functionality in the hard/soft segment, owing to the superior tolerance of the carboxylic acid functionality during RAFT polymerization.

**Morphology and Thermal Properties.** The thermal properties of the resulting triblock copolymers were analyzed by differential scanning calorimetry (DSC). Three styrene–acrylic triblock copolymers without (BP2 in Table 1) and with the AA unit in the middle soft segment (BP4 in Table 1) or end hard segments (BP6 in Table 2) were employed as representative samples. As shown in Figure 3, DSC measurements showed that the addition of the AA units into the middle poly(BA) units increased the \(T_g\) of the midblock, relative to that of the pristine triblock copolymer (\(T_g\) of the midblock changed from −37.1 to −32.6 °C for BP2 and BP4, respectively, BP4 in Table 1).
Table 2. Synthesis of ABA Triblock Poly(St-AA)-b-poly(nBA)-b-poly(St-AA) and Poly(St-r-AA)-b-poly(2EHA)-b-poly(St-r-AA) Copolymers by RAFT Polymerization Using Poly(St-r-AA) Macro-CTA
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| code | comonomer | [M]₀/[macro-CTA]₀/[I]₀ | conv. (%) | Mₙ (theory) | Mₙ (SEC) | Mₑ/Mₙ (SEC) | composition |
|------|-----------|-------------------------|-----------|-------------|----------|------------|-------------|
| BP6  | nBA       | 3,500/5/1               | 73        | 88,200      | 53,700   | 1.94       | 23:74:3     |
| BP7  | nBA       | 5,500/5/1               | 74        | 127,000     | 105,400  | 2.32       | 15:83:2     |
| BP8  | 2EHA      | 1,350/3/1               | 81        | 89,900      | 43,700   | 1.64       | 31:65:4     |

“Polymerization in ethyl acetate ([M] = 4.0 mol/L) at 85 °C for 10 h, poly(St-r-AA) macro-CTA 3: Mₙ = 22,800, Mₑ/Mₙ = 1.36. Calculated by GC. Theoretical molecular weight (Mₙ theory) = (MW of monomer) × [monomer]₀/[macro-CTA]₀ × conv. + (MW of macro-CTA). Measured by SEC using polystyrene standards in THF. Calculated by monomer conversion.

(a) Copolymers by RAFT Polymerization Using Poly(St-b-poly(GC).

Table 2. Synthesis of ABA Triblock Poly(St-r-AA)-b-poly(nBA)-b-poly(St-r-AA) and Poly(St-r-AA)-b-poly(2EHA)-b-poly(St-r-AA) Copolymers by RAFT Polymerization Using Poly(St-r-AA) Macro-CTA

| code | comonomer | [M]₀/[macro-CTA]₀/[I]₀ | conv. (%) | Mₙ (theory) | Mₙ (SEC) | Mₑ/Mₙ (SEC) | composition |
|------|-----------|-------------------------|-----------|-------------|----------|------------|-------------|
| BP6  | nBA       | 3,500/5/1               | 73        | 88,200      | 53,700   | 1.94       | 23:74:3     |
| BP7  | nBA       | 5,500/5/1               | 74        | 127,000     | 105,400  | 2.32       | 15:83:2     |
| BP8  | 2EHA      | 1,350/3/1               | 81        | 89,900      | 43,700   | 1.64       | 31:65:4     |

“Polymerization in ethyl acetate ([M] = 4.0 mol/L) at 85 °C for 10 h, poly(St-r-AA) macro-CTA 3: Mₙ = 22,800, Mₑ/Mₙ = 1.36. Calculated by GC. Theoretical molecular weight (Mₙ theory) = (MW of monomer) × [monomer]₀/[macro-CTA]₀ × conv. + (MW of macro-CTA). Measured by SEC using polystyrene standards in THF. Calculated by monomer conversion.

In contrast, the incorporation of AA units in poly(St) end blocks of the triblock copolymers (BP6 in Table 2) exhibited no significant change in Tᵩ′ which was attributed to the middle soft segment.

The atomic force microscopy (AFM) height and adhesive images of the surface of the three block copolymers were recorded under ambient conditions on a 1.5 × 1.5 μm² scale to investigate the phase separation between the hard and soft domains (Figure 4). In addition to the conventional height images, the PeakForce QNM technique gave further insights into the state of the adhesive properties. The bright and dark regions in the adhesive images were assigned to the soft poly(nBA) and hard poly(St) segments, respectively. AFM measurements of poly(St)-b-poly(nBA)-b-poly(St) (BP2) with longer poly(St) segments (Mₙ = 15,900) revealed spherical microphase separated structures, as shown in Figure 4a. In contrast, the same triblock copolymer (BP1) with relatively short poly(St) segments (Mₙ = 10,000) showed no microphase separation (Figure S2, Supporting Information), suggesting that a certain chain length of poly(St) hard segment was required to achieve microphase separation under the conditions.

As shown in Figures 4b,c, both spherical and cylindrical structures could be observed for poly(St-b-poly(nBA-AA)-b-poly(St) (BP4) and poly(St-r-AA)-b-poly(nBA-AA)-b-poly(St-r-AA) (BP6). These results indicated that the addition of AA units to poly(St)-b-poly(nBA)-b-poly(St) led to a change in the Flory–Huggins interaction parameters between poly(St) and poly(nBA), resulting in a self-assembled morphology. The same shapes and distributions were seen in the height images (Figure 4d–f), which provided further evidence for the presence of microphase separation structures. As shown in Figure S3 (Supporting Information), poly(St)-b-poly(nBA-AA)-b-poly(St) (BP5 in Table 1) and poly(St-r-AA)-b-poly(nBA-AA)-b-poly(St-r-AA) (BP7 in Table 2) with their longer middle soft segments exhibited spherical structures originating from a short hard segment, which were dispersed within the matrix of the soft segment. In the case of poly(St-r-AA)-b-poly(2EHA)-b-poly(St-r-AA) (BP8 in Table 2), continuous cylindrical structures were predominantly visible (Figure S4, Supporting Information). These AFM investigations indicated the formation of self-assembled structures on the polystyrene terephthalate (PET) substrate, in which the morphologies were governed by the chain lengths of the soft and hard segments, their composition, location of the AA unit, and flexibility of the middle soft segment.

**Evaluation of Adhesive Properties.** The adhesive properties and melt temperature of the synthesized triblock copolymers were evaluated in terms of 180° peeling adhesive strength and holding force, shear adhesion failure temperature (SAFT), dynamic viscoelasticity measurement (dynamic mechanical analysis (DMA)), and a Koka-type flow tester. The adhesive strength was initially evaluated by a 180° peel.
test, which corresponds to the force required to peel the adhesive from an adherend. Here, the holding force was evaluated by monitoring the temperature before the adhesive failed. In both cases, a flexible backing film was adhesively bonded to stainless steel. The SAFT determines the upper working limit temperature of a tape under static shear load. In the SAFT test, the heat-fail temperature of shear strength of a PSA was measured as an additional test for shear resistance. For practical applications, it is desirable to produce triblock copolymers with a holding force greater than 100 N/25 mm, SAFT > 100 °C, and no cohesive failure.

Initially, we attempted to prepare the heat-resistant ABA triblock copolymers with a high holding power even under a high-temperature environment by changing the molecular weight of poly(St) hard segments in poly(St)-b-poly(nBA)-b-poly(St). As shown in Table 3, poly(St)-b-poly(nBA)-b-poly(St) with relatively short poly(St) end chains (Mn = 10,000, BP1) exhibited low cohesive strength, and cohesive failure was detected in a 180° peeling adhesion strength test. Further, the melting temperature, which was defined as a softening point by a 1/2 method (T1/2), was determined to be less than 40 °C using a Koka-type flow tester (Figure 5). The ball tack test was also conducted to evaluate the tackiness of adhesive tape, and the result showed a similar tendency (the number of ball, which could be stuck to the adhesive tape, was 12).

An increase in the melting temperature (T1/2) to 79 °C was detected in the triblock copolymers composed of the poly(nBA) middle block and longer poly(St) chains (Mn = 15,900, BP2 and BP3). In a 180° peeling adhesion strength test, the delamination was interfacial failure, no stick-slip was detected, and the adhesive strength was observed to be 20 N/25 mm or less. However, the heat creep resistance test (1 kgf at 80 °C for 2 h) revealed a short holding time of 1 min, suggesting insufficient heat resistance. The same tendency was also observed in the ball tack test (ball number = 12).

The triblock copolymers with the AA unit in the middle block, poly(St)-b-poly(nBA-r-AA)-b-poly(St), and relatively longer poly(St) end chains (Mn = 15,900, BP4 and BP5) exhibited good adhesive strength (>20 N/25 mm), interfacial adhesive strength higher than 20 N/25 mm, SAFT > 100 °C, and no cohesive failure.

Table 3. Summary of Adhesive Properties

| code | 180° peel strength* | melting temp.°C | heat creep resistance† | inclined ball tack* | ball number |
|------|---------------------|----------------|-----------------------|--------------------|------------|
|      | N/25 mm             | T1/2           | (min)/creep distance (mm) |                  |            |
| BP1  | 20.0                | <40            | 1 min/25 mm           | 12                 |
| BP2  | 15.5                | 49             | 1 min/25 mm           | 12                 |
| BP3  | 15.0                | 46             | 2 min/25 mm           | 14                 |
| BP4  | 21.0                | 84             | 90 min/25 mm          | 11                 |
| BP5  | 22.0                | 68             | 90 min/25 mm          | 10                 |
| BP6  | 24.0                | 103            | non-creep             | 12                 |
| BP7  | 22.0                | 103            | non-creep             | 14                 |
| BP8  | 0.5                 | 106            | non-creep             | 16                 |

*Bond width = 24 mm, adhesive thickness a = 25.0 μm, temperature = 23 °C, relative humidity = 50%, rate of peel = 300 mm/min, and peel angle = 180°. †Load = 1 kg, heating rate = 0.5 °C/min, and pasting area = 24 × 10 mm². Die diameter = 1 mm, cylinder pressure = 0.98 MPa, and heating rate = 4 °C/min. ‡Load = 1 kg, pasting area = 25 × 25 mm², temperature = 80 °C, and measurement time = 2 h. §Bond width = 15 mm, adhesive thickness a = 25.0 μm, temperature = 23 °C, relative humidity = 50%, and inclination angle = 30°.

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Figure 4. AFM (a–c) adhesion and (d–f) height images of the triblock copolymers, (a,d) poly(St)-b-poly(nBA)-b-poly(St) (BP2 in Table 1), (b,e) poly(St)-b-poly(nBA-r-AA)-b-poly(St) (BP4 in Table 1), and (c,f) poly(St-r-AA)-b-poly(nBA)-b-poly(St-r-AA) (BP6 in Table 2).

Figure 5. Flow tester test results of the triblock polymers: (blue; BP2) poly(St)-b-poly(nBA)-b-poly(St), (green; BP4) poly(St)-b-poly(nBA-r-AA)-b-poly(St), and (red; BP6) poly(St-r-AA)-b-poly(nBA)-b-poly(St-r-AA).
failure, no stick-slip, and higher melting temperature ($T_{1/2} = 110 \, ^\circ\text{C}$). Because higher ball number corresponds to lower tackiness, the results of the ball tack test indicated higher tackiness (11 for BP4 and 10 for BP5, respectively) of the triblock copolymers with the AA unit in the middle block and relatively longer poly(St) end chains.

As shown in Table 3, the SAFT of BP5 is much lower than that of BP4, which may be due to the higher St content in BP4. As can be seen in AFM images, BP4 showed predominantly cylindrical structures (Figure 4b,e), whereas spherical structure was mainly detected in BP5 (Figure S3, Supporting Information). Similarly, higher SAFT of BP8 is caused by the cylindrical structures (Figure S4, Supporting Information). The difference in the nanomorphology may contribute to the significant difference in the SAFT between BP4 and BP5, in addition to the different St contents. In contrast, higher SAFT of BP6 may be due to the incorporation of the AA unit, which can contribute to the self-complementary hydrogen bonding, into poly(St) segments, resulting in the enhancement of pseudo-cross-linking. In this case, both cylindrical and spherical structures were clearly seen in the AFM images (Figure 4c,f), which can be attributed to high SAFT of BP6. In order to evaluate the surface composition, we also conducted contact angle measurements of a water droplet on the block copolymer surfaces. The contact angle of the block copolymers with AA units in the poly(St) segments (BP6 and BP7) were 100 and 107°, respectively. These values were comparable to those of the block copolymers without AA units (103 and 107° for BP2 and BP3), indicating that the outermost surface was covered predominantly with the hydrophobic St unit, independent of the AA contents. Poly(St-r-AA)-b-poly(nBA)-b-poly(St-r-AA) with relatively longer poly(St-r-AA) end chains ($M_n = 22,800$, BP6 and BP7) exhibited good adhesive strength (>20 N/25 mm), interfacial failure, and no stick-slip. The result of the ball tack test was 12 (BP6) and 14 (BP7), respectively.

The triblock copolymers with the AA unit in the end blocks, poly(St-r-AA)-b-poly(nBA)-b-poly(St-r-AA)s (BP6 and BP7), showed further increase in the melting temperature (130 °C) and no deviation under the measurement conditions. This result implied that good heat resistance was achieved by incorporating the AA unit in the poly(St) end chains. The results of the Koka-type flow tester, as shown in Figure 5, confirmed that both the increase in the melting temperature and heat resistance were dependent on the position of the introduced AA unit. Thus, by using the triblock copolymers with suitable AA units in the hard segments, the adhesiveness of the adhesive layer was enhanced, and the occurrence of the positional deviation between the substrate and flexible film was suppressed.

Figure 6 shows the results of DMA, giving an insight into the temperature dependence of the storage modulus ($G'$) and loss ($G''$) of the triblock copolymer. The triblock copolymer poly(St)-b-poly(nBA)-b-poly(St) was first measured as a reference. In Figure 6a, for the copolymer where the AA unit was not installed, the storage elastic modulus decreased markedly for temperatures above 60 °C. In Figure 6b,c, the decrease in the storage modulus at high temperatures was suppressed by the introduction of AA units at specific locations. Figure 7 shows a plot of the storage modulus data for each sample. Comparing BP4 and BP6, poly(St-r-AA)-b-poly(nBA)-b-poly(St-r-AA)s (triblock polymer with AA units in the end block, BP6) showed a lower storage modulus at higher temperatures than BP4. BP6 showed no deviation in the 120 °C holding power test. The melting temperature of the poly(St) hard segment that acted as a pseudo-cross-linking point was the main factor that determined the heat resistance temperature of the triblock polymer. In addition to the thermal stability of the original poly(St) segment, the hydrogen bonding strength between the AA units helped to further strengthen the network of the cross-linking points and improve heat resistance. Owing to the introduction of polar functional groups and optimization of the AA position, an elastomer with excellent heat resistance was obtained while still being a thermoplastic. BP8 with 2-EHA introduced in the soft segment.
showed excellent holding power like BP7, and $T_f$ of the soft segment had no effect on heat resistance. The adhesive strength (180° peeling strength) was less than 1/40 compared with BA and did not increase because of strong adhesiveness.

**CONCLUSIONS**

In this study, we demonstrated that incorporation of an AA unit in ABA triblock copolymers composed of poly(St) hard ends and poly(nBA) soft middle block leads to a novel PSA with thermoplastic property, good heat resistance, and strong tackiness. Poly(St) and poly(St-r-AA) end blocks were initially prepared as macro-CTAs, and subsequent chain extension via RAFT process afforded poly(nBA-r-AA) and poly(nBA) middle blocks, ultimately resulting in the formation of the target triblock copolymers. Poly(St-r-AA)-b-poly(nBA)-b-poly(St-r-AA) exhibited excellent adhesion properties and heat resistance in terms of a higher holding force at 120 °C, adhesion strength = 24.0 N/25 mm, $SAFT = 103 $°C, and no cohesive failure. The presence of free carboxylic acid groups increased the intermolecular interactions within the glassy poly(St) end blocks and promoted stronger pseudo-cross-links that ultimately improved the heat resistance and adhesive strength. Although similar peel adhesion and no cohesive failure were observed for poly(St)-b-poly(nBA-r-AA)-b-poly(St), in the heat creep resistance, the creep distance was 2.5 mm, and $SAFT = 84 $°C.

These results suggested that the hydrogen bonds between the AA units on the middle block served as dynamic stickers in the elastic strands of these elastomers under the applied conditions. Regardless of the location of the AA units, the triblock copolymers with incorporated functional carboxylic acids exhibited better heat resistance and adhesive strength than the pristine St-nBA-based triblock copolymer elastomers. Significant improvements in the adhesion and heat resistance properties of these triblock copolymers as a result of such noncovalent interactions allowed for an improved design of high-performance thermoplastic elastomers. In other words, this study demonstrates the enhancement effect of the noncovalent interactions, self-complementary hydrogen bond-

![Figure 7. Effect of storage modulus depending on the location of the AA unit. (green: BP2) poly(St)-b-poly(nBA)-b-poly(St), (red: BP4) poly(St)-b-poly(nBA-r-AA)-b-poly(St), and (blue: BP6) poly(St-r-AA)-b-poly(nBA)-b-poly(St-r-AA).](image-url)

**EXPERIMENTAL SECTION**

**Materials.** Styrene (St, Idemitsu Kosan, >99.6%), nBA (Mitsubishi Chemical Corporation, >99%), 2-EHA (Mitsubishi Chemical Corporation, >99%), and AA (Osaka Organic Chemical Industry, >98.5%) were used as received without purification. ABN-E (Japan Finechem Company, 98%), acetone (Taihei Kasei, >99%), methanol (Taihei Kasei, >99%), ethyl acetate (Mitsubishi Chemical Corporation, >99%), and $SS$-dibenzyl trithiocarbonate (CTA, Arkema, >95%) were also used as received.

**Synthesis of Poly(St)-b-poly(nBA-r-AA)-b-poly(St).** The triblock copolymer having poly(nBA-r-AA) as the midblock was synthesized as follows (BP4 in Table 1). St (100 g, 0.962 mol), CTA (0.697 g, 2.40 mmol), ABN-E (0.462 g, 2.40 mmol), and ethyl acetate (50 mL) were placed in a Schlenk reaction flask, and the solution was purged with nitrogen for 60 min at a flow rate of 200 mL/min. The reaction mixture was stirred at 80 °C for 12 h. Subsequently, conversion of St was calculated by gas chromatography (GC) to be 68%. The crude product was purified by reprecipitation into methanol, followed by filtration to afford poly(St) as a pale yellow solid (yield = 64%). The number-average molecular weight ($M_n$) (as determined by SEC) and PDI ($M_w/M_n$) of the prepared poly(St) were 15,900 and 1.25, respectively (Table S1, Supporting Information).

For the preparation of the block copolymer, trithiocarbonate-terminated poly(St) (50.0 g, 3.14 mmol), ABN-E (151 mg, 0.785 mmol), nBA (190 g, 1.48 mol), AA (8.50 g, 0.118 mol), and ethyl acetate (120 mL) were placed in a Schlenk reaction flask, and the solution was purged with nitrogen for 60 min at a flow rate of 200 mL/min. The reaction mixture was stirred at 85 °C for 10 h. The conversions of nBA and AA, as determined by GC, were 67 and 71%, respectively. The crude product was purified by reprecipitation into methanol and filtration afforded poly(St)-b-poly(nBA-r-AA)-b-poly(St) as a pale yellow solid (yield = 65%). The $M_n$SEC and PDI of the block copolymer were 46,000 and 1.76, respectively.

**Synthesis of Poly(St)-b-poly(nBA)-b-poly(St).** Synthesis of the triblock copolymer to be used as a standard sample was performed as follows (BP2 in Table 1). The trithiocarbonate-terminated poly(St) macro-CTA ($M_n = 15,900, M_w/M_n = 1.25$) synthesized by the method described above was employed. For the preparation of the block copolymer, trithiocarbonate-terminated poly(St) (50.0 g, 3.14 mmol), ABN-E (151 mg, 0.786 mmol), nBA (181 g, 1.42 mol), and ethyl acetate (110 mL) were placed in a Schlenk flask, and the solution was purged with nitrogen for 60 min at a flow rate of 200 mL/min. The reaction mixture was stirred at 85 °C for 10 h and the conversion, as determined by GC, was 75%. The crude product was purified by reprecipitation into methanol and filtration-afforded poly(St)-b-poly(nBA)-b-poly(St) as a pale yellow solid (yield = 71%). The $M_n$SEC and PDI of the block copolymer were 43,100 and 1.79, respectively.

**Synthesis of Poly(St-r-AA)-b-poly(nBA)-b-poly(St-r-AA).** The triblock copolymer having poly(St-r-AA) end blocks was synthesized as follows (BP6 in Table 2). St (88.0 g, 0.846 mol), AA (12.0 g, 0.166 mol), CTA (0.734 g, 2.53 mmol), ABN-E (0.486 g, 2.53 mmol), and ethyl acetate (50 mL) were placed in a Schlenk flask, and the solution was purged with nitrogen for 60 min at a flow rate of 200 mL/min. The reaction...
mixture was stirred at 80 °C for 12 h. Subsequently, the conversions of St and AA were determined by GC to be 86 and 99%, respectively. The crude product was purified by reprecipitation into methanol, followed by filtration to afford poly(St-r-AA) as a yellow solid (yield = 85%). The resulting poly(St-r-AA) had $M_n$ (as determined by SEC) and PDI of 22,800 and 1.36, respectively (Table S1, Supporting Information).

For the synthesis of the block copolymer, the triiocarbonatedermate-terminated poly(St-r-AA) (50.0 g, 2.19 mmol), ABN-E (84.1 mg, 0.438 mmol), nBA (196 g, 1.53 mol), and ethyl acetate (120 mL) were placed in a Schlenk flask, and the solution was purged with nitrogen for 60 min at a flow rate of 200 mL/min. The reaction mixture was stirred at 85 °C for 10 h. The conversion (based on nBA) calculated by GC was 73%. The crude product was purified by reprecipitation into methanol, followed by filtration to obtain poly(St-r-AA)-b-poly(nBA)-b-poly(St-r-AA) as a pale yellow solid (yield = 67%). The $M_n$, SEC, and PDI of the block copolymer were 53,700 and 1.94, respectively.

**Instruments.** $M_n$ and $M_p/M_n$ were estimated by SEC at 40 °C, using a SHODEX GPC-101 system equipped with refractive index and UV detectors. The column set consisted of four consecutive hydrophilic vinyl polymer-based gel columns (TSK-GELS, bead size, exclusion limits): GMHXL (9 μm, 4 × 103), G-2000 (5 μm, 1 × 104), and a guard column (TSK-guard column HXL-L, 4.0 cm). The system was operated at a flow rate of 1.0 mL/min using tetrahydrofuran (THF). Polystyrene standards were used for calibration. The residual monomer content was measured by GC (Agilent GC7890) using the HP-5 (% phenyl methyl-polysiloxane) column and a flame ionization detector. The system was operated at a carrier gas flow rate of 1.0 mL/min.

AFM experiments were performed with the Bruker Multi-Mode 8 microscope by the PeakForce QNM technique in air, using silicon nitride cantilevers with a force constant of approximately 0.4 N/m. The sample was prepared as follows. The block copolymer solution was diluted to 40% with ethyl acetate, applied to a PET film (Lumirror #50 - S10 Toray Industries, Inc.) using a Baker film applicator (150 μm gap and 25 μm film thickness), and dried at 100 °C for 5 min.

Measurements of peel strength were all made on a tensile testing machine (Toyoseiki Strograph VG1-E) using a modified form of a variable-angle peeling device, following a standard Japanese Industrial Standards (JIS) procedure (JISZ0237:2009). The stainless steel substrate was cleaned with acetone. The specimens were cut to a width of 24 mm and a length of 300 mm using an adhesive tape test piece made by the above-mentioned preparation method. The specimens were a SUS304 steel plate with bright annealed finish and surface roughness of Ra 50 ± 25 nm. The dimensions of the test plate were 2 mm (thickness) × 50 mm (width) × 125 mm (length). The test plate was cleaned by soaking absorbent cotton in acetone and wiping the surface of the specimen and then drying by wiping with new cotton wool. The cleaning procedure was repeated three times or more, until the washing solvent was visually removed from the surface of the substrate. Then, the block copolymer specimen was pressed onto the stainless steel substrate using two passes of a 2 kg rubber roller and stored at room temperature for over 24 h. The 180 peel strength of the specimens was measured after coating onto the PET film. The crosshead speed was 300 mm/min at room temperature. The average force in the debonding process was measured as the peel strength.

The SAFT indicates the resistive ability under a constant shear load at an elevated temperature and can be measured following a standard JIS procedure (ASTMD-4498). The specimen was pressed onto a stainless steel substrate using two passes of a 2 kg rubber roller and was 24 mm wide and 10 mm long. The load attached to the specimen was 1 kg, and the heating rate was 0.5 °C/min. The SAFT results indicated the temperature at which the bonding failed.

Heat creep resistance was measured using a creep tester (Testor Industries), according to a standard JIS procedure (JISZ0237:2009). The test piece prepared by the method described above was cut into a 25 mm wide and 300 mm long test piece, which was placed at the center of a 25 mm × 25 mm stainless steel plate without applying pressure. The roller was pressed four times from above the test piece. At 24 h after crimping, one end of the stainless steel plate was stopped such that the stainless steel plate and the test piece were vertical, and a 1 kg weight could be attached. The test piece was then placed in an oven adjusted to a temperature of 80 °C, and the time elapsed until the test piece completely peeled off the stainless steel plate after 2 h from the attachment of the weight, or the shifted distance after a predetermined time, was measured.

Inclined ball tack was measured using a ball tack tester (Testor Industries), according to a standard JIS procedure (JISZ0237:2009). The test piece prepared by the method described above was cut into a 15 mm wide and 300 mm long test piece and was set on an inclined surface of the tack tester. The inclination angle of the inclined ball tack tester was 30°. After washing the ball with acetone using high-carbon chromium bearing steel (SUJ2), the ball was rolled from the inclined surface and evaluated whether it stopped on the adhesive surface. The ball number shall be 32 for a 1 inch diameter and 1 for 1/32. The test results were expressed as the number of the largest ball found, and the average of three test pieces was determined.

The dynamic viscoelasticity measurements (DMA) were performed using ARES-G2 (TA Instruments) at 1 Hz and −50 to 150 °C with the temperature increasing at a rate of 3 °C/min. The outflow temperature by the 1/2 method using a Koka-type flow tester was measured using a rising flow tester (Shimadzu Corporation). The die diameter was 1 mm, cylinder pressure was 0.98 MPa, heating rate was 4 °C/min, and the measurement started at 40 °C.

**ASSOCIATED CONTENT**

**Supporting Information**
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b04282.

1H NMR spectra, AFM images, and synthesis of macrochain-transfer agents (PDF).

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Notes
The authors declare no competing financial interest.

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