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Yanzhao Wang and Marc A. Hillmyer*

Facile preparation of linear amorphous hydroxy-telechelic poly(ethylene-*co*-isobutylene) (PEIB) was enabled by ROMP of a new monomer, (*Z*)-5,5-dimethylcyclooct-1-ene (Me$_2$COE). Control of the isobutylene content and the resulting thermal properties was accomplished via copolymerization with COE. The applicability as a prepolymer was demonstrated by the synthesis of a tough, elastic and free-standing polyurethane film.

Polyisobutylene (PIB) is widely applied in a variety of industrial areas because of its attractive properties: extremely low permeability, excellent oxidative stability and chemical resistance. PIB was also shown to be biocompatible and approved by the Food and Drug Administration (FDA) for food-related applications.[1] PIB-based thermoplastic polyurethane (PU) elastomers represent particularly interesting class of biomaterials and have attracted much attention.[2,3] Due to the PIB component, the oxidative, hydrolytic, and thermal stability along with the barrier properties of these PUs are far superior to conventional PUs containing polyesters and polyethers as soft segments.[4]

As early as in 1970, Zapp *et al.* prepared PIB-based PUs utilizing *sec*-hydroxy-telechelic PIB. However, this reaction produced byproducts like biurets and allophanates due to the low reactivity of the secondary hydroxyl end-groups.[5] Kennedy *et al.* reported the synthesis of PIB-based PUs by the use of well-defined hydroxy-telechelic PIB (HO-PIB-OH), diisocyanates and chain extenders;[6] those materials exhibited excellent chemical and thermal stability.[7] Shortly after this, Faust and Kennedy *et al.* reported the first living carbocationic polymerization of isobutylene (IB);[8] this breakthrough led to the preparation of well-defined hydroxy-/amino-telechelic PIBs with low dispersity. Subsequently these PIBs were used to prepare the corresponding PUs.[9,10] In addition, poly(styrene)-*b*-poly(isobutylene)-*b*-poly(styrene) (SIBS) block polymers have been used as polymeric coatings in a drug-eluting coronary stents.[11]

We proposed that controlled versions of poly(ethylene-*co*-isobutylene) (PEIB) can potentially provide similar properties and applications to PIB. Such copolymers can be easily obtained by ring-opening metathesis polymerization (ROMP), a powerful tool to access a variety of linear polyolefins with controllable molar mass and architecture.[12] In these cases, the polymers are analogues to those derived from the polymerization of isobutylene, but are distinct in that no isobutylene is used in their synthesis. In 1995, Wu and Grubbs prepared an alternating PEIB with high regioselectivity by ROMP of 3,3-dimethylcyclobutene followed by hydrogenation.[13] More recently, Binder *et al.* synthesized poly(*homo*-isobutylene) from 3,3-dimethylcyclopropene utilizing a similar strategy,[14] and this *pseudo*-PEIB had a moderate dispersity (1.9–3.9) and a melting temperature (T_m) of 108 °C. To date telechelic PEIB synthesized via ROMP has not been reported. In this work, we describe the synthesis of hydroxy-telechelic PEIBs via ROMP from a new, more accessible cyclooctene monomer, and its application as a soft segment in the synthesis of elastomeric PUs.

The new monomer, (*Z*)-5,5-dimethylcyclooct-1-ene (Me$_2$COE **5**), was synthesized in five steps staring from inexpensive 1,5-cyclooctadiene (1,5-COD), as shown in Scheme 1. *Tert*-butyl ester **1** was prepared in 84% yield through Pd-catalyzed alkoxy carbonylation, followed by LDA promoted methylation, giving the α-methyl *tert*-butyl ester **2** in 92% yield. LiAlH$_4$ reduction provided alcohol **3**, and subsequent treatment with 4-toluenesulfonyl chloride in the presence of pyridine and 4-dimethylaminopyridine (DMAP) afforded tosylate **4**; both steps gave near quantitative yields. Monomer **5** was prepared in 54% yield via LiAiH$_4$ reduction of **4** (69% based on recovered **3**). Notably, 22% of **3** was isolated as well, indicating there was a competition between the reduction of the C-O and S-O bond. Monomer **5** was obtained on a multigram scale in 40% overall yield and this synthesis can be carried out using efficient, column-free processes (distillation or aqueous work-up only); only one silica plug was used in the last step. See the Supporting Information for synthetic and characterization details.

The homopolymerization of Me$_2$COE **5** was performed in anhydrous chloroform with 0.04 mol % Grubbs second-generation

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Department of Chemistry, University of Minnesota, Minneapolis, Minnesota, 55455-0431, USA. E-mail: hillmyer@umn.edu

† Footnotes relating to the title and/or authors should appear here.
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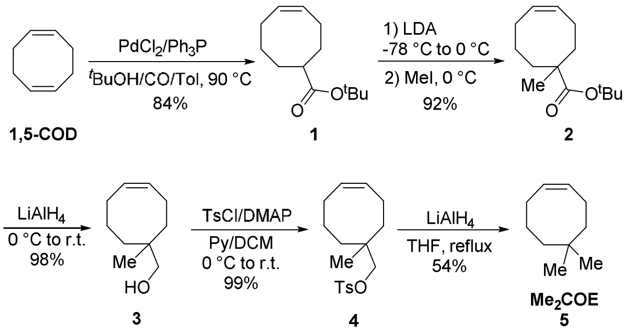
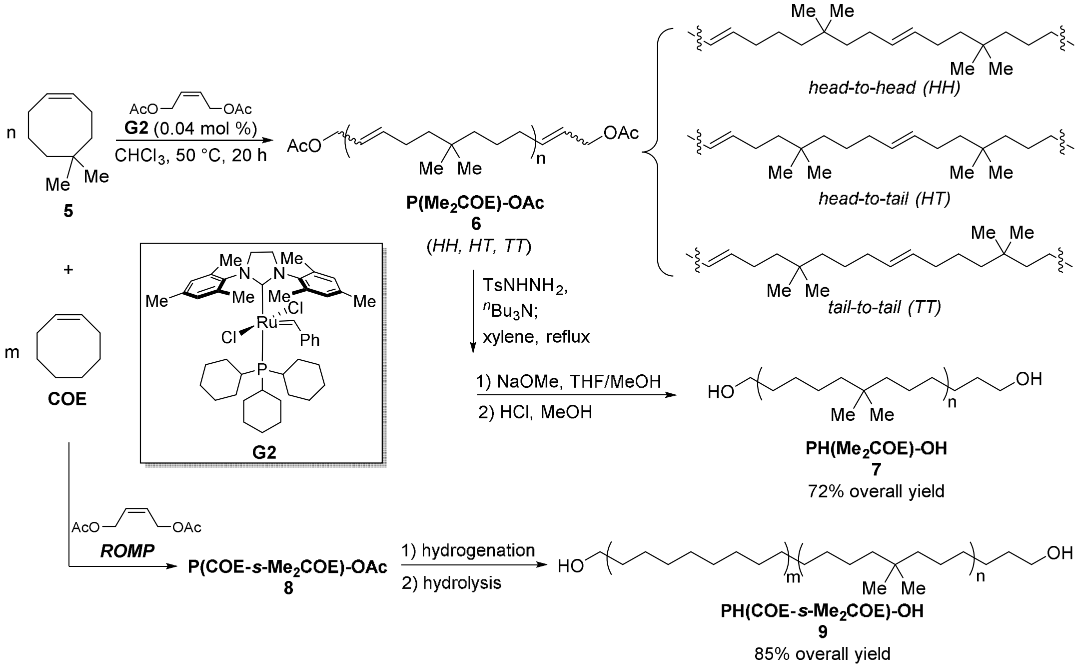


Scheme 1 Synthesis of the monomer Me$_2$COE **5**

catalyst (**G2**) at 50 °C (Scheme 2). Since 1,4-diacetoxy-*cis*-2-butene proved to be an excellent chain transfer agent (CTA) allowing for further functionalization,[15-18] it was chosen to tune the number-average molar mass (M_n) of the polymer (target M_n = 5.0 kg mol^{-1}). The reaction initiated in less than 10 seconds as suggested by the viscosity increase and monomer conversion was quantitative after 20 h according to the crude ^{1}H NMR spectrum (90% isolated yield) in spite of the Thorpe–Ingold effect of the *gem*-dimethyl groups.[19] The M_n of the resulting P(Me$_2$COE)-OAc **6** was close the target value as verified by SEC ($M_{n,LS\text{-}SEC}$ = 6.6 kg mol^{-1}) and ^{1}H NMR end-group analysis ($M_{n,NMR}$ = 5.0 kg mol^{-1}). The molar mass dispersity was approximately 2 as expected for the ROMP of an eight-membered cyclic olefin after relatively long reaction times (Table 1).



Scheme 2 Synthesis of hydroxy-telechelic PEIBs PH(Me$_2$COE)-OH **7** and PH(COE-*s*-Me$_2$COE)-OH **9**: ROMP, hydrogenation and hydrolysis

Table 1 Characterization data of the hydroxy-telechelic PEIBs and unsaturated prepolymers

Polymer	M_n (kg mol^{-1})				Đ (M_w/M_n)	T_g	T_m	T_d
	Calc.[c]	SEC[d]	LS-SEC[e]	NMR[f]	SEC[d]	(°C)[g]	(°C)[h]	(°C)[i]
P(Me$_2$COE)-OAc **6**[a]	5.0	6.6	6.6	5.0	2.00	−56	-	359
PH(Me$_2$COE)-OH **7**[b]	5.0	8.8	6.9	5.8	1.61	−45	-	384
P(COE-*s*-Me$_2$COE)-OAc **8**[a]	5.1	8.8	8.6	6.1	1.98	−73	−13	382
PH(COE-*s*-Me$_2$COE)-OH **9**[b]	5.1	9.4	8.2	6.6	1.97	−37	31[j]	396

[a]Targeted M_n = 5 kg mol^{-1}. [b]>99% Hydrogenation achieved. [c]$M_{n,calc.}$ = (M_w of **5**)×[**5**]/([CTA]+[G2]) + (M_w of CTA). [d]Determined by SEC in CHCl$_3$ versus polystyrene standards. [e]Determined by LS-SEC in THF. [f]Determined by NMR end-group analysis [g]Determined by DSC (2nd heating cycle) at 10 °C min^{-1}. [h]Determined by DSC (2nd heating cycle) at 2 °C min^{-1}. [i]5% mass loss determined by TGA at 20 °C min^{-1} under N$_2$. [j]This material has a broad melting transition (−15 to +77 °C).

Unsaturated polymer **6** was then hydrogenated using diimide generated *in situ* by the thermolysis of *p*-toluenesulfonylhydrazide.[20] The extent of hydrogenation was >99% according to the ^{1}H NMR spectrum (Fig 1), and 12% of the acetoxyl (OAc) end-group were hydrolyzed under these reaction conditions. To obtain the fully hydroxy-telechelic polymer, the hydrogenated polymer was treated with NaOMe in tetrahydrofuran and subsequently acidified using methanolic HCl. The final product, PH(Me_2COE)-OH **7**, was collected as slightly yellow viscous liquid in 80% yield over two steps and decolorized by simple filtration over silica gel and activated carbon. The M_n of this hydroxy-telechelic polymer was slightly higher than that of the unsaturated prepolymer **6** (Table 1), possibly due to some fractionation during precipitation.

P(COE-*s*-Me_2COE)-OAc **8**, a 1:1 statistical copolymer of *cis*-cyclooctene (COE) and Me_2COE **5**, was also obtained in excellent isolated yield (94%) under the same ROMP conditions (Scheme 2). We expect that the long reaction time (20 h) should allow for relatively equal distribution of the two monomers in the backbone by cross-metathesis. The final telechelic polymer PH(COE-*s*-Me_2COE)-OH **9** was afforded as a white solid after hydrogenation and hydrolysis in 90% overall yield. The values of M_n for PEIB **9** and its precursor **8** were consistent according to SEC and NMR end-group analysis (Table 1). Notably, the overall yield of **9** was higher than that of the homopolymer **7** (85% *vs.* 72%), most likely due to the lower solubility and thus more efficient isolation.

SEC traces of the hydrogenated polymers were unimodal and very similar to their parent materials (Fig S1),[21] indicating that minimum side-reactions occurred during hydrogenation and end-group hydrolysis. The slightly lower dispersity of the PH(Me_2COE)-OH **7** is attributed to the loss of lower molar mass species in sequential precipitations.

The ^{1}H NMR spectrum also supports that Me_2COE **5** was successfully polymerized to P(Me_2COE)-OAc **6** using **G2** (Fig 1). The two sets of olefinic protons from the monomer **5** shifted upfield and merged to a broad peak with a shoulder, indicating that the ring was opened and both *E* and Z double bonds were present. Furthermore, the methylene protons from the OAc end-groups located at 4.62 and 4.51 ppm signify the incorporation of the CTA into the polymer. The peaks between 1.37–1.09 ppm belong to the methylene groups of the polymer backbone while the peaks associated with the *gem*-dimethyl protons were observed at 0.84 ppm. In the ^{13}C NMR spectrum, multiple peaks appear in the olefinic area due to head-to-head, head-to-tail, and tail-to-tail repeating units as well as the presence of *E*- and *Z*-configuration of the double bonds (see supporting Information).[22] Complete hydrogenation and hydrolysis were confirmed by both ^{1}H and ^{13}C NMR spectroscopy as the peaks in the olefinic and allylic regions as well as the acetyl groups were no longer evident, while the methylene protons of the end-groups shifted upfield. The ^{1}H NMR spectrum of the copolymer P(COE-*s*-Me_2COE)-OAc **8** indicates that Me_2COE **5** and COE were fully incorporated (Fig 2), consistent with the feed ratio of 1:1 for the two monomers. Additionally, the subsequent hydrogenation and hydrolysis were shown to reach full conversion based on the ^{1}H (Fig 2) and ^{13}C NMR spectra (see supporting Information) of PH(COE-*s*-Me_2COE)-OH **9**.

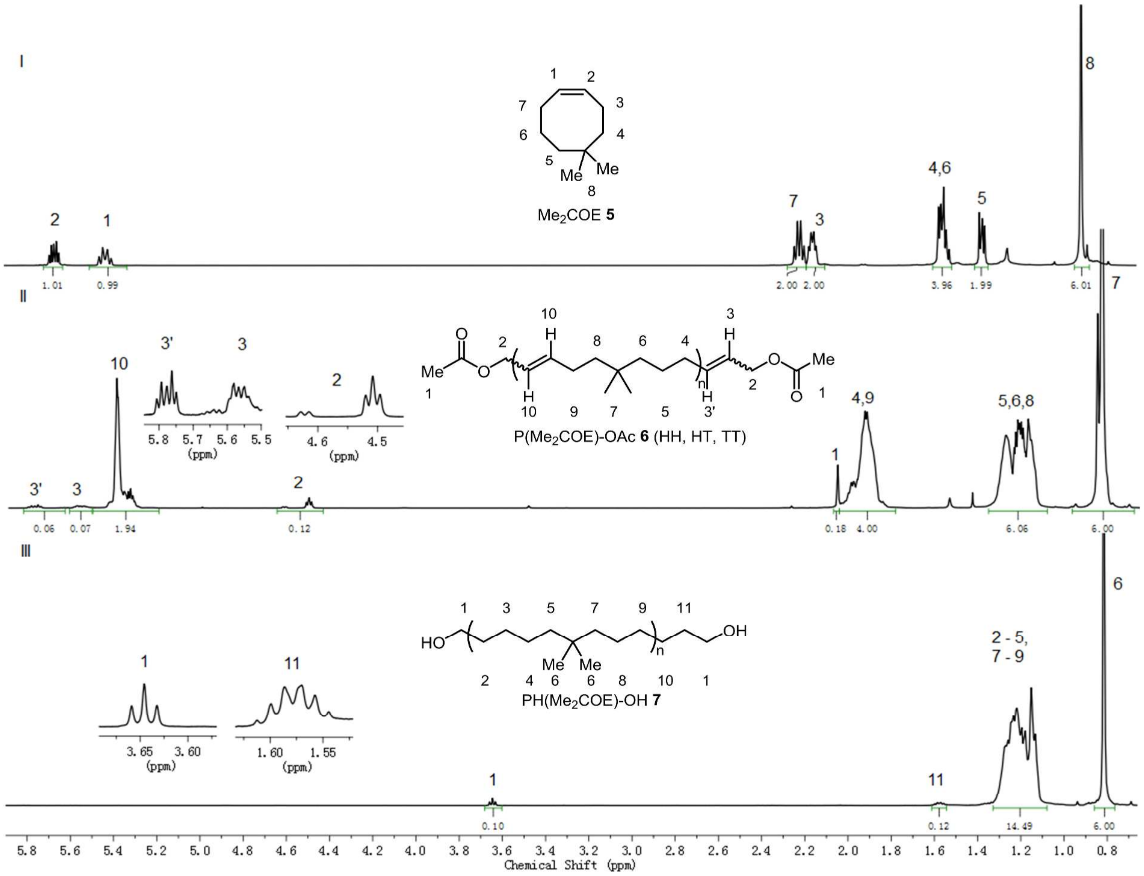


Fig 1 ^{1}H spectra of (I) Me_2COE **5**; (II) P(Me_2COE)-OAc **6** and (III) PH(Me_2COE)-OH **7** measured in $CDCl_3$

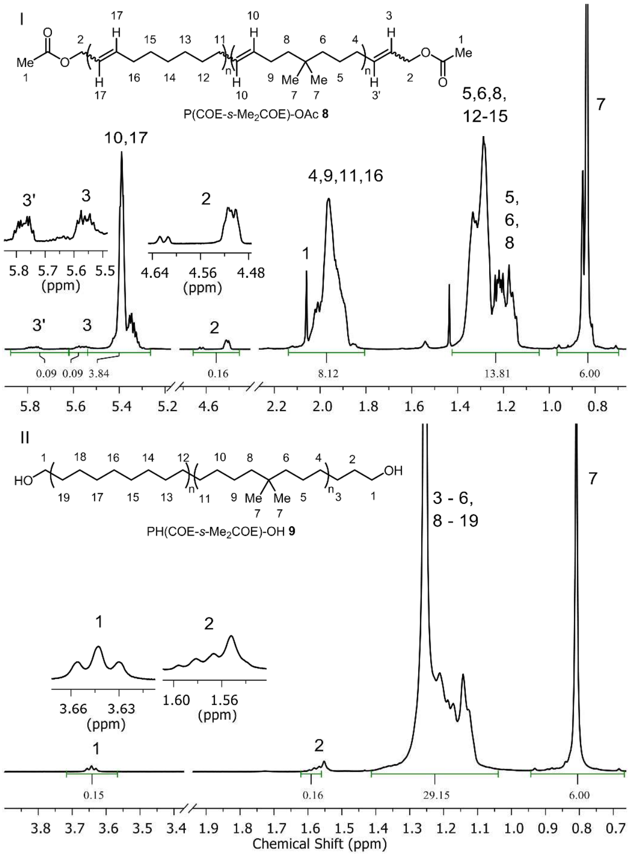


Fig 2 ^{1}H spectra of (I) P(COE-*s*-Me$_2$COE)-OAc **8** and (II) PH(COE-*s*-Me$_2$COE)-OH **9** measured in CDCl$_3$

As expected, DSC analysis indicates that telechelic PEIB **7** is completely amorphous with a low glass transition temperature (T_g) of –45 °C; no crystallization or melting behaviour was observed. PH(COE-*s*-Me$_2$COE)-OH **9** is semicrystalline material, exhibiting a peak T_m at about 31 °C (ΔH_m = 40 J/g) with a slightly higher T_g at –37 °C; the broadness of the melting transition (from −15 to +77 °C) indicates that this copolymer is not regioregular (Fig 3).

PH(Me$_2$COE)-OH **7** can be considered as a copolymer of ethylene (75 mol %) and isobutylene (25 mol %) with precise molar ratio control. In 1998, Shaffer *et al.* reported the T_g of a PEIB (M_n = 27 kg mol^{-1}) with 24 mol % incorporation of IB from the copolymerization of ethylene and IB catalyzed by metallocene to be 8 °C higher (T_g = –37 °C),[23] which was possibly due to the increased running length of ethylene segment on the backbone from this statistical copolymerization. Schwendeman *et al.* reported two PEIBs made by acyclic diene metathesis (ADMET),[24,25] bearing a *gem*-dimethyl moiety on every 9th and 15th carbon along the backbone (T_g = –47 °C, –42°C respectively); the IB content of these polymers were 22.2 mol % and 13.3 mol %, respectively. Although ROMP of Me$_2$COE **5** was non-regioselective, the distance between every two *gem*-dimethyls could only be 6, 7 or 8 methylene groups, which may suggest why PH(Me$_2$COE)-OH **7** behaves similarly to the precisely alternating PEIB rather than the corresponding statistical copolymer, and retains a T_g close to that of the ADMET PEIB (M_n = 56 kg mol^{-1}) with 22.2% IB content (–45 °C *vs.* –47 °C). For PH(COE-*s*-Me$_2$COE)-OH **9** (12.5 mol % IB content), the material also has a comparable T_g (–37 °C *vs.* –42 °C) and T_m (31 °C *vs.* 32 °C) to that of the corresponding ADMET PEIB (M_n = 49 kg mol^{-1}) with 13.3 mol % IB content. Thermal gravimetric analysis (TGA) of these hydroxy-telechelic PEIBs and prepolymers revealed high thermal stability with temperatures of decomposition (T_d, 5% mass loss) from 359–398 °C under nitrogen (Table 1 and Fig S3).[26]

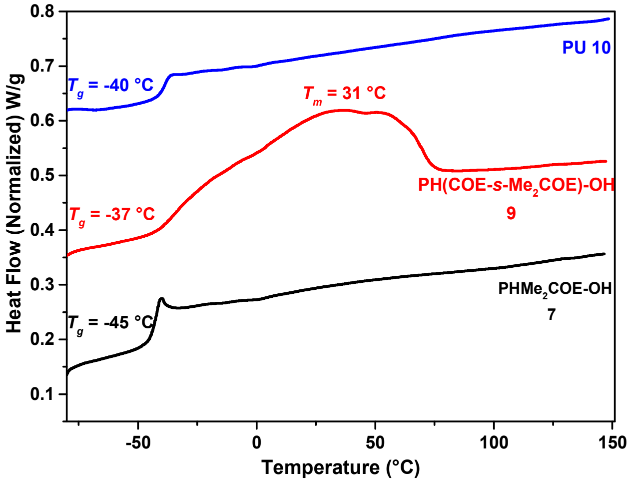
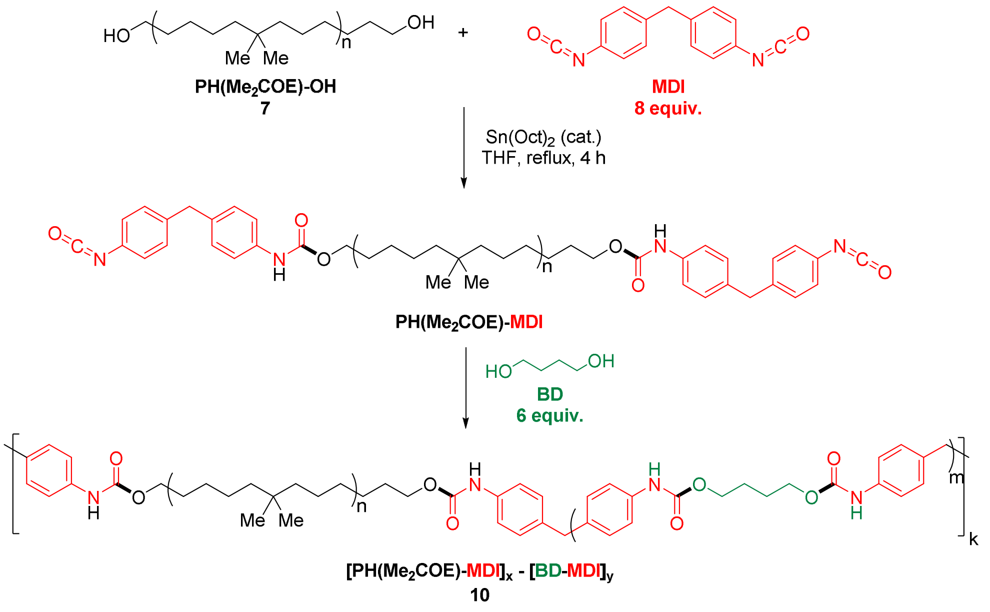


Fig 3 DSC thermograms of hydroxy-telechelic PEIBs **7**, **9** and PU **10** at the heating rate of 10 °C/min

A PEIB-based PU sample targeting 30% hard segment was obtained in a two-step sequence from amorphous hydroxy-telechelic PEIB **7**, methylene diphenyl diisocyanate (MDI) and 1,4-butanediol (BD) (Scheme 3). The prepolymer **7** was first dissolved in THF and then charged into a vial containing MDI at 72 °C under a N$_2$ atmosphere. Stannous (II) octoate (Sn(Oct)$_2$) in THF was then added to catalyze the addition reaction and the resulting reaction mixture was stirred for 4 h to achieve the isocyanate-terminated intermediate, PH(Me$_2$COE)-MDI (See Supporting Information for details). Subsequently a solution of BD, the chain-extender, in THF was added and the reaction was allowed to react at the same temperature. The NCO/OH ratio was 1.14:1. After 12 hours, some precipitates formed and the addition of methanol led to further precipitation, yielding the PU **10** in 93% isolated yield as off-white solid.

The FT-IR spectrum of PU **10** shows a strong band at 1702 cm^{-1}, which is rather typical for the carbonyl stretching of H-bonded carbamate linkages (Fig 4). The N-H stretching frequency of the urethane linkages was observed at 3325 cm^{-1} and another strong band at 1228 cm^{-1} was attributed to the C-O stretch. These data are consistent with successful preparation of PU **10** from PH(Me$_2$COE)-OH **7**.



Scheme 3 Synthesis of PU **10** based on PH(Me_2COE)-OH **7**

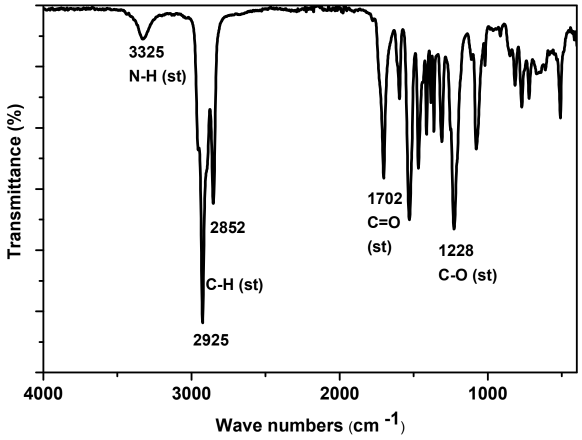


Fig 4 FT-IR spectrum of PU **10**

In the ^{1}H NMR spectrum of PU **10** (Fig 5), a new broad signal at 4.26 ppm clearly corresponds for CH_2O-CO-NH, again indicating the successful PU synthesis. The multiple peaks at 4.02–3.78 ppm are attributable to the benzylic methylene protons originating from MDI and the peaks from 1.90–1.63 ppm correspond to the OCH_2-CH_2-CH_2-CH_2O resonances. The disappearance of the triplet at 3.64 ppm for CH_2-OH of PH(Me_2COE)-OH **7** indicates complete consumption of the hydroxyl end-groups during the reaction.

A low T_g was observed at –40 °C from DSC thermogram of PU **10** (Fig 3) and a T_d at 295 °C was determined by the TGA data (Fig S3).[26] Due to the limited solubility of **10** in typical SEC solvents (*e.g.* $CHCl_3$, DMF, THF, 1,2,4-TCB, HFIP), molar mass data were not obtained. Although allophanate and biuret motifs are common in PU, the sample PU 10 was very soluble in the solvent mixture of CHCl3 and TFA, consistent with the lack of significant crosslinking. Nevertheless, a tough, elastic and free-standing PU film was obtained by solvent casting from a solvent pair of $CHCl_3$ and TFA (90:10),[27] and the characteristics of this film indicated that a relatively high molar mass was achieved (Fig S4).

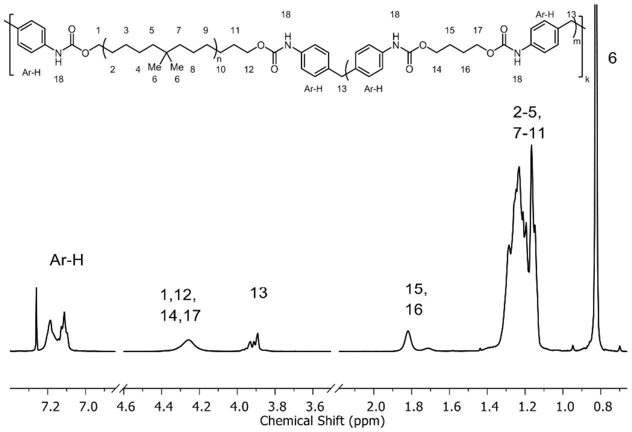


Fig 5 ^{1}H spectrum of PU **10** measured in $CDCl_3$/TFA-d_1 (90:10)[28]

In conclusion, we have described the efficient synthesis of a new monomer, (*Z*)-5,5-dimethylcyclooct-1-ene (Me_2COE **5**), from 1,5-COD. Linear amorphous hydroxy-telechelic poly(ethylene-*co*-isobutylene), PH(Me_2COE)-OH **7**, was obtained via ROMP of Me_2COE followed by hydrogenation and hydrolysis. The IB content, T_g and crystallinity of PEIB could be tuned by the copolymerization of Me_2COE and COE. The use of *cis*-1,4-diacetoxy-2-butene as the CTA allowed for control of the molar mass via ROMP and more importantly, further transformation to the hydroxyl telechelic material. The hydroxy-telechelic PEIBs showed low T_g values and high thermal resistance. One application of these telechelic PEIBs was demonstrated by the synthesis of PEIB-based PU **10** from PH(Me_2COE)-OH **7**, MDI and BD.

Acknowledgement

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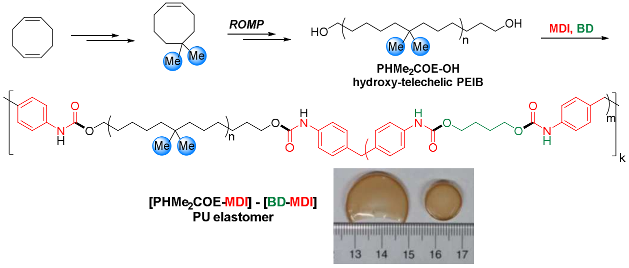
Graphic



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