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Introduction

Thermoplastic elastomers (TPEs) are of high utility and interest for a wide variety of applications, ranging from adhesives and electronics to clothing and automotive parts due to their highly processable structures.¹ With the ability to fine-tune the chemical TPE architecture and properties, triblock copolymers with an ABA architecture can be designed to comprise of a soft/rubbery middle segment (B) with two hard/glassy blocks at the ends (A). By selecting immiscible A and B blocks, the

Sustainable glucose-based block copolymers exhibit elastomeric and adhesive behavior†

Mohammadreza Nasiri and Theresa M. Reineke*

Herein, we present the direct modification of glucose, an abundant and inexpensive sugar molecule, to produce new sustainable and functional polymers. Glucose-6-acrylate-1,2,3,4-tetraacetate (GATA) has been synthesized and shown to provide a useful glassy component for developing an innovative family of elastomeric and adhesive materials. A series of diblock and triblock copolymers of GATA and n-butyl acrylate (n-BA) were created via Reversible Addition-Fragmentation Chain Transfer (RAFT) polymerization. Initially, poly(GATA)-b-poly(n-BA) copolymers were prepared using 4-cyano-4-[(ethylsulfanylthiocarbonyl)sulfanyl] pentanoic acid (CEP) as a chain transfer agent (CTA). These diblock copolymers demonstrated decomposition temperatures of 275 °C or greater and two glass transition temperatures (T_{o}) around -45 °C and 100 °C corresponding to the PnBA and PGATA domains, respectively, as measured by differential scanning calorimetry (DSC). Triblock copolymers of GATA and n-BA, with moderate dispersities (D = 1.15-1.29), were successfully synthesized when S,S-dibenzyl trithiocarbonate (DTC) was employed as the CTA. Poly(GATA)-b-poly(nBA)-b-poly(GATA) copolymers with 14-58 wt% GATA were prepared and demonstrated excellent thermomechanical properties ($T_d \ge 279$ °C). Two well-separated glass transitions near the values for homopolymers of n-BA and GATA (~-45 °C and ~100 °C, respectively) were measured by DSC. The triblock with 14% GATA exhibited peel adhesion of 2.31 N cm⁻¹ (when mixed with 30 wt% tackifier) that is superior to many commercial pressure sensitive adhesives (PSAs). Use of 3,5-bis(2-dodecylthiocarbonothioylthio-1oxopropoxy)benzoic acid (BTCBA) as the CTA provided a more efficient route to copolymerize GATA and n-BA. Using BTCBA, poly(GATA)-b-poly(nBA)-b-poly (GATA) triblock copolymers containing 12–25 wt% GATA, with very narrow molar mass distributions ($D \leq$ 1.08), were prepared. The latter series of triblock copolymers showed excellent thermal stability with $T_{d} \ge$ 275 °C. Only the T_q for the PnBA block was observed by DSC (~-45 °C), however, phase-separation was confirmed by small-angle X-ray scattering (SAXS) for all of these triblock copolymers. The mechanical behavior of the polymers was investigated by tensile experiments and the triblock with 25% GATA content demonstrated moderate elastomeric properties, 573 kPa stress at break and 171% elongation. This study introduces a new family of glucose-based ABA-type copolymers and demonstrates functionality of a glucose-based feedstock for developing green polymeric materials.

soft/rubbery B segments will form intermolecular physical cross-links between the A segments.² Self-assembly of the glassy endblocks into microstructures at ambient temperatures, with the rubbery blocks bridging between the hard domains, creates a superior resistance to flow, resulting in a material with elastomeric properties.¹ Variations in the block lengths and component ratios allows for preparation of elastomeric materials with different nanopatterns (spheres, cylinders, *etc.*)³ and the molecular compositions can be tuned to achieve the desired properties for any specific applications.

Currently, the most common and widely used ABA triblock copolymers for TPE applications are styrene-based copolymers, such as poly(styrene)-*b*-poly(butadiene)-*b*-poly(styrene) (SBS) and poly(styrene)-*b*-poly(isoprene)-*b*-poly(styrene) (SIS).¹ Although, these styrene-based materials possess valuable and functional



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properties for their intended applications, they are derived from nonrenewable feedstocks. Yet, the manufacturing and disposal of these petroleum-based materials (particularly, styrene) has a clear negative environmental impact,⁴ which affirms the need for developing TPEs from more sustainable and plant-based feedstock sources.^{5–11}

To date, sustainable TPE research has primarily focused on lactide and lactone derivatives.¹ For example, Qian et al.¹² and Cohn et al.¹³ have used poly(lactide) (PLA) as the glassy component in tri- and multiblock copolymers, also consisting of rubbery poly(ethylene glycol) blocks, to create thermoplastic elastomers. PLA has been used in association with poly(isoprene) segments, a traditional soft segment, to prepare elastomeric materials,14,15 and Lebarbé et al. have reported ABA triblock copolymers of PLA with poly(ricinoleic acid).¹⁶ Additionally, α -methylene- γ -butyrolactone (MBL) has been copolymerized with n-butyl acrylate (n-BA) to prepare ABA triblock copolymers for TPE applications.¹⁷ Moreover, Gallagher et al. have used an acetylated methacrylic isosorbide (AMI) as a glassy sustainable monomer, to synthesize a series of welldefined di- and triblock copolymers utilizing n-BA as the soft segment; this work has enabled development of new elastic and adhesive materials.^{18,19} In another effort to create biorenewable thermoplastic elastomers, Robertson and coworkers have developed ABA linear triblock copolymers with fatty acid-derived midblock and salicylic acid-derived endblocks.²⁰ Also, Bolton *et al.* reported using α -methyl-*p*-methylstyrene and myrcene in their triblock system to create sustainable TPEs.21

Researchers have also sought alternative rubbery blocks from sustainable feedstocks.²²⁻²⁹ For example, ABA triblock copolymers of menthide and lactide monomers have been created via sequential ring-opening polymerizations to produce renewable and hydrolytically degradable pressure sensitive adhesives (PSAs).² Wang et al. have utilized soybean oil derived monomers in their triblock copolymers to incorporate sustainable soft segments into styrene-based TPEs.^{29,30} Shin and coworkers copolymerized ɛ-decalactone with L-lactide to produce renewable triblock thermoplastic elastomers.³¹ Additionally, copolymers of ε-caprolactone and ε-decalactone were used as the midblock for ABA triblocks with PLA endblocks.³² Block polymers have also been created from substituted δ -valerolactone monomers and studied in detail for their structure activity relationships for sustainable material design.³³ Moreover, block copolymers from menthide and tulipalin A (α -methylene- γ -butyrolactone) have been examined for thermoplastic elastomer applications.³⁴ Ding et al. recently reported the preparation of $poly(\gamma-methyl-\alpha-methylene-\gamma-butyro$ lactone)-*b*-poly-(menthide)-*b*-poly(γ -methyl- α -methylene- γ -butyrolactone) ABA triblock copolymers that offer a significant enhancement in the adhesive properties compared to the previously reported sustainable elastomers.35 Despite the enormous research efforts to create sustainable elastomeric materials, creating these materials to exhibit comparable properties to commercial petroleum-derived structures, at a reasonable cost, remains a great challenge.

Herein, we report a new family of thermoplastic elastomers based on the direct functionalization of glucose, an abundant and low cost sugar. The glucose-based monomer, glucose-6acrylate-1,2,3,4-tetraacetate (GATA), was created to impart a sustainable glassy segment into block copolymers that have been copolymerized with rubbery n-butyl acrylate (n-BA). Reversible Addition-Fragmentation Chain Transfer (RAFT) polymerization of the GATA monomer, in conjunction with its copolymerization with n-BA, allowed preparation of fine-tuned diblock and triblock copolymers. Controlled radical polymerization methods such as RAFT provide a powerful tool to target copolymers with tailored architecture, composition, and molar mass to examine structure-activity relationships to achieve targeted properties. Furthermore, triblock copolymers with the desired ABA architecture were investigated for the fidelity of phase-separation in the bulk and were initially examined for their adhesion and mechanical properties. Although different modifications of glucose have previously been explored for various biomaterials applications,³⁶⁻⁴⁰ this study is the first to utilize GATA in TPE applications. Indeed, the new family of materials introduced here in provides a green feedstock for the development of sustainable elastomeric materials that can be utilized in a wide variety of applications.

Results and discussion

Synthesis and polymerization of the GATA monomer

The synthesis of the sugar-based monomer, glucose-6-acrylate-1,2,3,4-tetraacetate (GATA), was inspired from previously reported procedures.^{39,41} The primary hydroxyl group on glucose was protected with a trityl group followed by full acetylation of the remaining hydroxyl groups. The trityl protecting group was then selectively removed using trifluoroacetic acid (TFA). Lastly, the acrylate functionality was installed on the primary alcohol position *via* esterification with acryloyl chloride (Scheme 1).

RAFT polymerization of the GATA monomer was employed to synthesize the glassy block. Using 4-cyano-4-[(ethylsulfanylthiocarbonyl)sulfanyl] pentanoic acid (CEP) as the chain transfer agent (CTA), the poly(GATA) macro-CTA was synthesized (Scheme 2, Table 1: denoted as P1 "polymer 1"). Subsequently, *n*-butyl acrylate (n-BA) was sequentially added to the P1 macro-CTA to yield poly(glucose-6-acrylate-1,2,3,4-tetraacetate)-*b*-poly(*n*-butyl acrylate) (PGATA-*b*-PnBA) diblock copolymers with low molar mass distributions (Table 1, see the ESI, Fig. S4,† for the size exclusion chromatography results). All diblock copolymers were created from the P1 macro-CTA.

To examine the ability to target different block lengths with high control, a series of diblocks with various component ratios were synthesized (P4–P6, Table 1). These systems displayed thermal stability ($T_d \ge 275$ °C). Additionally, in all cases, the diblocks exhibited two well-separated glass transition temperatures (T_g), which are near the T_g values of the respective homopolymers (104 °C and -50 °C (ref. 42) for poly(GATA) and poly(n-BA), respectively), indicating microphase



Glucose-6-acrylate-1,2,3,4-tetraacetate (GATA)

Scheme 1 Synthesis of glucose-6-acrylate-1,2,3,4-tetraacetate (GATA).



Scheme 2 Schematic synthesis of the PGATA macro-CTA followed by copolymerization with *n*-butyl acrylate (n-BA).

Polymer	Sample code	$M_{\rm n}{}^a$ (kDa, NMR)	${M_{\rm n}}^b$ (kDa, SEC)	D^b	GATA wt% (NMR)	GATA wt% (SEC)	T_{d}^{c} (°C)	T_{g}^{d} (°C)
PGATA	P1	21	19	1.17	100	100	283	104
	P2	22	25	1.17	100	100	278	104
	P3	21	23	1.09	100	100	275	100
PGATA-b-PnBA ^e	P4	40	53	1.12	52	35	275	-45,103
	P5	86	96	1.20	24	20	279	-45,105
	P6	106	130	1.20	20	15	280	-43, 92
PGATA- <i>b</i> -PnBA- <i>b</i> -PGATA ^{<i>f</i>}	P7	38	54	1.15	58	46	279	-45, 105
	P8	134	99	1.29	16	24	298	-44, 107
	P9	147	124	1.16	14	18	312	-43, 105

Table 1 Data summary of the GATA homopolymers and the respective diblock and triblock copolymers of GATA and n-BA

^{*a*} Number average molar mass determined by ¹H NMR spectroscopy. ^{*b*} Number average molar mass and polydispersity determined by SEC-MALLS in THF at room temperature. ^{*c*} Decomposition temperature at 5% weight loss determined by thermal gravimetric analysis (TGA). ^{*d*} Glass transition temperature determined by differential scanning calorimetry (DSC). ^{*e*} All diblock copolymers were synthesized using P1 as the macro-CTA. ^{*f*} Corresponding macro-CTA for P7 was P2, and P3 was chain extended to achieve the other two triblock copolymers (P8 and P9).

separation between the PGATA and PnBA domains. These results indicated that these segments were promising for further study by synthesizing ABA-type triblock copolymers, to enable physically cross-linked networks for TPE applications. Thus, we were inspired to proceed with the sequential polymerization to construct PGATA-*b*-PnBA-*b*-PGATA triblock copolymers with this same synthetic procedure. However, attempts to sequentially add a third block *via* RAFT polymerization on the PnBA end of the diblock macro-CTA were unsuccessful. To this end, we explored the use of a symmetric



Scheme 3 Two-step synthesis of the PGATA-b-PnBA-b-PGATA triblock copolymers using a symmetric trithiocarbonate as the CTA.

trithiocarbonate CTA to build the desired PGATA-*b*-PnBA-*b*-PGATA triblocks. As shown in Scheme 3, we employed *S*,*S*-dibenzyl trithiocarbonate (DTC) as the chain transfer agent for this two-step synthesis. P2 and P3 homopolymers were synthesized using DTC and were subsequently chain extended with *n*-butyl acrylate to yield the triblock copolymers listed in Table 1 (P7–P9). Similar to the diblock analogs, the triblock copolymers showed excellent thermal stability (with decomposition temperatures higher than 279 °C) along with two well-separated T_g values (~–45 °C and ~105 °C for the PnBA and PGATA domains, respectively). Close inspection of the size exclusion chromatography (SEC) traces shows that there is a lower molar mass shoulder with the triblocks, which can be attributed to the dead chains from the macro-CTA synthesis (Fig. 1).

Both the di- and triblock polymers presented in Table 1 were prepared in various GATA weight percentages and with low dispersities, which supports a successful utilization of the RAFT mechanism for copolymerization of GATA and n-BA. Although this approach offers a simple two-step synthesis for the desired triblocks, the resulting copolymers carry a trithio-carbonate functionality within the midblock. This internal trithiocarbonate can impact the processability of the materials at high temperatures as this group is susceptible to degradation *via* high temperature or hydrolysis. Yet, this simple preparation method offered a facile means to produce and study this family of triblock copolymers and evaluate their properties for further study.

The ABA architecture of these triblock copolymers, which are comprised of a rubbery and low T_g midblock (PnBA) and two hard and high T_g end-segments (PGATA), provides a template that can form a network *via* physical cross-linking between the two domains when phase-separated at room temperature. ABA-type copolymers are appealing for TPE applications and P9, as an illustrative example, was selected to be examined for its PSA properties. With 14% GATA, this triblock is a tacky material at room temperature and was tested for its



Fig. 1 Representative SEC traces of the PGATA-b-PnBA-b-PGATA triblock copolymers (P8 and P9), using DTC as the CTA, and the corresponding macro-CTA, P3 (eluent: THF, at room temperature).

peel adhesion. The force required to remove an adhesive from a substrate is responsible for the peel strength.² For adhesion testing, solutions of 30 wt% of the polymers were uniformly spread on a polyethylene terephthalate (PETE) film. After complete evaporation of the solvent, the coated films were adhered onto a stainless steel plate and the peel resistance was measured by pulling the adhered films off the plate at an angle of 180°. Polymer P9 (PGATA-PnBA-PGATA: 11-125-11 kDa) exhibited a peel strength of 1.05 \pm 0.12 N cm⁻¹ when the neat polymer was examined as an adhesive material. The peel adhesion was also tested with a mixture of the polymer and a tackifier. The use of a tackifier moderates the plateau modulus by diluting the entanglements in the midblock leading to more effective PSAs.^{2,43,44} Addition of a rosin ester tackifier, 30 mass percent of the polymer weight, boosted this value to 2.31 ± 0.14 N cm⁻¹. As a comparison, paper tape, scotch tape, electrical tape, and Post-it® note commercial products offer peel adhesion values of 2.4, 1.9, 1.8, and 0.3 N cm⁻¹, respectively, under similar experimental conditions.² The adhesion results were very promising and encouraged us to further improve the polymerizations to more efficiently increase the scalability and stability of this system.

To improve the potential scalability, stability, and processability of the triblock TPEs, another polymerization pathway was explored (Scheme 4) that employed 3,5-bis(2-dodecylthiocarbonothioylthio-10x0propoxy)benzoic acid (BTCBA) as the CTA.⁴⁵ This bifunctional CTA leaves the cleavable trithiocarbonate groups on the ends of the polymer chains (Scheme 4), while maintaining a facile two-step synthesis to yield the desired triblocks. Final triblock copolymer structures were achieved with excellent control as low dispersities ($D \leq 1.08$) were obtained. Using BTCBA as the CTA demonstrated that this strategy offers an efficient and effective route for advanced development of these materials. Fig. 2 shows the clear shift to higher molar mass elution times with the increase in the GATA content. A summary of the characteristics for this new family of triblock copolymers is provided in Table 2.

Similar thermal stability to the previous analogous copolymers were observed ($T_{\rm d} \ge 264$ °C). Triblocks with 12, 19 and 25% of GATA content were prepared in a controlled manner. The glass transition for the soft domains (PnBA block) was evidently observed in differential scanning calorimetry (DSC),



Fig. 2 SEC traces of the PGATA-*b*-PnBA-*b*-PGATA triblock copolymers, synthesized with BTCBA as the CTA, and their corresponding macro-CTA (eluent: THF, at room temperature).

however, a clear transition was not observed for the hard domains (GATA blocks) (representative DSC traces of the two triblock copolymer groups are shown in ESI, Fig. S5†). One possible explanation for this lack of clear PGATA T_g in the DSC could be small heat change during the glass transitions for these polymers, attributed to their short PGATA segments



Scheme 4 Two-step synthesis of the PGATA-b-PnBA-b-PGATA triblocks using BTCBA as the chain transfer agent.

 Table 2
 Data summary of the *n*-butyl acrylate homopolymers and the respective triblock copolymers of GATA and n-BA with BTCBA chain transfer agent

Polymer	Sample code	$M_{\rm n}{}^a$ (kDa, NMR)	${M_{\rm n}}^b$ (kDa, SEC)	D^b	GATA wt% (NMR)	GATA wt% (SEC)	T_{d}^{c} (°C)	T_{g}^{d} (°C)
PnBA	P10	56	56	1.04	_	_	276	-43
PGATA- <i>b</i> -PnBA- <i>b</i> -PGATA	P11	64	61	1.06	12	9	268	-42
	P12	69	67	1.07	19	16	287	-44
	P13	75	75	1.08	25	25	264	-43

^{*a*} Number average molar mass determined by ¹H NMR spectroscopy. ^{*b*} Number average molar mass and polydispersity determined by SEC-MALLS in THF at room temperature. ^{*c*} Decomposition temperature at 5% weight loss determined by thermal gravimetric analysis (TGA). ^{*d*} Glass transition temperature determined by differential scanning calorimetry (DSC).

(approximately 4, 6, and 9 kDa endblocks, compared to PGATA segments greater than 11 kDa for the previous di and triblocks). It should be noted that even the glass transitions observed for the previous triblocks, with endblocks \geq 11 kDa, represented very small transitions. Lack of a second glass transition could also be attributed to presence of the dodecyl alkyl chains on the hard ends of the triblock copolymers.

Small-angle X-ray scattering (SAXS) was employed to further investigate the fidelity of phase-segregation in these triblock copolymer materials. After solvent casting, the polymer samples were annealed at 140 °C for two hours for SAXS analysis. The SAXS profile for a bulk sample generated from P9 is shown in Fig. 3(a). A strong principal reflection (q^*) indicates phase-separation between the two segments in this copolymer. Although the higher order reflections are not very well-defined, the peak position ratios of the observed broad features suggest a disorganized spherical morphology.34,46 SAXS analysis of P12 revealed an intense primary peak along with higher order broad reflections (Fig. 3(b)). The relative peak positions $(q/q^*) = \sqrt{3}$ and $\sqrt{7}$ can be associated with a cylindrical structure.^{17,46-48} Principal reflections corresponding to phasesegregation were also observed for bulk samples generated from P11 and P13 (see Fig. S6[†] for the SAXS profiles).

After synthesizing polymers with the desired ABA architecture and confirming their phase-separation, we also conducted initial examinations of the TPE properties of these triblock copolymers. Samples with lower GATA content in the polymer series were evaluated for their adhesion properties in a similar manner as previously studied. As shown in Table 3, the peel adhesion significantly drops from P11 to P12 with an increase in GATA content (12 and 19 wt%, respectively). Addition of more GATA in P13 (25 wt%) resulted in a dry/rubbery material with nearly no tack. P9 and P11 exhibited excellent adhesion properties (with peel adhesion of 2.31 and 2.01 N cm⁻¹, respectively) that are comparable or superior to many commercial PSA products (such as scotch tape, electrical tape, paper tape, *etc.*).²

The tensile properties of these triblocks were also investigated. Due to the high tack in P11 and P9 (12 and 14 wt% GATA, respectively) at ambient temperature, only samples of P12 and P13 were able to be prepared for tensile testing (Fig. 4). As shown in Fig. 4, at low strain, a linear response was observed in the stress-strain curves for both P12 and P13



Fig. 3 (a) Experimental 1D synchrotron SAXS profile of P9 (PGATA-PnBA-PGATA: 11-125-11 kDa) at 25 °C. The higher order reflections are approximately positioned at $\sqrt{2}$ and $\sqrt{7}$ relative to the principal peak. (b) Experimental 1D synchrotron SAXS profile of P12 (PGATA-PnBA-PGATA: 6-56-6 kDa) at 25 °C. The higher order reflections are approximately positioned at $\sqrt{3}$ and $\sqrt{7}$ relative the principal peak.

triblocks, which represents a Young's modulus of 440 and 560 kPa, respectively (Table 3). The stress at break and maximum elongation for these two triblocks (Table 3) are comparable to previously reported examples with similar n-BA midblock length and very high T_g end blocks, such as PMBL.¹⁷ However, the triblock copolymers used in this proof of concept study are comprised of mostly short block lengths; because elastomeric properties are tightly tied to polymer length and entanglements,² this ABA copolymer system can significantly benefit from triblock copolymers with longer block segments. Indeed, exploring the role of longer block lengths on the bulk polymer

Table 3 Tensile and peel tests summary

Sample	NMR M_n^a , kDa (GATA wt%)	SEC M_n^b , kDa (GATA wt%)	Peel adhesion (N cm ⁻¹)	E^{d} (kPa)	σ^{e} (kPa)	e^f (% elongation)
Р9	147 (14)	124 (18)	2.31 ± 0.14^{c}	NA^{g}	\mathbf{NA}^{g}	NA^g
P11	64 (12)	61 (9)	2.01 ± 0.38^{c}	NA^{g}	\mathbf{NA}^{g}	\mathbf{NA}^{g}
P12	69 (19)	67 (16)	0.29 ± 0.05	440 ± 100	312 ± 10	123 ± 8
P13	75 (25)	75 (25)	NA^h	560 ± 50	573 ± 48	171 ± 12

^{*a*} Number average molar mass determined by ¹H NMR spectroscopy. ^{*b*} Number average molar mass determined by SEC-MALLS in THF at room temperature. ^{*c*} This value is for the mixture of the polymer and 30 weight percent of a tackifier (see ESI) and the peel adhesion for neat polymer was 1.05 ± 0.12 and 1.44 ± 0.31 for P9 and P11, respectively. ^{*d*} Young's modulus calculated at the first 5% elongation. ^{*e*} Average stress at break for 5 measurements. ^{*f*} Average maximum elongation. ^{*g*} The tensile properties were not measured due to high tack at room temperature. ^{*h*} Dry, non-tacky material not relevant for adhesion testing.



Fig. 4 Stress-strain curves of P12 (PGATA-PnBA-PGATA: 6-56-6 kDa) and P13 (PGATA-PnBA-PGATA: 9-56-9 kDa). Experiments were conducted at room temperature at 5 mm min⁻¹; failure point marked with x. Five replicate tensile bars of each polymer sample were conducted.

morphology, such as the ability to form highly cross-linked networks, and/or incorporation of functional groups to promote non-covalent interactions within the soft network, $(i.e., hydrogen bonding)^{49,50}$ to improve elastomeric properties, are certainly warranted and currently in progress.

Conclusion

In summary, this study is the first to report the use of GATA, a glucose-based monomer, for the design of sustainable thermoplastic elastomers. Alternative polymerization pathways were explored and both diblock and triblock copolymers with narrow molar mass distributions were synthesized by RAFT polymerization. BTCBA, a bifunctional chain transfer agent, provided a simple and straightforward two-step synthesis for the desired ABA (PGATA-*b*-PnBA-*b*-PGATA) triblock copolymers. Phase-separation of the blocks was found by SAXS analysis and the triblock copolymers demonstrated moderate mechanical properties with excellent thermomechanical and adhesion properties. Indeed, the work herein demonstrates a new bio-based feedstock to produce greener elastomeric materials particularly for TPE applications. The role of block length and chemistry is currently being optimized to drive further improvements in the mechanical properties towards replacement of petroleumderived elastomeric materials.

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