

Polymerization

Bifunctional Carbanionic Synthesis of Fully Bio-Based Triblock Structures Derived from β -Farnesene and LL-Dilactide: Thermoplastic Elastomers

Moritz Meier-Merziger, Jan Imschweiler, Frank Hartmann, Bart-Jan Niebuur, Tobias Kraus, Markus Gallei, and Holger Frey*

Abstract: Current environmental challenges and the shrinking fossil-fuel feedstock are important criteria for the next generation of polymer materials. In this context, we present a fully bio-based material, which shows promise as a thermoplastic elastomer (TPE). Due to the use of β -farnesene and L-lactide as monomers, bio-based feedstocks, namely sugar cane and corn, can be used. A bifunctional initiator for the carbanionic polymerization was employed, to permit an efficient synthesis of ABA-type block structures. In addition, the “green” solvent MTBE (methyl *tert*-butyl ether) was used for the anionic polymerisation, enabling excellent solubility of the bifunctional anionic initiator. This afforded low dispersity ($\bar{D}=1.07$ to 1.10) and telechelic polyfarnesene macroinitiators. These were employed for lactide polymerization to obtain *H*-shaped triblock copolymers. TEM and SAXS revealed clearly phase-separated morphologies, and tensile tests demonstrated elastic mechanical properties. The materials featured two glass transition temperatures, at -66°C and 51°C as well as gyroid or cylindrical morphologies, resulting in soft elastic materials at room temperature.

Thermoplastic elastomers (TPEs) are extensively studied because of their advantages over classically vulcanized elastomers for specific applications. Especially in terms of their potential recyclability, TPEs are superior and therefore important to respond to current environmental challenges. They offer thermoplastic processability, retaining elastomeric properties at service temperatures.^[1] The finite availability of fossil resources and their enormous impact on the environment lead to one of the key objectives of current research: the search for alternatives to fossil fuel-based materials. Established thermoplastic elastomers of the SBS or SIS type consist of two glassy polystyrene (PS) end-blocks, which are covalently connected to a rubber-like polybutadiene (PB) or polyisoprene (PI) mid-block. Hillmyer et al.^[2] showed that the PS-phase can be substituted with another high glass transition temperature (T_g) material, e.g., polylactide (PLLA), to obtain partly bio-based TPE structures. They demonstrated the combination of different polymerization techniques to create new materials of clearly phase-separated block copolymers. Further, some examples of fully bio-based TPE structures have recently been presented in literature, showing materials that can be obtained from purely renewable raw material. They cover materials based on polyesters, polyurethanes and polyamides.^[3,4] Herein, terpenes offer great potential as alternative sources for sustainable materials.^[4] For instance, β -myrcene (Myr) has been considered as a bio-based substitute for the soft phase in TPEs in various works. Anionic polymerization,^[5] subsequent LA grafting^[6] and also RAFT^[7] were used to develop bio-based TPE structures derived from diene monomers.

A major challenge for actual application is to identify scalable processes with monomers that can be produced on large scale.^[3] We recently presented a partly bio-based material with a low T_g PI midblock, flanked by outer high T_g lactide blocks.^[8] Here we aim at fully bio-based TPEs, which are synthesized by combining carbanionic and ring-opening polymerization.

A rather less considered, bio-based monomer can be found in the group of terpenes: the diene β -farnesene (Far) is already produced on an industrial scale.^[9] β -Farnesene is based on the renewable feedstock sugar cane, and the corresponding polyfarnesene (PFar) shows different thermal and rheological properties in bulk compared to its homologues, PI and PB. The unusual bottlebrush-like architecture

[*] M. Meier-Merziger, J. Imschweiler, Prof. H. Frey
 Johannes Gutenberg University, Mainz, Chemistry Department
 Duesbergweg 10–14, 55128 Mainz (Germany)
 E-mail: hfrey@uni-mainz.de

F. Hartmann, Prof. M. Gallei
 Saarland University, Chair in Polymer Chemistry
 Campus C4 2, 66123 Saarbrücken (Germany)

B.-J. Niebuur, Prof. T. Kraus
 INM - Leibniz-Institute for New Materials
 Campus D2 2, 66123 Saarbrücken (Germany)

Prof. T. Kraus
 Saarland University, Colloid and Interface Chemistry
 Campus D2 2, 66123 Saarbrücken (Germany)

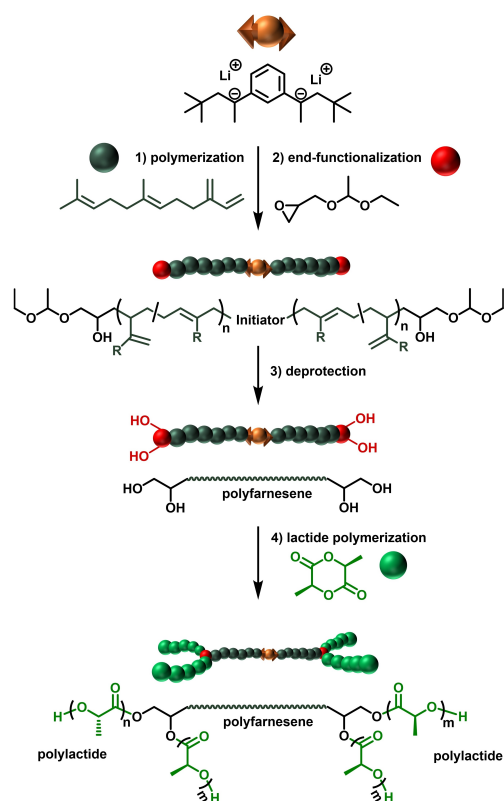
Prof. M. Gallei
 Saarene, Saarland Center for Energy Materials and Sustainability
 Campus C4 2, 66123 Saarbrücken (Germany)

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leads to a significantly higher entanglement molecular weight (M_c) of PFar of $\approx 49.7 \text{ kg}\cdot\text{mol}^{-1}$ and an even higher critical molecular weight (M_c) of $>10^5 \text{ g}\cdot\text{mol}^{-1}$.^[10] In comparison the M_c values of PB ($5.6 \text{ kg}\cdot\text{mol}^{-1}$)^[11] and PI ($14 \text{ kg}\cdot\text{mol}^{-1}$)^[12] are much lower. Further, both PI and PB show a strong T_g dependency on their microstructure ratio. The T_g of PI with 9 % of vinyl content can be found at -67°C and increases to 0°C at a vinylic fraction of 85%.^[13] In comparison, polyfarnesene (PFar), retains a low T_g below -70°C independent of the vinylic content up to 52%.^[13] Therefore, Far is a highly suitable monomer for carbanionic polymerization in polar aprotic media (i.e., ethers), in which polydienes with a high vinylic content $>52\%$ are obtained. This further facilitates the use of a bifunctional initiator for the carbanionic polymerization, which reduces the number of necessary monomer addition steps, but is known to be hardly soluble in pure hydrocarbons. As polar solvents lead to an increase in the vinylic fraction, this normally limits their relevance for widely used dienes, such as butadiene (B) and isoprene (I). Even though there are several reported bifunctional initiators available for non-polar solvents,^[14] their preparation is rather complex and challenging to implement in scale-up procedures.^[15] Here we demonstrate that it is possible to take full advantage of both the characteristics of Far as a building block and the use of a polar solvent for efficient dissolution of the bifunctional initiator.

We employed 1,3-diisopropenylbenzene (DIB), a commercially available initiator precursor, for our synthesis route, which is transformed to the dilithiated species by the addition of two equivalents of *tert*-BuLi.^[16] To further overcome undesired decomposition reactions, observed in widely used polar solvents like THF and diethyl ether in the presence of carbanionic species, methyl *tert*-butyl ether (MTBE) was investigated as an more inert alternative.^[17] Besides its stability against side reactions with the nucleophilic chain end, it also established as a more sustainable solvent.^[18] Even though large-scale production is currently based on the fossil resources isobutene and methanol, some partly bio-based variants, e.g. *bio*-MTBE, are already available on the market.^[19] Other advantages, such as safer handling (no peroxide formation), have found attention in organic chemistry, but surprisingly have never gained importance in polymer chemistry.^[20]

Polyfarnesyl lithium was transformed to hydroxy functional telechelics by end-functionalization of the living chain ends with a glycidyl ether, namely ethoxy ethyl glycidyl ether (EEGE). After acidic deprotection, telechelic tetrahydroxy macroinitiators with a high degree of end-functionalization are accessible in a highly controlled manner.^[21] The targeted 100 % bio-based A_2BA_2 -type triblock-type structure was further generated by polymerization of LL-dilactide (LLA), one of the most abundant bio-based materials to date. The corresponding poly-(L)-lactide (PLLA) has a T_g of $\approx 60^\circ\text{C}$ and therefore acts as a suitable candidate for the “hard” block of TPEs.^[22] By simply varying the respective glycidyl ether, different and more elaborate structures are accessible. The step-by-step synthesis route can be followed in Scheme 1. Pitet et al. recently demonstrated that lactide



Scheme 1. Synthesis pathway: Far initiated by DIB/*tert*-BuLi and subsequent end-functionalization using EEGE, then deprotection followed by organocatalyzed ROP of LLA to form *H*-shaped A_2BA_2 -type triblock copolymers.

polymerization onto PFar macroinitiators is also suitable for flow synthesis, highlighting the potential for scale-up.^[23]

The successful preparation of the active initiator species derived from the reaction of DIB/*tert*-BuLi was tracked by ^1H NMR spectroscopy. Full conversion of the respective benzylic double bonds was observed within the first monitored time frame ($<1 \text{ min}$) (Figure S1). The deep red colored solution was diluted, and the color faded to a slightly yellowish color upon the addition of Far, showing the crossover from the benzylic carbanions of the initiator to the farnesyl lithium chain ends. After full monomer consumption, the addition of a tenfold excess of EEGE led to an instant decolorization due to the introduction of alkoxide groups at the chain ends and formation of a highly viscous organo-gel. Upon protonation of the chain ends by addition of degassed methanol a polymer solution of low viscosity was obtained. Since end-group determination by NMR spectroscopy leads to reliable results only for low-molecular masses (M_n), a low M_n sample of $5000 \text{ g}\cdot\text{mol}^{-1}$ was prepared. An end-group functionality of 94 % for EEGE-PFar(5k)-EEGE was determined by comparison of the signal of the methyl groups ($\approx 0.88 \text{ ppm}$) of the initiating species with the proton signals of the end-group in the respective ^1H NMR (Figure S2). Likewise, the spectra can be used to determine the M_n by NMR. The obtained M_n^{NMR} of $6600 \text{ g}\cdot\text{mol}^{-1}$ differs slightly from the size-exclusion

chromatography (SEC) results ($M_n^{SEC} = 5700 \text{ g}\cdot\text{mol}^{-1}$), which can be explained by the utilization of a PI-calibration for the SEC measurement. Both methods lead to a value close to the expected M_n . Combining all observations leads to the conclusion that a highly controlled bifunctional polymerization and subsequent termination occurs.

Consequently, three additional high molar mass macroinitiators (targeted M_n : 30k, 50k and 80k) were synthesized for the preparation of triblock copolymers. The SEC traces of the telechelic EEGE-PFar-EEGE samples are displayed in Figure 1, showing low dispersity (\mathcal{D}) of 1.07 to 1.10, reflecting the controlled and living behavior of the synthesis. A slight shoulder is observed for the higher molar mass samples, which is caused by inevitable initiation of *tert*-BuLi utilized for the preparation of the bifunctional initiator. This, however, indicates the presence of a mainly bifunctional species during the polymerization. The remaining low dispersity of the samples emphasizes a negligible monofunctional content.

Characterization results are summarized in Table 1, including the ratio of the different microstructures of all samples determined by ^1H NMR spectroscopy, see Supporting Information. The 1,4-PFar content decreases to approximately 61%. In non-polar solvents, e.g., heptane, a 1,4-PFar

content of 91% is obtained.^[10] It is interesting to note that only 3,4-PFar is observed, and 1,2-PFar units were absent. In a next step, the partially acetal-protected hydroxyl groups at the chain ends were deprotected under acidic conditions via addition of ion-exchange resin (DOWEX) to the polymer solution. It is important to note that these reaction conditions are applicable for larger scales, due to the straight-forward separation of the resin via filtration.

Complete disappearance of the methine proton signals of the protecting group at 4.55 ppm in the ^1H NMR spectrum (Figure S3) confirmed successful cleavage. In the following step, the desired fully bio-based block copolymer structure was obtained via organobase catalyzed ring opening polymerization (ROP) of LLA with 1,8-diazabicyclo-(5.4.0)undec-7-ene (DBU), using the telechelic multihydroxy functional PFar. The polymerization technique is known to provide narrow molar mass distributions and short reaction times despite the mild reaction conditions.^[24]

After work-up, a solid material was isolated. The expected shift towards higher molar masses was observed by SEC, see Figure 2 (a–c). As the methine proton signals of PLLA and the 3,4-PFar signals overlap in the ^1H NMR spectrum, determination of the PLLA volume fraction is not straightforward. Since the 1,4-PFar to 3,4-PFar ratios of the macroinitiators are known, the 3,4-PFar proton content can be subtracted from the combined ^1H NMR signal. The remaining integral of the signal is due to the methine signal of PLLA. Thereby, the molar ratio can be calculated. The volume fraction of PLLA (Φ_{LA}) is approximated by the literature-known densities of the PFar and PLLA, $\rho(\text{PFar})$: $0.900 \text{ g}\cdot\text{cm}^{-3}$,^[10] $\rho(\text{PLLA})$: $1.264 \text{ g}\cdot\text{cm}^{-3}$.^[25]

Based on the ^1H NMR results shown in Table 1, PLLA volume fractions between 18 and 29 vol% were determined that are near the theoretical values. A slight broadening is observed in the SEC diagram (see Figures 2 and S9–11), which is explained by the presence of different initiating species. However, as the SEC distribution remains unimodal, successful chain extension is confirmed. The absence of a PLLA homopolymer species in diffusion-ordered-spectroscopy measurements (Figure S5) indicates successful and controlled initiation by the PFar macroinitiator.

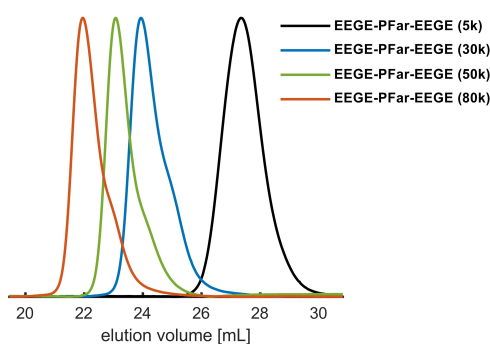


Figure 1. SEC traces of all end-capped EEGE-PFar-EEGE telechelics targeting 5k, 30k, 50k and 80k (eluent: THF, PI-calibration).

Table 1: Data of the synthesized A_2BA_2 -type triblock copolymers and their respective macro initiators.

| Sample | $M_n^{\text{target}} [\text{g}\cdot\text{mol}^{-1}] / \Phi_{LA}^{\text{targeted}}$ | $M_n^{\text{SEC[a]}} [\text{g}\cdot\text{mol}^{-1}]$ | $\mathcal{D}^{\text{[a]}}$ | 1,4-Far ^[b] [%] | $\Phi_{LA}^{\text{[c]}}$ [%] | $T_g^{\text{[d]}}$ [°C] | $T_g^{\text{[d]}}$ [°C] | $T_m^{\text{[e]}}$ [°C] | SAXS ^[f] | TEM ^[f] |
|--|--|--|----------------------------|----------------------------|------------------------------|-------------------------|-------------------------|-------------------------|---------------------|--------------------|
| EEGE-PFar-EEGE (5k) | 5000 | 5700 | 1.17 | 59.0 | – | – | – | – | – | – |
| EEGE-PFar-EEGE (30k) | 30000 | 24100 | 1.10 | 61.2 | – | – | – | – | – | – |
| ($\text{PLLA}_{2.6k}$) ₂ - <i>b</i> -PFar(30k)- <i>b</i> -($\text{PLLA}_{2.6k}$) ₂ | +20% PLLA | 30200 | 1.17 | 61.2 | 18.3 | – | – | – | mix | H |
| ($\text{PLLA}_{4.5k}$) ₂ - <i>b</i> -PFar(30k)- <i>b</i> -($\text{PLLA}_{4.5k}$) ₂ | +30% PLLA | 39100 | 1.14 | 61.2 | 28.6 | –64 | 50 | 149 | H | G |
| EEGE-PFar-EEGE (50k) | 50000 | 36300 | 1.07 | 61.8 | – | – | – | – | – | – |
| ($\text{PLLA}_{4.4k}$) ₂ - <i>b</i> -PFar(50k)- <i>b</i> -($\text{PLLA}_{4.4k}$) ₂ | +20% PLLA | 43600 | 1.19 | 61.8 | 20.0 | – | – | – | H | #NA |
| ($\text{PLLA}_{7.5k}$) ₂ - <i>b</i> -PFar(50k)- <i>b</i> -($\text{PLLA}_{7.5k}$) ₂ | +30% PLLA | 54600 | 1.18 | 61.8 | 28.5 | –66 | 51 | 136 | #NA | #NA |
| EEGE-PFar-EEGE (80k) | 80000 | 57400 | 1.09 | 63.5 | – | – | – | – | – | – |
| ($\text{PLLA}_{7.0k}$) ₂ - <i>b</i> -PFar(80k)- <i>b</i> -($\text{PLLA}_{7.0k}$) ₂ | +20% PLLA | 59800 | 1.36 | 63.5 | 20.6 | – | – | – | S | S |
| (PLLA_{12k}) ₂ - <i>b</i> -PFar(80k)- <i>b</i> -(PLLA_{12k}) ₂ | +30% PLLA | 79400 | 1.27 | 63.5 | 23.6 | –66 | 51 | 134 | L | G |

[a] Eluent: THF, calibration: PI. [b] Calculated from ^1H NMR, see SI. [c] Calculated from PFar:PLLA ratio from ^1H NMR assuming the homopolymer density $\rho(\text{PFar})$: $0.900 \text{ g}\cdot\text{cm}^{-3}$ [10] and $\rho(\text{PLLA})$: $1.264 \text{ g}\cdot\text{cm}^{-3}$ [25]. [d] From second heating curve measured by DSC, with a heating rate of 10 K/min. [e] DSC value of the first heating curve. [f] Determined by TEM and SAXS, S: spherical, G: gyroidal, H: hexagonally packed cylinders, L: lamellar.

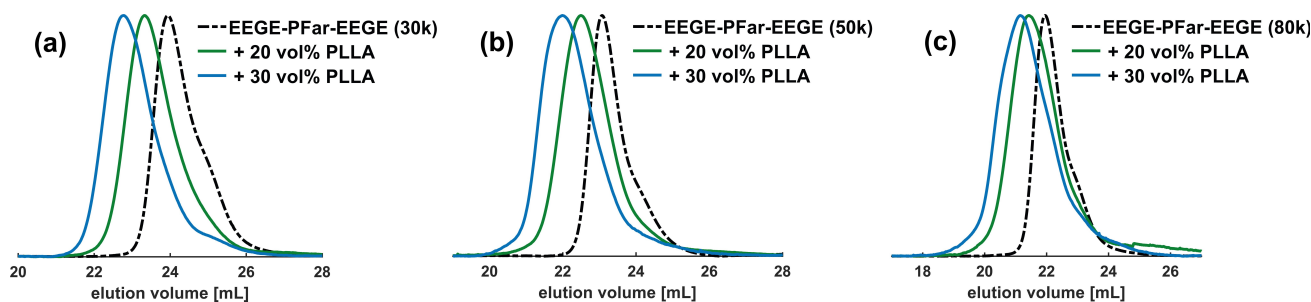


Figure 2. SEC traces of all telechelic macroinitiators and their corresponding triblock copolymers: (a) EEGE-PFar-EEGE (30k) with +20 vol% and +30 vol% PLLA; (b) EEGE-PFar-EEGE (50k) with +20 vol% and +30 vol% PLLA; (c) EEGE-PFar-EEGE (80k) with +20 vol% and +30 vol% PLLA; (eluent: THF, PI-calibration).

The successful triblock copolymer synthesis motivated further studies of the newly formed materials with respect to TPE properties. Evidence for phase-separation was found by differential scanning calorimetry (DSC) measurements (Figure 3), showing two distinct T_g s for each sample. The lower T_g between -66°C and -64°C is caused by the PFar phase and the higher one at around 50°C can be attributed to PLLA. In addition to the observed T_g s, all samples showed a melting point (T_m) in the temperature range of 134°C to 149°C , see Figures S6–8. However, the melting endotherms were only visible in the first heating run of the measurements. The time frame or cooling rate upon cooling was therefore not sufficient to allow for (re)crystallization of PLLA. A recrystallization peak was also absent in the cooling curve.

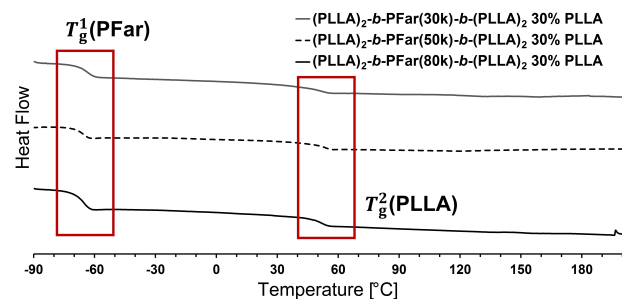


Figure 3. Second DSC heating curve of all $(\text{PLLA})_2$ - b -PFar- b - $(\text{PLLA})_2$ with a targeted PLLA volume fraction of 30 vol%, (heating rate of 10 K/min).

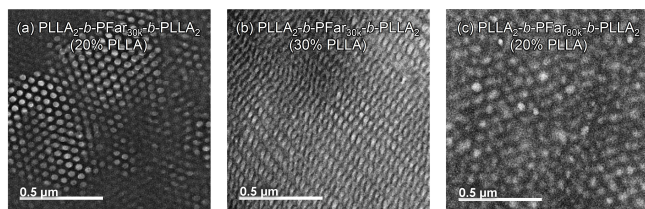


Figure 4. TEM Images of $(\text{PLLA})_2$ - b -PFar- b - $(\text{PLLA})_2$ samples of different compositions, solvent cast, 16 h annealing at 80°C and OsO₄ stained; (a) $(\text{PLLA})_2$ - b -PFar(30k)- b - $(\text{PLLA})_2$ 20% PLLA; (b) $(\text{PLLA})_2$ - b -PFar(30k)- b - $(\text{PLLA})_2$ 30% PLLA; (c) $(\text{PLLA})_2$ - b -PFar(80k)- b - $(\text{PLLA})_2$ 20% PLLA.

Phase-separation was confirmed by transmission electron microscopy (TEM) for most samples, see Figure 4 and S15. Hexagonal (Figure 4a), gyroidal (Figure 4b) and spherical (Figure 4c) morphologies were observed, some of which comprise phase-separation of several domain sizes within one sample. Remarkably, the complex gyroid morphology was present in two of the samples, which is explained by the elaborate H -shaped architecture that leads to curvature at the interface.^[26]

The different architecture of the polymers leads to a deviation of the morphology from the phase diagram of classical linear block copolymers at given volume ratios. In some cases, the determination of the phase-separation resulted in some deviation between the applied analytical techniques. DSC results suggest phase-separation for all measured samples, but in case of the 50k PFar samples no phase-separation was observed in the TEM images. Despite well-defined phase-separation for most samples, the morphology could not be determined in every case. Therefore, additional validation studies were performed using small angle X-ray scattering (SAXS), which probes the bulk structural properties and averages over larger sample volumes compared to TEM. As is described in the SI, the SAXS measurements revealed different morphologies compared to the ones assigned by TEM for most samples. PFar(30k) with 20 vol% PLLA (Figure S16a) even showed a combination of reflections that can be attributed to a mixed morphology. The obtained volume fraction of PLLA appears to be at the transition point of two morphologies in the phase diagram. To which extent the H -shaped architecture plays a peculiar role for the morphology will be a subject of future work. The determined morphologies for all samples are listed in Table 1.

ABA-type triblocks are widely used thermoplastic elastomers, based on domain bridging due crosslinking by the vitrified high T_g domains.^[27] Tensile tests were performed for the samples with a targeted Φ_{PLA} of 30%. Films were prepared via solvent casting process. The measurements revealed almost exclusively elastic deformation for the sample with the lowest M_n (Figure 5). The elongation at break (ϵ_{break}) was 66%, and at lower deformation the samples showed full elastic recovery. The higher M_n samples exhibited plastic deformation and strain hardening in addition to elastic deformation. This is in line with the

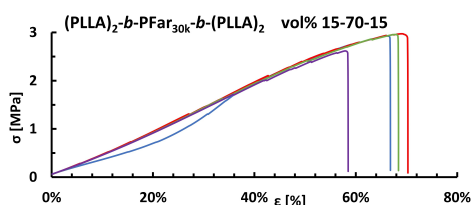


Figure 5. Stress-strain experiments of $(\text{PLLA})_2\text{-b-PFar}_{30\text{k}}\text{-b-(PLLA)}_2$ 30 vol% PLLA, four measurements for each sample.

behavior of non-bio-based SIS-rubbers.^[28] The mentioned results and the Young's modulus (E) are shown in Table S1, and all remaining stress-strain curves are presented in Figures S12–13.

The obtained values are low compared to the characteristics of triblocks consisting of styrene copolymerized with isoprene or myrcene.^[28] This is most likely due to the aforementioned, considerably higher M_e of PFar, which requires even longer PFar midblocks to achieve higher strength and elongation.^[29] Further, by distributing the lactide units over 4 arms of the H -shaped architecture, each arm of the respective chain has still a rather low molecular weight of $2.6 \text{ kg}\cdot\text{mol}^{-1}$ up to $12 \text{ kg}\cdot\text{mol}^{-1}$. This could explain the low degree of crystallization of PLLA observed in the DSC measurements. Thus, the obtained mechanical characteristics can clearly be attributed to the targeted structure and the moderate molecular weights. Further tailoring and improvement of the material properties for specific applications and to obtain stronger TPEs is possible via the synthesis sequence introduced in this work.

In summary, we capitalize on the hardly used, slightly polar bio-based solvent MTBE for the bifunctional, anionic initiation and at the same time rely on the low T_g of PFar, despite its increased vinyl content in this solvent. Telechelic multi α,ω -hydroxy PFar macroinitiators were generated via controlled end-functionalization of the living anionic chain ends. By using LA for the subsequent polymerization, H -shaped A_2BA_2 -type copolymers were accessible. These materials showed microphase-segregation, manifest in two distinct T_g s for all samples, covering a broad service temperature range from -66°C to 51°C . Longer PLLA chains that crystallize may considerably increase the upper service temperature of the TPEs in the future. TEM and SAXS of the copolymers showed different morphologies e.g. gyroid and hexagonal cylinders, and surprisingly also mixtures of those. As the obtained morphologies deviate from expectation for classical linear polymers, these results pave the way for a variety of further materials by varying the content of both components and even the nature of the diene and the aliphatic polyester. Since the monomers β -farnesene and LL-dilactide are derived from renewable feedstocks, the materials are an example of fully bio-based thermoplastic elastomers.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Anionic Polymerization • Bifunctional • Phase Separation • Polyfarnesene • Thermoplastic Elastomer

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