

Synthesis and Characterization of Biobased Polyesters with Tunable  $T_g$  by ROCOP of Beta-Element Oxides and Phthalic Anhydride

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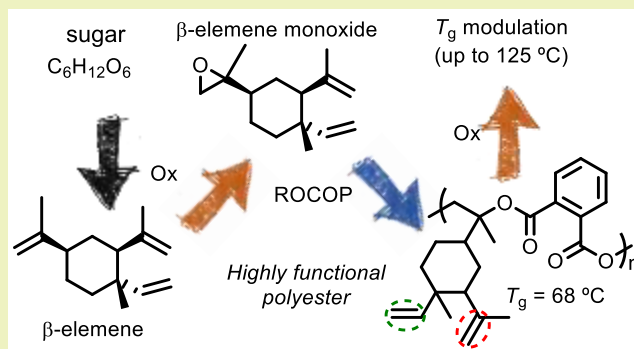
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Supporting Information

**ABSTRACT:** The use of terpene-based oxides derived from  $\beta$ -elemene is reported in the context of new functional semiaromatic polyester development. In particular, poly( $\beta$ -elemene monoxide-*alt*-phthalic anhydride) featuring two double bonds per repeating unit having distinct reactivity is conveniently prepared by iron- and aluminum-mediated ring-opening copolymerization (ROCOP). Sequential and selective transformation of each of these double bonds is addressed by epoxidation allowing one to precisely manipulate the degree and nature of the functionality in the polymer backbone while modulating the  $T_g$  from 68 to 121 °C. Direct access to cross-linked polyesters is demonstrated by ROCOP of bifunctional  $\beta$ -elemene dioxide and phthalic anhydride furnishing a material with a  $T_g$  of 125 °C.

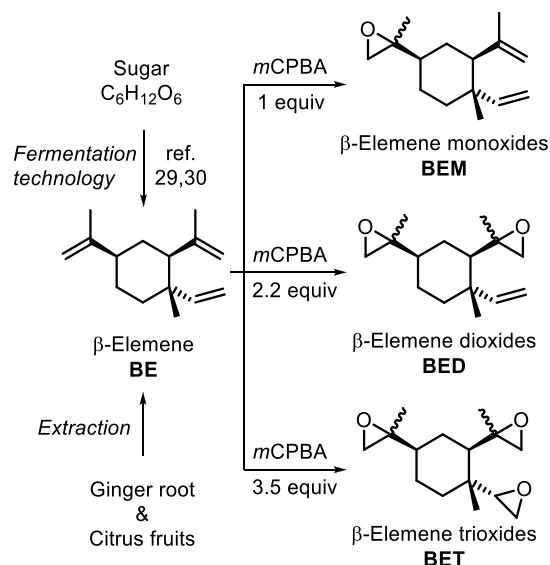
**KEYWORDS:** Beta-elemene, Biopolymers, Homogeneous catalysis, Polyesters, Ring opening copolymerization



## INTRODUCTION

Societal demand for more sustainable and renewable monomers and polymers is gaining momentum due to depletion of oil reserves, a raising awareness about the environmental impact of certain raw materials, and problems associated with end-of-life plastic disposal.<sup>1–3</sup> In this context, polyesters (PEs) represent one of the most appealing polymer ingredients for plastic materials because of their general biocompatibility and facile hydrolytic degradation.<sup>4,5</sup> The metal-mediated ring-opening copolymerization (ROCOP) of epoxides and cyclic anhydrides offers a highly effective technique for PE synthesis.<sup>6,7</sup> However, current ROCOP and related ROP processes still suffer from the lack of more structurally diverse monomers that can widen the scope of PE properties (such glass-to-liquid transitions,  $T_g$ ). Amplification of existing and new materials with an improved sustainability footprint is highly attractive, and in this regard, the consideration of alternative renewable and accessible bio-sourced monomers for PE synthesis remains important to explore while expanding the structural and molecular diversity space.

Terpenes are attracting increasing attention in the synthesis of new biobased polymers,<sup>8,9</sup> with recent contributions reporting on novel types of polyolefin,<sup>10–12</sup> polycarbonate,<sup>13–15</sup> and polyurethane structures.<sup>16–18</sup> However, integration of terpene scaffolds into PE architectures is relative unexplored,<sup>8,19–23</sup> especially toward the development of functional polymers having postsynthetic/curing potential.<sup>24–27</sup> Inspired by this apparent limitation, we envisioned the use of the relatively rigid terpene  $\beta$ -elemene (BE, Scheme 1) for the synthesis of new

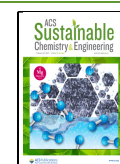
Scheme 1. Epoxidation of  $\beta$ -Elemene to  $\beta$ -Elemene Mono-, Bis-, and Tri-oxides<sup>4</sup>

<sup>4</sup>For the sake of clarity, only one regioisomer of BEM is shown.

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functional PEs. **BE** is a sesquiterpene compound present in citrus fruit such as grapefruit, that is mainly extracted from ginger root. It was demonstrated to have anticancer activity.<sup>28</sup> In recent years, **BE** has become available on a multiton scale as a byproduct of a fermentation process directed to the production of fragrances.<sup>29,30</sup>

Its structure features three double bonds, which can be properly engineered by epoxidation chemistry, providing the requisite monomers for the formation of functional PEs.

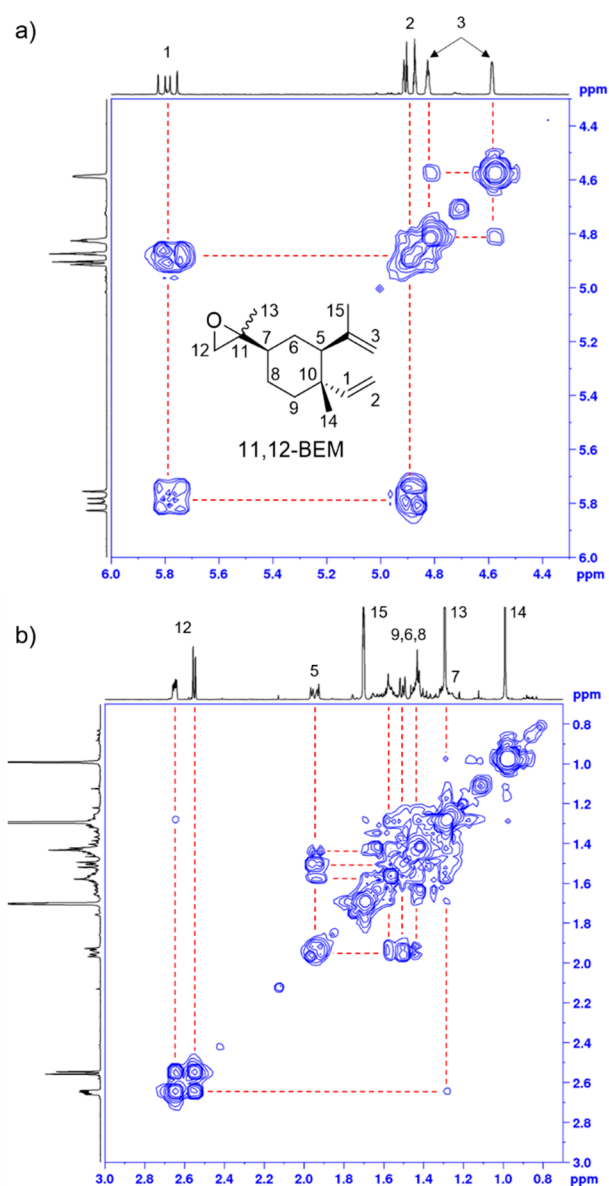
In this letter, we report the synthesis of  $\beta$ -elemene oxide monomers and their use in the ROCOP with phthalic anhydride (PA) mediated by iron and aluminum aminotriphenolate complexes. This copolymerization reaction marks a rare example of a multifunctional terpene-derived monomer in polymer synthesis, with clear potential to engineer the PE properties by sequential postmodification of the pendent double bonds resulting in polyesters with tunable  $T_g$  values of up to 125 °C.

## RESULTS AND DISCUSSION

The epoxidation of **BE** can generate various products and stereoisomers depending on the oxidation degree (Supporting Information, SI, Scheme S1). Our initial target was to selectively prepare both  $\beta$ -elemene monoxide (**BEM**) and  $\beta$ -elemene dioxide (**BED**) by a judicious choice of the reaction conditions (Scheme 1). The **BEM** synthesis was reported in the early 1970s by epoxidation with peracetic acid, but the <sup>1</sup>H NMR of only one product was provided.<sup>31</sup> We selected *meta*-chloroperbenzoic acid (*m*CPBA) as the oxidizing agent because it is known to selectively react with electron-rich double bonds.<sup>32</sup> We investigated the preparation of **BEM** by varying the amount of *m*CPBA (SI, Table S1). Due to comparable reactivity of the two disubstituted double bonds, the concomitant formation of **BED** was observed even at low *m*CPBA/**BE** ratios. Under optimal conditions (1 equiv *m*CPBA, 0 °C, 1 h), **BEM** was obtained in 54% yield as a 7:3 mixture of two regioisomers and characterized by NMR (SI, Figures S14–S19). GC-MS analyses confirmed the formation of four diastereoisomers (SI, Figures S60 and S61). **BEM** is easily prepared to up to 3.5 g, allowing one to examine its potential in ROCOP. Unreacted **BE** can be recovered and reused for further transformations.

A pure sample of the major isomer (11,12-**BEM**) was isolated by column chromatography and characterized in detail by NMR (SI, Figures S20–S25). The <sup>1</sup>H–<sup>1</sup>H COSY NMR spectrum of 11,12-**BEM** is shown in Figure 1. In the olefinic region, an AB<sub>2</sub> spin system was detected for the coupling of protons in positions 1 and 2, in addition with signals due to coupling of geminal protons in position 3 (Figure 1a). The coupling of protons 12 of the epoxide ring is clearly detected between 2.7 and 2.5 ppm (Figure 1b). The presence of a complex multiplet at 2.65 ppm is due to the presence of two diastereoisomers, as confirmed by GS-MS analysis (Figure S61). The chemical shifts of protons in positions 5 and 7 were attributed with the help of <sup>1</sup>H–<sup>13</sup>C HSQC NMR and comparison with the NMR spectra of  $\beta$ -elemene, while the methyl resonances were assigned similarly. The –CH<sub>2</sub> protons 6, 8, and 9 of the cyclohexane ring resonate between 1.3 and 1.7 ppm, but they could not be unequivocally assigned because of the presence of different diastereoisomers causing overlapping peaks. However, cross-peaks for the coupling between –CH 5 with –CH<sub>2</sub> 6 were clearly detected between 1.4 and 1.6 ppm.

Oxidation of **BE** in the presence of 2.2 equiv of *m*CPBA gives **BED** up to a 97% yield as a mixture of stereoisomers, while attempts to isolate pure isomers were unsuccessful. The use of

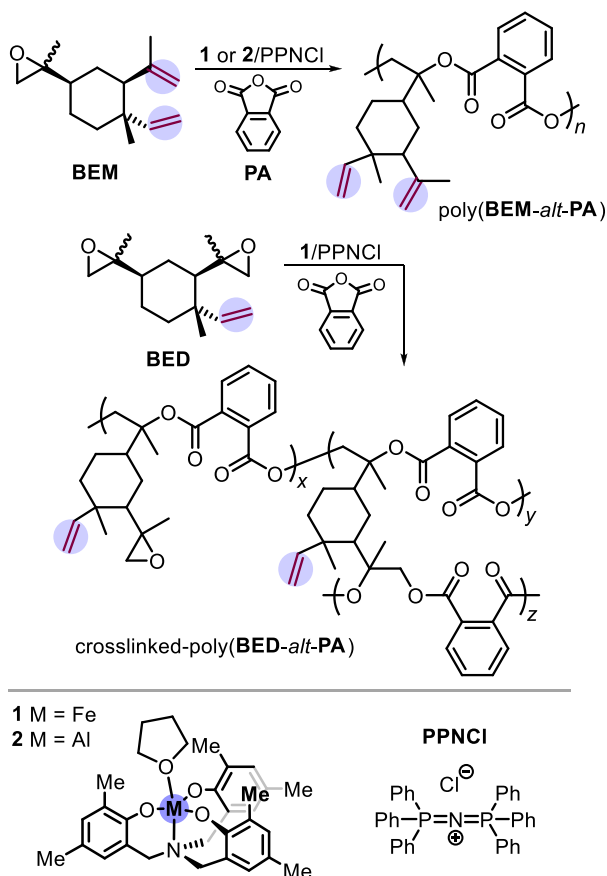


**Figure 1.** <sup>1</sup>H–<sup>1</sup>H COSY NMR spectrum of 11,12-**BEM** in CDCl<sub>3</sub> in the selected spectral regions from 4.3 to 6.0 (a) and from 0.7 to 3.0 ppm (b).

**BED** as an ACE inhibitor has been investigated,<sup>33</sup> but no detailed characterization data were provided. We thus analyzed our product in detail by NMR (SI, Figures S26–S31). The  $\beta$ -elemene trioxide (**BET**) was also obtained for the first time using an excess of the same oxidant (3.5 equiv), but in this case, a relatively low isolated yield was obtained (33%) probably due to some degree of epoxide hydrolysis under the reaction conditions (SI, Figures S32–S35).

For the ROCOP of **BEM** (i.e., the mixture of regioisomers) and PA, we selected the iron and aluminum aminotriphenolate complexes **1** and **2** in combination with bis-(triphenylphosphine)iminium chloride (PPNCl) (Scheme 2). These systems were previously demonstrated to be effective in the ROCOP of sterically encumbered monomers.<sup>22,34</sup> Optimization of the reaction conditions was performed (SI, Table S2), and selected results from this optimization phase are reported in Table 1. First, copolymerization reactions were performed at 60 °C in THF using an equimolar mixture of

**Scheme 2. Synthesis of Poly(BEM-*alt*-PA) and Cross-Linked Poly(BED-*alt*-PA) by ROCOP and Structures of Complexes 1 and 2 and PPNCI<sup>a</sup>**



<sup>a</sup>For the sake of clarity, only the one regioisomer of BEM is shown, and relevant double bonds are highlighted.

comonomers and a PA/catalyst ratio of 100 (SI, entries 1 and 2, Table S2). Under these conditions, low monomer conversions were observed after 1.5 days with both catalyst systems probably

due to the steric demand of the terpene oxide. Thus, reactions were then conducted at higher temperature in toluene, thereby achieving good conversions in 17 h yielding a perfectly alternating poly( $\beta$ -elemene monoxide-*alt*-phthalic anhydride) [poly(BEM-*alt*-PA), entries 1 and 2, Table 1]. In both latter cases, relatively narrow molecular weights distributions (low  $\bar{D}$  values of <1.2) were obtained. However, a bimodal distribution was observed for poly(BEM-*alt*-PA) when utilizing complex 1 (SI, Figures S62 and S63). An increase of the reaction time led to similar results, probably due to high viscosity of the reaction mixture (entries 3 and 4, Table S2) resulting in diffusion limitation effects. In an attempt to reach full conversion, we carried out the copolymerization under neat conditions using an excess of epoxide (BEM/PA = 2) and reaction temperatures ranging from 60 to 100 °C (SI, entries 5–8, Table S2; entries 3–4, Table 1). Under these settings, iron complex 1 performed much better than the aluminum one giving full and 52% conversion of PA, respectively, after 17 h at 100 °C. A number average molecular weight ( $M_n$ ) of 7.8 kDa was obtained with complex 1. The PA/catalyst ratio was further increased up to 300 in an attempt to obtain a higher  $M_n$ . At a lower catalyst concentration in toluene, 40 h were needed to reach good PA conversion without a noticeable increase of the  $M_n$  (entries 9–12, Table S2). Under neat conditions, 98% PA conversion was achieved in 24 h providing a  $M_n$  of 6.4 kDa (compare entry 5, Table 1, with entries 14 and 15, Table S2). Larger quantity samples of poly(BEM-*alt*-PA) could be obtained from gram-scale reactions under both solution and neat conditions (entries 6 and 7, Table 1).

The formation of the desired alternating copolymer was confirmed by NMR analyses (SI, Figures S36–S41). In addition, matrix-assisted laser ionization/desorption (MALDI) analyses of poly(BEM-*alt*-PA) were performed. The polymer obtained with complex 1 under neat conditions revealed the presence of two hydroxyl-terminated polymer chain distributions terminated by  $\beta$ -elemene-ol and  $\beta$ -elemene-diol, with a mass-to-mass peak increment of 368 Da (SI, Figure S70). The  $\beta$ -elemene-ol terminus can be explained by a Meerwein–Ponndorf–Verley–Oppenauer (MPVO) reaction at the beginning of the copolymerization as previously suggested for the same catalytic

**Table 1. Ring-Opening Copolymerization of BEM and BED with PA<sup>a</sup>**

Entry	M	Catalyst	[PA]/[Cat]	Solvent	Temp. (°C)	Time (h)	Conversion <sup>b</sup> (%)	$M_n^c$ (kDa)	$\bar{D}^c$	$T_g^d$ (°C)
1	BEM	1	100	toluene	100	17	75	7.0	1.19	n.d.
2	BEM	2	100	toluene	100	17	48	3.5	1.13	n.d.
3 <sup>e</sup>	BEM	1	100	neat	100	17	>99	7.8	1.28	75
4 <sup>e</sup>	BEM	2	100	neat	100	17	52	3.7	1.16	64
5 <sup>e</sup>	BEM	1	300	neat	100	24	98	6.4	1.25	68
6 <sup>f</sup>	BEM	1	100	toluene	100	24	55	6.9	1.21	79
7 <sup>g</sup>	BEM	1	300	neat	100	24	>99	4.4	1.21	68
8 <sup>h</sup>	BED	1	100	toluene	60	48	57	6.8 <sup>j</sup>	1.77	125
9 <sup>h</sup>	BED	1	100	toluene	80	24	82	8.8 <sup>j</sup>	1.21	n.d.
10 <sup>i</sup>	BED	1	100	neat	60	24	56	3.5 <sup>j</sup>	3.12	n.d.
11 <sup>i</sup>	BED	1	100	neat	80	24	91	4.1 <sup>j</sup>	2.48	117

<sup>a</sup>M stands for terpene monomer. Reaction conditions: PA = 100 mg ( $6.75 \times 10^{-4}$  mol); BEM = 149 mg ( $6.75 \times 10^{-4}$  mol); solvent = 200  $\mu$ L; PPNCI/complex = 1/1; temperature = 100 °C. All the samples show >99% polyester linkages as evidenced by <sup>1</sup>H NMR analyses. <sup>b</sup>Determined by <sup>1</sup>H NMR on the basis of comparison of the aromatic proton signals of PA and the PE. <sup>c</sup>Determined by GPC in THF calibrated with polystyrene standards. <sup>d</sup>Determined by DSC analysis at a 10 °C/min heating/cooling rate; data are for the second heating cycle. <sup>e</sup>BEM = 298 mg ( $1.35 \times 10^{-3}$  mol). <sup>f</sup>PA = 1.00 g ( $6.75 \times 10^{-3}$  mol); BEM = 1.49 g ( $6.75 \times 10^{-3}$  mol); solvent = 2.0 mL. <sup>g</sup>PA = 0.950 g ( $6.41 \times 10^{-3}$  mol); BEM = 2.83 g ( $1.28 \times 10^{-2}$  mol). <sup>h</sup>PA = 100 mg ( $6.75 \times 10^{-4}$  mol); BED = 160 mg ( $6.75 \times 10^{-4}$  mol); solvent = 200  $\mu$ L; PPNCI/complex = 1/1. <sup>i</sup>PA = 100 mg ( $6.75 \times 10^{-4}$  mol); BED = 319 mg ( $1.35 \times 10^{-3}$  mol); PPNCI/complex = 1/1. <sup>j</sup>From GPC measurements conducted on the THF-soluble fraction; n.d. is not determined.



system,<sup>22</sup> and previously reported in the ROCOP of limonene oxide.<sup>35</sup> However, its formation by elimination of chloride end groups (that would result from PPNCl-mediated initiation) cannot be excluded. The  $\beta$ -elemene-diol terminal groups can be formed by reaction of **BEM** with adventitious water. In this case, the growth of two polymer chains on this diol scaffold is more likely, explaining the presence of bimodal distributions. The polymer obtained from ROCOP reactions in the presence of complex **2** revealed the same MALDI distributions (SI, Figure S71). In this latter scenario, the presence of both even and odd chains (terminated by either **BEM**- or **PA**-based units) was observed suggesting the occurrence of transesterification phenomena. As described in Table 1,  $M_n$  values less than 10 kDa were obtained in all cases. This result is in line with the behavior of the catalytic system used in this study. For example, cyclohexene oxide-based polyesters produced by catalyst **1**/PPNCl exhibit modest  $M_n$  in the range of 4–12 kDa.<sup>22</sup> The formation of small amounts of  $\beta$ -elemene-ol byproducts under the reaction condition increases the concentration of initiating species and, consequently, decreases the molecular weight. Nevertheless, aminotriphenolate complexes remain one of the few systems capable to promote the ROCOP of sterically demanding epoxides.<sup>8</sup> The low  $M_n$  values attained in our work for poly(**BEM-*alt*-PA**) will limit its use in potential applications. However, low(er) molecular weight polyester polyols find industrial applications (e.g., in polyurethane production),<sup>36</sup> and the preparation of structurally new polyols is currently an attractive topic of research.<sup>37</sup> In addition, the high density of functional groups in the poly(**BEM-*alt*-PA**) backbone renders this PE highly attractive for postfunctionalization and curing reactions.

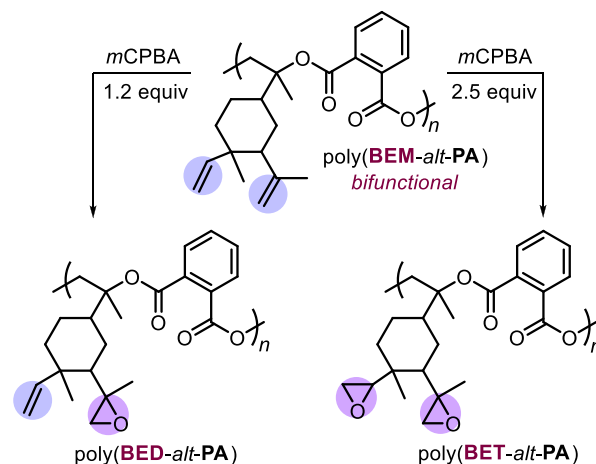
Differential scanning calorimetry (DSC) analysis of poly(**BEM-*alt*-PA**) samples showed  $T_g$  values between 64 and 79 °C. It is known that the  $T_g$  strongly depends on the  $M_n$  in low molecular weight polymers. Consequently, the observed variance can be attributed to the different  $M_n$  values obtained for the polymer samples. Also, samples obtained with complex **1** show a bimodal molecular weight distribution, and a different ratio between the higher and lower  $M_n$  distributions may also affect the  $T_g$ . In addition, the incorporation of both **BEM** regioisomers at high monomer conversion can result into more flexible polymer chains.

Copolymerization of **BED** with **PA** was also investigated under both solution and neat conditions under similar conditions used for **BEM**. **BED** is more reactive than **BEM** as a result of the presence of two epoxide groups per molecule, and good **PA** conversions were thus obtained even at 60 °C (entries 8 and 10, Table 1). In these cases, the reaction mixtures became very viscous after the selected reaction times. After coagulation in acidified MeOH, a nearly THF-insoluble product was isolated, and GPC analyses conducted on the THF-soluble fractions showed increased molecular weight distributions ( $1.21 \leq D \leq 3.12$ ; SI, Figures S66 and S67). This hints to the formation of cross-linked poly( $\beta$ -elemene dioxide-*alt*-phthalic anhydride) [poly(**BED-*alt*-PA**)], and in line with this notion is the broadened NMR peaks observed for the CDCl<sub>3</sub>-soluble fractions (SI, Figures S42–S47). Finally, the possibility to selectively and sequentially functionalize the two pendant double bonds on poly(**BEM-*alt*-PA**) was pursued by epoxidation as a proof-of-principle demonstration of the synthetic value of the two double bonds in each repeat unit.

Reactions in the presence of 1.2 or 2.5 equiv of *m*CPBA resulted in the formation of linear poly(**BED-*alt*-PA**) and

poly( $\beta$ -elemene trioxide-*alt*-phthalic anhydride) [poly(**BET-*alt*-PA**)] with an overall 94% and 90% double bond functionalization degree, respectively (Scheme 3). The selective formation of

**Scheme 3.** Selective Epoxidation of Poly(**BEM-*alt*-PA**) toward Poly(**BED-*alt*-PA**) and Poly(**BET-*alt*-PA**)



the epoxide groups was confirmed by comparing NMR spectra of polymers with those of model epoxides (SI, Figures S48–S59). A comparison of selected regions of the <sup>1</sup>H NMR spectra of poly(**BEM-*alt*-PA**), cross-link-free poly(**BED-*alt*-PA**), and poly(**BET-*alt*-PA**) is reported in Figure 2.

In the case of poly(**BED-*alt*-PA**), the disappearance of the vinylic signals at 4.6 and 4.8 ppm together with the appearance of an epoxide resonances around 2.5 ppm are in line with the notion of selective epoxidation of the disubstituted double bond. In addition, the <sup>1</sup>H NMR spectrum of poly(**BED-*alt*-PA**) is rather similar to that of the soluble fraction of cross-linked poly(**BED-*alt*-PA**) obtained from the ROCOP of **BED** (SI, Figures S42 and S48). Notably, the signal of vinylic proton **1** was split into two between 5.7 and 6.0 ppm. The same was observed in the <sup>1</sup>H NMR of the **BED** monomer (SI, Figure S26). We ascribe this to the formation of different diastereoisomers after epoxidation of **BEM** and poly(**BEM-*alt*-PA**). In the case of poly(**BET-*alt*-PA**), the almost full disappearance of the diagnostic vinyl signal at 5.8 ppm and the appearance of a new epoxide peak around 2.7 ppm are clear support for the epoxidation of the monosubstituted double bond. Thermal analyses of the epoxidized PE polymers were conducted to compare their behavior with that of the parent polymer. Comparisons were made between epoxidized polyesters derived from the same sample of poly(**BE-*alt*-PA**) sample in order to eliminate any effect due to different molecular weight distribution. In particular, DSC analyses show that the  $T_g$  increases from 68 to 97 and 121 °C in the case of poly(**BED-*alt*-PA**) and poly(**BET-*alt*-PA**), respectively (Figure 3). Thermogravimetric analyses (TGA), conducted under air atmosphere, also showed a significant increase of the decomposition temperature ( $T_d^5$ ) from 232 °C up to 253 °C (SI, Figures S79, S83, and S84). These relatively low values may be ascribed to the presence of hydroxyl-terminated polymer chains susceptible toward backbiting reactions at high temperatures. However, similar results were also observed for the structurally related polyester poly(limonene oxide-*alt*-phthalic anhydride).<sup>34</sup> In addition, we observed a  $T_g$  of 125 °C for the cross-linked poly(**BED-*alt*-PA**), which is in line with the higher

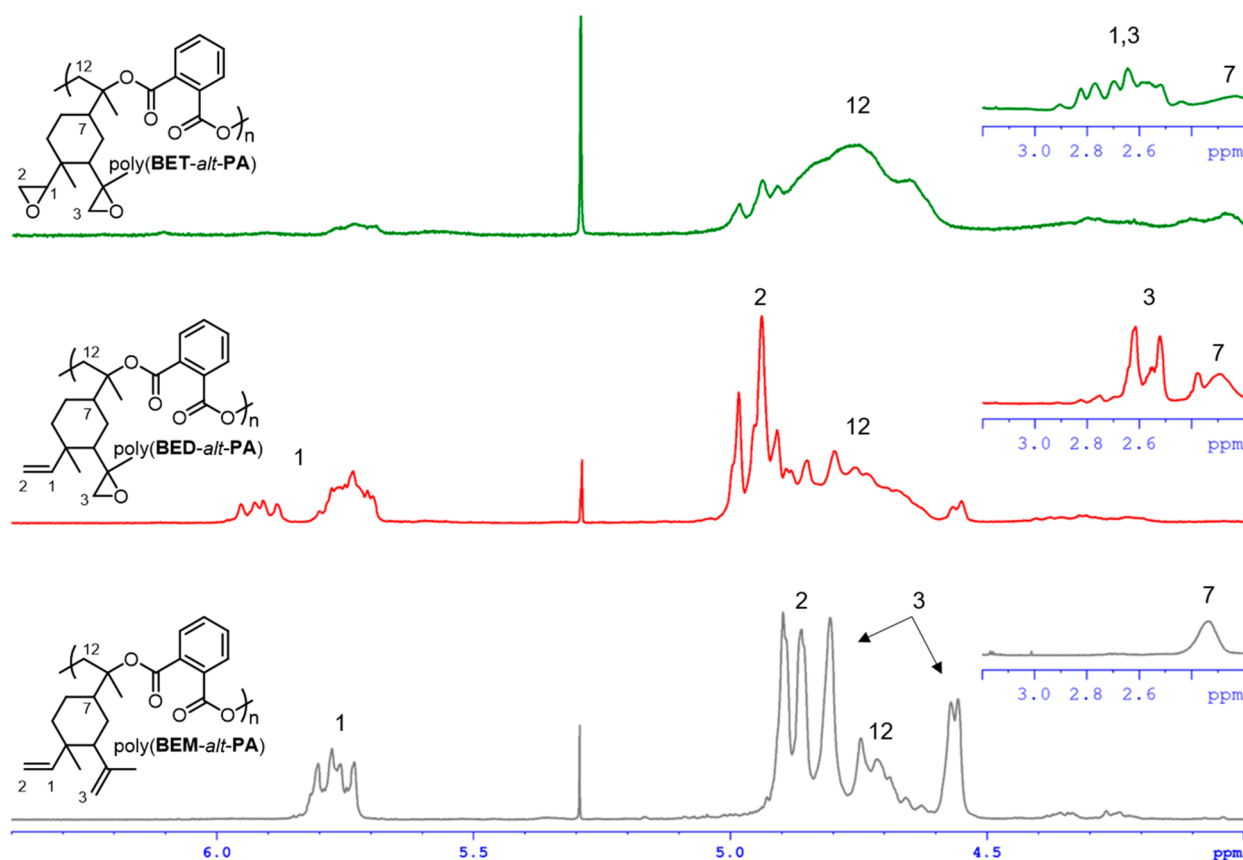


Figure 2.  $^1\text{H}$  NMR spectral comparison between poly(**BEM-alt-PA**), poly(**BED-alt-PA**), and poly(**BET-alt-PA**) in selected regions.

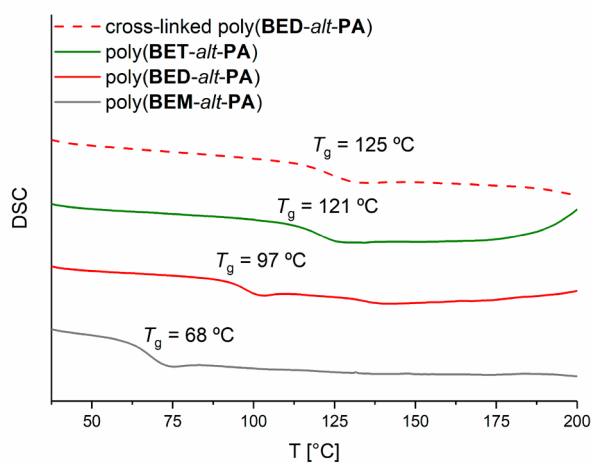


Figure 3. Comparison of DSC thermograms of poly(**BEM-alt-PA**), poly(**BED-alt-PA**), poly(**BET-alt-PA**), and cross-linked poly(**BED-alt-PA**).

structural rigidity expected for a cross-linked material although with a clearly different microstructure compared to linear poly(**BED-alt-PA**). This underlines the flexible nature of these functional PEs in choosing the appropriate postmodification strategy enabled by the functionality present in the repeat units. It also emphasizes the versatile nature of **BE** in the creation of functional materials with modular properties that are not easily accessible by ROCOP of conventional monomers.

Despite the current efforts in the assessment of new biobased polyesters, the industrial production is currently dominated by

few biopolymers, such as poly(3-hydroxybutyrate), PHB, and polylactide, PLA.<sup>38</sup> The properties of these semicrystalline PEs, with  $T_g$  values of 5 and 57 °C, respectively, are usually tuned by copolymerization with other (often petrol-based) comonomers.<sup>39–41</sup> In the case of poly(**BEM-alt-PA**), the starting  $T_g$  values are somewhat higher than that of PLA, but simple postmodification reactions allow for the modulation of this value up to 121 °C. Also, cross-linked networks are easily obtained by use of the bifunctional **BED** monomer. Further studies are ongoing toward different postsynthetic modifications in order to expand the window of thermal and mechanical properties of  $\beta$ -elemene-based PEs.

## CONCLUSIONS

The use of the terpene oxides derived from  $\beta$ -elemene as versatile comonomers for the catalytic synthesis of the new functional polyester, poly(**BEM-alt-PA**), is described using Fe- and Al-mediated ROCOP. This new type of PE features two double bonds in each repeating unit having different reactivity, allowing for selective and sequential postfunctionalization using epoxidation, thereby tuning the glass transition temperature from 68 °C up to 125 °C. This novel strategy allows one to prepare highly functional polyester structures which are not accessible by ROCOP of conventional monomers devoid of functionality that permits easy postsynthetic transformations or curing. The use of  $\beta$ -elemene dioxides under similar copolymerization conditions leads to the direct formation of cross-linked poly(**BED-alt-PA**) with a distinct thermal resistance ( $T_g = 125$  °C) compared to its cross-link-free analogue ( $T_g = 97$  °C). The present results serve to inspire future research devoted to the development of new functional materials based

on renewable terpenoid scaffolds and their use to access a wider range of polymer formulations.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.0c09189>.

Materials; methods; synthetic procedures; and MS, NMR, GC-MS, MALDI, GPC, DSC, and TGA analyses, including copies of relevant spectra (PDF)

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### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

- (1) Zhang, X.; Fevre, M.; Jones, G. O.; Waymouth, R. M. Catalysis as an Enabling Science for Sustainable Polymers. *Chem. Rev.* **2018**, *118*, 839–885.
- (2) Llevot, A.; Dannecker, P.-K.; von Czapiewski, M.; Over, L. C.; Söyler, Z.; Meier, M. A. R. Renewability is not Enough: Recent Advances in the Sustainable Synthesis of Biomass-Derived Monomers and Polymers. *Chem. - Eur. J.* **2016**, *22*, 11510–11521.
- (3) Zhu, Y.; Romain, C.; Williams, C. Sustainable polymers from renewable resources. *Nature* **2016**, *540*, 354–362.
- (4) Gross, R. A.; Kalra, B. Biodegradable Polymers for the Environment. *Science* **2002**, *297*, 803–807.
- (5) Vert, M.; Li, S. M.; Spenlehauer, G.; Guerin, P. Bioresorbability and biocompatibility of aliphatic polyesters. *J. Mater. Sci.: Mater. Med.* **1992**, *3*, 432–446.

(6) Longo, J. M.; Sanford, M. J.; Coates, G. W. Ring-Opening Copolymerization of Epoxides and Cyclic Anhydrides with Discrete Metal Complexes: Structure–Property Relationships. *Chem. Rev.* **2016**, *116*, 15167–15197.

(7) Paul, S.; Zhu, Y.; Romain, C.; Brooks, R.; Saini, P. K.; Williams, C. K. Ring-opening copolymerization (ROCOP): synthesis and properties of polyesters and polycarbonates. *Chem. Commun.* **2015**, *51*, 6459–6479.

(8) Della Monica, F.; Kleij, A. W. From terpenes to sustainable and functional polymers. *Polym. Chem.* **2020**, *11*, 5109–5127.

(9) Winnacker, M. Pinenes: Abundant and Renewable Building Blocks for a Variety of Sustainable Polymers. *Angew. Chem., Int. Ed.* **2018**, *57*, 14362–14371.

(10) Wahlen, C.; Blankenburg, J.; von Tiedemann, P.; Ewald, J.; Sajkiewicz, P.; Müller, A. H. E.; Floudas, G.; Frey, H. Tapered Multiblock Copolymers Based on Farnesene and Styrene: Impact of Biobased Polydiene Architectures on Material Properties. *Macromolecules* **2020**, *53*, 10397–10408.

(11) Lamparelli, D. H.; Paradiso, V.; Della Monica, F.; Proto, A.; Guerra, S.; Giannini, L.; Capacchione, C. Toward More Sustainable Elastomers: Stereoselective Copolymerization of Linear Terpenes with Butadiene. *Macromolecules* **2020**, *53*, 1665–1673.

(12) Sahu, P.; Sarkar, P.; Bhowmick, A. K. Synthesis and Characterization of a Terpene-Based Sustainable Polymer: Poly-allocimene. *ACS Sustainable Chem. Eng.* **2017**, *5*, 7659–7669.

(13) Wambach, A.; Agarwal, S.; Greiner, A. Synthesis of Biobased Polycarbonate by Copolymerization of Menth-2-ene Oxide and CO<sub>2</sub> with Exceptional Thermal Stability. *ACS Sustainable Chem. Eng.* **2020**, *8*, 14690–14693.

(14) Kindermann, N.; Cristòfol, À.; Kleij, A. W. Access to Biorenewable Polycarbonates with Unusual Glass-Transition Temperature ( $T_g$ ) Modulation. *ACS Catal.* **2017**, *7*, 3860–3863.

(15) Hauenstein, O.; Agarwal, S.; Greiner, A. Bio-based polycarbonate as synthetic toolbox. *Nat. Commun.* **2016**, *7*, 11862.

(16) Maltby, K. A.; Hutchby, M.; Plucinski, P.; Davidson, M. G.; Hintermair, U. Selective Catalytic Synthesis of 1,2- and 8,9-Cyclic Limonene Carbonates as Versatile Building Blocks for Novel Hydroxyurethanes. *Chem. - Eur. J.* **2020**, *26*, 7405–7415.

(17) Schimpf, V.; Ritter, B. S.; Weis, P.; Parison, K.; Mühlhaupt, R. High Purity Limonene Dicarboxylate as Versatile Building Block for Sustainable Non-Isocyanate Polyhydroxyurethane Thermosets and Thermoplastics. *Macromolecules* **2017**, *50*, 944–955.

(18) Firdaus, M.; Meier, M. A. R. Renewable polyamides and polyurethanes derived from limonene. *Green Chem.* **2013**, *15*, 370–380.

(19) Thomsett, M. R.; Moore, J. C.; Buchard, A.; Stockman, R. A.; Howdle, S. M. New renewably-sourced polyesters from limonene-derived monomers. *Green Chem.* **2019**, *21*, 149–156.

(20) Nsengiyumva, O.; Miller, S. A. Synthesis, characterization, and water-degradation of biorenewable polyesters derived from natural camphoric acid. *Green Chem.* **2019**, *21*, 973–978.

(21) Quilter, H. C.; Hutchby, M.; Davidson, M. G.; Jones, M. D. Polymerisation of a terpene-derived lactone: a bio-based alternative to  $\epsilon$ -caprolactone. *Polym. Chem.* **2017**, *8*, 833–837.

(22) Sanford, M. J.; Peña Carrodegua, L.; Van Zee, N. J.; Kleij, A. W.; Coates, G. W. Alternating Copolymerization of Propylene Oxide and Cyclohexene Oxide with Tricyclic Anhydrides: Access to Partially Renewable Aliphatic Polyesters with High Glass Transition Temperatures. *Macromolecules* **2016**, *49*, 6394–6400.

(23) Van Zee, N. J.; Coates, G. W. Alternating Copolymerization of Propylene Oxide with Biorenewable Terpene-Based Cyclic Anhydrides: A Sustainable Route to Aliphatic Polyesters with High Glass Transition Temperatures. *Angew. Chem., Int. Ed.* **2015**, *54*, 2665–2668.

(24) Yi, N.; Chen, T. T. D.; Unruangsri, J.; Zhu, Y.; Williams, C. K. Orthogonal functionalization of alternating polyesters: selective patterning of (AB)<sub>n</sub> sequences. *Chem. Sci.* **2019**, *10*, 9974–9980.

(25) Sanford, M. J.; Van Zee, N. J.; Coates, G. W. Reversible-deactivation anionic alternating ring-opening copolymerization of epoxides and cyclic anhydrides: access to orthogonally functionalizable multiblock aliphatic polyesters. *Chem. Sci.* **2018**, *9*, 134–142.

(26) Fournier, L.; Robert, C.; Pourchet, S.; Gonzalez, A.; Williams, L.; Prunet, J.; Thomas, C. M. Facile and efficient chemical functionalization of aliphatic polyesters by cross metathesis. *Polym. Chem.* **2016**, *7*, 3700–3704.

(27) Hillmyer, M. A.; Tolman, W. B. Aliphatic Polyester Block Polymers: Renewable, Degradable, and Sustainable. *Acc. Chem. Res.* **2014**, *47*, 2390–2396.

(28) Adio, A. M. (–)-*trans*- $\beta$ -Elemene and related compounds: occurrence, synthesis, and anticancer activity. *Tetrahedron* **2009**, *65*, 5145–5159.

(29) *Isobionics*. <https://www.isobionics.com/index-Beta%20Elemene.html> (accessed Dec 18, 2020).

(30) Beekwilder, M. J.; Van Houwelingen, A. M. M. L.; Bosch, H. J.; Lentzen, G. F.; Melillo, E. Terpene synthase producing patchoulol and elemol, and preferably also pogostol. World Patent WO2019045568A1, March 7, 2019.

(31) Thomas, A. F.; Vial, C.; Ozainne, M.; Ohloff, G. The Oxidation of the Double Bonds of  $\beta$ -Elemene. *Helv. Chim. Acta* **1973**, *56*, 2270–2279.

(32) Hussain, H.; Al-Harrasi, A.; Green, I. R.; Ahmed, I.; Abbas, G.; Rehman, N. U. meta-Chloroperbenzoic acid (mCPBA): a versatile reagent in organic synthesis. *RSC Adv.* **2014**, *4*, 12882–12917.

(33) Pei, J.; Zhou, J.; Xie, G.; Chen, H.; He, X. PARM: A practical utility for drug design. *J. Mol. Graphics Modell.* **2001**, *19*, 448–454.

(34) Peña Carrodeguas, L.; Martín, C.; Kleij, A. W. Semiaromatic Polyesters Derived from Renewable Terpene Oxides with High Glass Transitions. *Macromolecules* **2017**, *50*, 5337–5345.

(35) Nejad, E. H.; Paoniasari, A.; van Melis, C. G. W.; Koning, C. E.; Duchateau, R. Catalytic Ring-Opening Copolymerization of Limonene Oxide and Phthalic Anhydride: Toward Partially Renewable Polyesters. *Macromolecules* **2013**, *46*, 631–637.

(36) Akindoyo, J. O.; Beg, M. D. H.; Ghazali, S.; Islam, M. R.; Jeyaratnam, N.; Yuvaraj, A. R. Polyurethane types, synthesis and applications – a review. *RSC Adv.* **2016**, *6*, 114453–114482.

(37) Stöber, T.; Sulley, G. S.; Gregory, G. L.; Williams, C. K. Easy access to oxygenated block polymers via switchable catalysis. *Nat. Commun.* **2019**, *10*, 2668.

(38) Meereboer, K. W.; Misra, M.; Mohanty, A. K. Review of recent advances in the biodegradability of polyhydroxyalkanoate (PHA) bioplastics and their composites. *Green Chem.* **2020**, *22*, 5519–5558.

(39) Sharma, R.; Ray, A. R. Polyhydroxybutyrate, its Copolymers and Blends. *J. Macromol. Sci., Polym. Rev.* **1995**, *35*, 327–359.

(40) Stirling, E.; Champouret, Y.; Visseaux, M. Catalytic metal-based systems for controlled statistical copolymerisation of lactide with a lactone. *Polym. Chem.* **2018**, *9*, 2517–2531.

(41) Della Monica, F.; Luciano, E.; Buonerba, A.; Grassi, A.; Milione, S.; Capacchione, C. Poly(lactide-*co*- $\epsilon$ -caprolactone) copolymers prepared using bis-thioetherphenolate group 4 metal complexes: synthesis, characterization and morphology. *RSC Adv.* **2014**, *4*, 51262–51267.