# Sustainable Thermoplastic Elastomers from Terpene-Derived Monomers

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S *Supporting Information*

ABSTRACT: ABA triblock polymers were prepared by living anionic polymerization of the pinene-derivable monomers α-methyl-*p*-methylstyrene and myrcene. The resulting thermoplastic elastomers displayed microphase separation at moderate molar mass, an upper service temperature about 70 °C higher than traditional petroleum-derived styrenic thermoplastic elastomers, competitive tensile strengths of up to 10 MPa, impressive ultimate elongations of up to 1300%, and remarkably low energy loss recovery attributes.
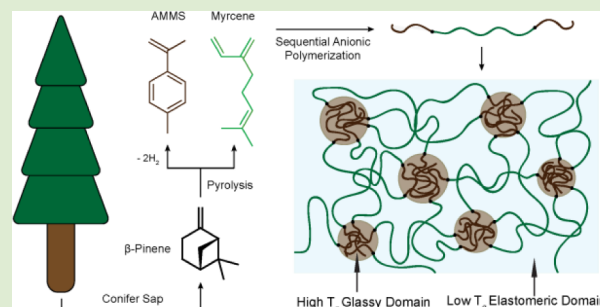
Thermoplastic elastomers (TPEs) are used in wide ranging applications including personal care products, pressure-sensitive adhesives, footwear, asphalt, and coatings. Since the 1960s, styrenic triblock polymer-based TPEs such as poly-(styrene)-*block*-poly(butadiene)-*block*-poly(styrene) (or SBS) have been a mainstay in the consumer market.[1] Over 1.7 billion kilograms of SBS and related poly(isoprene)-based TPEs are forecasted for production in 2017.[2] TPEs have properties similar to cross-linked rubbers, yet they can be melt-processed as thermoplastics. This is because the high glass transition temperature (T_g) poly(styrene) (PS, $T_g \approx 100$ °C) end blocks that flank the low T_g poly(butadiene) (PB, $T_g \approx -80$ °C) midblocks microphase segregate and act as physical cross-links that reinforce the rubbery matrix. This yields a strong elastomeric material that has a service temperature range dictated by the T_gs of the PS and PB segments. Contemporary styrenic triblock polymers are derived from finite oil-based feedstocks and thus belong to the large family of petrochemicals that are inspiring efforts to shift toward sustainable alternatives.[3,4] Moreover, the T_g of PS limits the upper service temperatures, because the physical cross-links weaken when the hard domains soften.

One strategy for extending the service temperature of styrenic TPEs is to substitute the PS blocks with a higher T_g polymer such as poly(α-methylstyrene) (PMS, $T_g = 172$ °C)[5] or poly[(cyclohexyl)ethylene] (PCHE, $T_g = 147$ °C).[6] However, neither PMS nor PCHE are renewably sourced. Advances toward sustainable TPEs have begun to emerge. One example is an all polyester-based triblock comprising poly-(lactide) hard blocks and a poly(methyl caprolactone) elastomeric midblock.[7] Although these triblocks possess excellent mechanical properties, they suffer from thermal as well as hydrolytic instability and, correspondingly, reduced upper service temperatures and lifetimes.[8,9] All-renewable poly(α-methylene-γ-butyrolactone)-*block*-poly(menthide)-*block*-poly(α-methylene-γ-butyrolactone) triblocks exhibit a noticeably improved upper service temperature due to the high T_g (≈195 °C) of their hard blocks.[10] These TPEs also show impressive ultimate elongations (>1800%) and continued performance at elevated temperatures where styrenic TPEs lose strength.

With the aim of developing new, high-performing, and sustainable TPEs, we explored the use of terpenes as a naturally occurring feedstock. Both limonene and myrcene are derivable by pyrolysis of β-pinene, a major constituent of turpentine.[11−13] Limonene can be dehydrogenated to yield α-methyl-*p*-methylstyrene (AMMS, **1**, Figure 1),[14] a compound that has
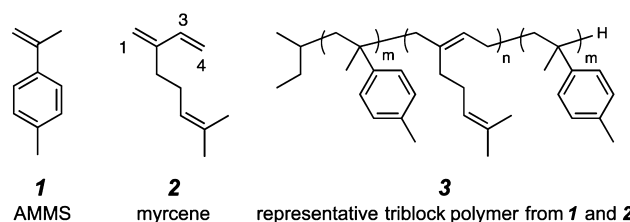

Figure 1. Structures of the monomers α-methyl-*p*-methylstyrene (**1**) and myrcene (**2**) and of a derived triblock copolymer **3**.

only rarely been polymerized.[15,16] Myrcene (**2**) is a 2-substituted-1,3-butadiene that previously has been incorporated [as poly(myrcene) (PMYR)] as the rubbery midblock in a styrenic TPE that showed promising mechanical properties.[17,18] We hypothesized that an ABA triblock such as **3**, having high T_g poly(AMMS) (PAMMS) end blocks flanking a PMYR central block, has potential value as a sustainable TPE.

Poly(α-methylstyrene) (PAMS) has a considerably lower ceiling temperature than PS because of additional steric compression between the substituents on adjacent quaternized carbon centers within the PAMS backbone.[19] This enthalpic penalty limits the extent of monomer conversion and largely defines the ceiling temperature. We devised a No-D ^{1}H NMR experiment[20] to assess the ceiling temperature associated with the (living anionic) polymerization of AMMS. A 1.0 M solution of AMMS in THF was treated with *sec*-butyllithium (ca. 10 mol %) to initiate anionic polymerization. The ^{1}H NMR spectrum of the resulting blood-red-colored solution at −78 °C showed essentially complete conversion of the AMMS to PAMMS-Li (Figure 2). Monomer evolution through depolymerization was
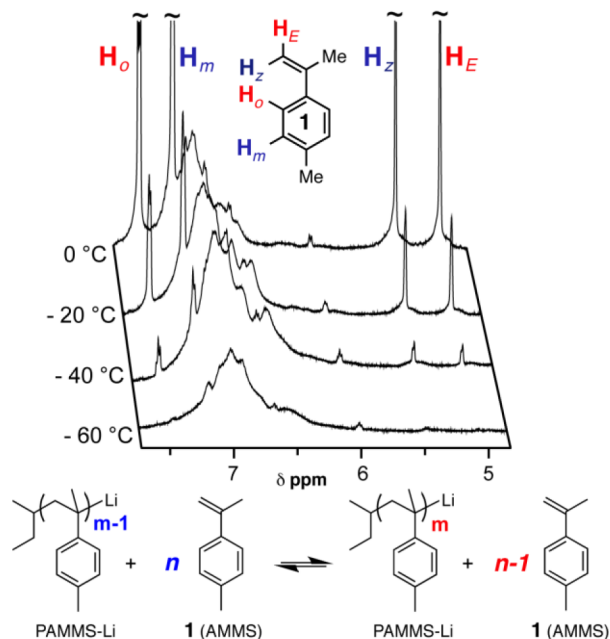

Figure 2. Direct observation by No-D ^{1}H NMR spectroscopy of the anionic polymerization of **1** to PAMMS-Li. $[1]_0 = 1.0$ M in anhydrous THF-h_8 over the temperature range of −60 to 0 °C (for a more complete set of spectra at additional temperatures, see Figure S5).

then monitored by the increase in relative intensity of the alkene resonances at δ 5.13 and 5.50 ppm as the solution was incrementally warmed. A plot of the natural logarithm of the ratio of the equilibrium to a standard state concentration of **1** $\{\ln([1]_{eq}/[1]_{ss})$ with $[1]_{ss} = 1.0$ M$\}$ versus inverse temperature (Figure S1) provided values for the enthalpy and entropy of polymerization (−31 kJ mol^{-1} and −110 J mol^{-1} K^{-1}, respectively). The ratio of these values gives a ceiling temperature of 15 °C for $[1]_0 = 1.0$ M, a value similar to that reported for PMS (4 °C).[19,21] At −78 °C the calculated equilibrium monomer concentration is 0.003 M, consistent with the observed high conversion of 1.0 M AMMS at this temperature.

Expectedly, the anionic homopolymerization of **1** in THF was well controlled and two predominantly atactic (Figure S8[22]) samples of PAMMS with $M_n = 68.2$ ($Đ = 1.07$) and 28.8 kg mol^{-1} ($Đ = 1.07$) (see Figures S2 and S3) were prepared. By differential scanning calorimetry (DSC), these samples exhibited high T_g values of 182 and 161 °C (Figures S6 and S7). Furthermore, the higher molar mass PAMMS sample showed virtually no weight loss until 310 °C by thermal gravimetric analysis (TGA, under N$_2$, Figure S8).

The complementary anionic homopolymerization of myrcene (**2**) at 10 °C in THF using *sec*-butyllithium as the initiator gave a yellow-green solution of the living anion (PMYR-Li). The resulting PMYR sample (after methanol termination) had a low dispersity ($Đ = 1.02$) and a molar mass ($M_n = 18.4$ kg mol^{-1}) close to the targeted value ($M_n = 20$ kg mol^{-1}; Figure S9). Its regiochemical composition was assessed by ^{1}H NMR analysis (Figure S10) to have 4,1/1,4-, 4,3-, and 1,2-contents of about 30, 60, and 10%, respectively, consistent with a previous report.[23] Finally, this sample of PMYR had a low T_g of −39 °C by DSC (Figure S11).

Synthesis of an ABA triblock was first attempted by sequential addition of myrcene (**2**) and then AMMS (**1**) to a solution of living PAMMS-Li. However, only PAMMS−PMYR diblock polymer was obtained upon quenching, indicating that the living PAMMS−PMYR-Li was not sufficiently reactive to reinitiate polymerization of **1**. Therefore, an alternative strategy was adopted to produce the desired ABA triblocks. Namely, addition of dichlorodimethylsilane to a solution of living PAMMS−PMYR-Li served as a coupling agent and successfully led to PAMMS−PMYR−PAMMS triblocks (Figure 3).[24,25]
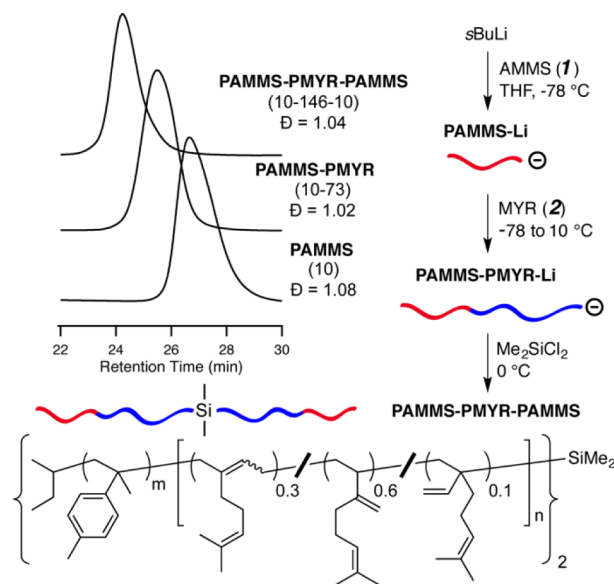

Figure 3. Synthesis of PAMMS−PMYR−PAMMS triblock copolymers by sequential anionic polymerization of AMMS and myrcene followed by coupling with dichlorodimethylsilane. The SEC data (upper left) of PAMMS, PAMMS−PMYR, and PAMMS−PMYR−PAMMS are of aliquots from the same polymerization experiment. The set of numbers in parentheses correspond to block sizes in kg mol^{-1}.

The use of precisely 0.5 equiv of Me$_2$SiCl$_2$ via titration that was guided by dissipation of the yellow-green color of the PAMMS−PMYR-Li solution was important in achieving high coupling efficiency. A representative set of SEC traces of aliquots corresponding to each of the three synthesis stages showed the sequential growth in molar mass. A series of PAMMS−PMYR−PAMMS triblock polymers of varying block sizes (in kg mol^{-1}) was produced: 10−146−10, 10−83−10, 10−58−10, 19−77−19, 17−101−17, 36−168−36 (see the SI for a discussion of how molar mass and coupling efficiency was determined and Table S1 for molecular characterization data and mechanical properties of each triblock).

Solvent cast samples of the PAMMS−PMYR−PAMMS triblock polymers were analyzed by small-angle X-ray scattering (SAXS) at 25 °C (Figures S16a−f). All samples exhibited a principal scattering peak with domain spacings ranging from 18.5 to 40.5 nm. As an example, the 36−168−36 sample gave a sharp principal reflection and weaker second order peaks consistent with a hexagonally packed cylindrical morphology (Figure 4). A bulk sample of this material was sectioned by
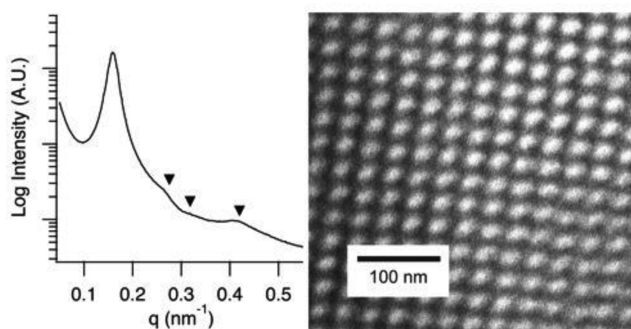

Figure 4. Left, SAXS profile of PAMMS−PMYR−PAMMS (36−168−36), D = 40.5 nm, expected secondary peaks for hexagonally packed cylinders are denoted with arrows. Right, TEM image of the same sample sectioned by microtome and stained with OsO$_4$. The image shows PAMMS cylinders (white, D_{cyl} = 23.2 ± 1.2 nm) in a PMYR matrix (gray).

cryomicrotome, stained with OsO$_4$, and imaged using transmission electron microscopy (TEM). The TEM micrograph in Figure 4 (other images are given in Figure S17) shows circular features with an average diameter of 23.2 ± 1.2 nm. This feature size is consistent with the calculated cylinder diameter of 20.9 from the SAXS data based on a PAMMS volume fraction of 0.333 and estimated densities of 1.04 g cm^{-1} for PMS and 0.891 g cm^{-1} for PMYR.[26]

The thermal properties of the PAMMS−PMYR−PAMMS triblocks were analyzed by DSC (S18a−f). All samples showed a T_g for the PMYR midblock at about −39 °C; however, no signals corresponding to the T_g of the PAMMS end blocks were observed. To further elucidate thermal behavior along with viscoelastic properties, the triblocks were subjected to dynamic mechanical analysis (Figures S19a−f).[27,28] Figure 5 shows the dynamic elastic modulus (G') data as a function of temperature
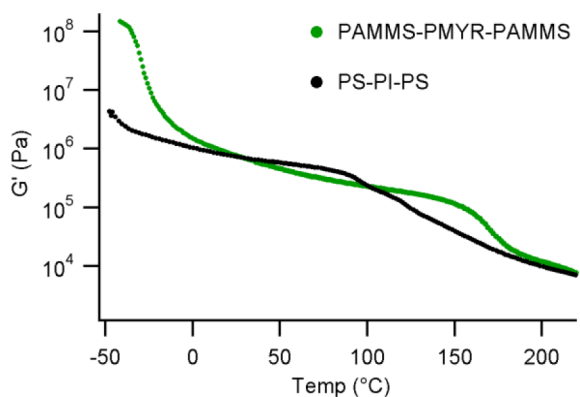

Figure 5. Elastic moduli (G') of PS−PI−PS (23−164−23; black) vs PAMMS−PMYR−PAMMS (36−168−36; green); ω = 1 rad s^{-1} with an initial strain of 10% and a 3 °C min^{-1} temperature ramp rate.

for both a representative PS−PI−PS (23−164−23) sample and a PAMMS−PMYR−PAMMS (36−168−36) sample with similar molar mass and styrene volume fraction (0.245 for the former and 0.333 for the latter). The PS−PI−PS sample has a modulus of approximately 1 MPa between −40 and 90 °C, at which point the modulus drops due to softening of the PS phase, as expected (black trace). On the other hand, the PAMMS−PMYR−PAMMS sample (green trace), shows a drop in modulus during heating through the T_g of the PMYR midblock at about −40 °C. The rubbery plateau (also ca. 1 MPa) for this material extends to 160 °C before a drop in the modulus is observed at the softening point of the PAMMS block. This suggests that these biosourced TPEs may well have an attractively high service temperature.

Tensile testing for the PAMMS−PMYR−PAMMS samples (summarized in Table S1) showed ultimate tensile stress (UTS) values ranging from 0.5 to 10.8 MPa and elongations at break ranging from 525 to 1340% (Figure 6). This suggests that
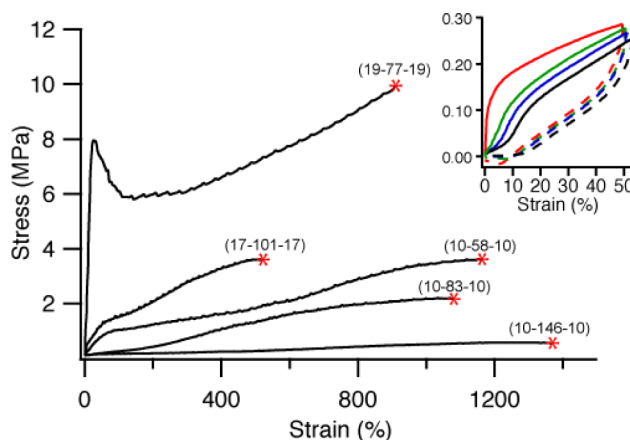

Figure 6. Representative stress−strain curves of PAMMS−PMYR−PAMMS samples at room temperature and 10 mm min^{-1}. *Denotes failure point. The inset shows stress recovery of the 17−101−17 sample from 0 to 50% strain at 5 mm min^{-1} over 20 cycles (cycle #1 is red, 2 is green, 5 is blue, and 20 is black; extensions are indicated by solid lines and retractions are indicated by dashed lines).

properties in this family of TPEs can be tuned based on composition. The distinct properties of the 19−77−19 sample suggests that this material adopts a morphology with a continuous PAMMS phase unlike the other more elastomeric samples. Styrenic TPEs typically have elongations of 800% and UTS values up to about 30 MPa. Despite similar values of elongation at break, the PAMMS−PMYR−PAMMS polymers exhibit lower UTS values.[29] This can be attributed to the higher entanglement molar mass for PMYR (24.8 kg mol^{-1}) in comparison to PI (5.1 kg mol^{-1}), which has been shown to be a major factor in determining UTS in TPEs.[25,30] This higher entanglement molar mass is manifest in the lower modulus values in the plateau region as compared to PS−PI−PS (Figure 5). However, the lower values of plateau modulus are attractive for applications such as pressure sensitive adhesives, where the lower values at typical use temperatures can be advantageous.[30]

A sample of PAMMS−PMYR−PAMMS (17−101−17) was also subjected to 20 cycles of 50% strain at a constant rate of displacement to evaluate elastic recovery. The behavior at cycle numbers 1, 2, 5, and 20 is shown in Figure 6. Comparison of the stress−strain profiles between cycles 1 and 2 shows a drop in Young's modulus, indicating that plastic deformation

occurred between these first few cycles, consistent with expected TPE behavior.[31] There is also a reduction of the extensional stress at constant strain levels between cycles 1 and 2. However, for the remaining cycles (5−20) the stress−strain behavior remains nearly constant, with only a slight reduction in stress at 50% extension. From these data we deemed these materials to be elastomeric in nature with overall good recovery.

In summary, the ceiling temperature, thermal stability, and T_g of the homopolymer PAMMS, prepared by anionic polymerization in THF, was characterized. In addition, the microstructure and thermal properties of PMYR, prepared in similar fashion, were determined. These types of blocks were then incorporated into an ABA triblock polymer of PAMMS−PMYR−PAMMS by sequential anionic polymerization followed by dichlorodimethylsilane coupling with high efficiencies. Members of a series of triblock copolymers were comprehensively analyzed. Through these studies we have shown that this biorenewable thermoplastic elastomer exhibits improved performance at higher temperature compared to current styrenic TPEs, making it attractive for applications requiring higher service temperatures.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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