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Divergent Catalytic Strategies for the *Cis/Trans* Stereoselective Ring-Opening Polymerization of a Dual Cyclic Carbonate/Olefin Monomer

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Ⓢ *Supporting Information*

ABSTRACT: A dual seven-membered cyclic carbonate/olefin monomer was synthesized from CO_2 and *cis*-1,4-butenediol and polymerized. The properties of the polymer were controlled using divergent catalytic strategies toward the stereochemistry of the olefin. Ring-opening polymerization of the cyclic carbonate using an organocatalytic approach retained the *cis*-stereoconfiguration of the olefin and yielded a hard semicrystalline polymer (T_m 115 °C). Ring-opening metathesis polymerization using Grubbs' catalyst proceeded with high *trans*-stereoregularity (95%) and produced a soft amorphous polymer (T_g −22 °C). *Cis* to *trans* isomerization of the polymer was possible using Cu(I) salts under UV light. In all polymers, the C=C double bond remained available for postpolymerization modification and thermoset resins were formed by cross-linking. From this single monomer, *cis-trans-cis* triblock copolymers, with potential applications as thermoplastic elastomers, were synthesized by combining both strategies using *cis*-1,4-butenediol as a chain transfer agent.

Controlling polymer stereochemistry is a powerful strategy to manipulate its physical properties.[1−8] The influence of the stereochemistry of alkene bonds in polymer chains is particularly remarkable. In nature, poly(*cis*-isoprene) (natural rubber) has thus vastly superior elastomeric properties compared with poly(*trans*-isoprene) (gutta percha).[9−11] Catalysis has been an efficient way to control synthetic polymers' stereochemistry by generating chain tacticity, yet examples of its application in *cis/trans* isomerism remain comparatively rare. Hillmyer and co-workers for example demonstrated the stereoselective ring-opening metathesis polymerization of *cis*-cyclooctene monomers using Ru catalysts (*trans*-selective)[12] and Mo catalysts (*cis*-selective).[13] Becker and Dove reported an organocatalytic stereocontrolled synthesis of unsaturated polyesters, resulting in a tunable *cis/trans* ratio, crystallinity, and mechanical properties.[14] Postpolymerization catalysis was also exploited to isomerize poly(propylene maleate) into poly(propylene fumarate) toward 3D printing and medical applications.[15−17]

The ability to drastically change polymer properties through *cis/trans* isomerization, e.g. from hard to soft materials, is particularly appealing in the context of synthetic thermoplastics elastomers (TPEs), which have a wide range of applications including 3D printing, elastomers (e.g., in footwear), pressure-sensitives adhesives, and coatings.[18,19] TPEs have similar properties to chemically cross-linked rubbers,[20] but they can be melt-(re)processed like thermoplastics. TPEs are usually ABA triblock copolymers in which hard/crystalline end-blocks (A) can microphase-separate from the soft/amorphous midblock (B) and act as physical cross-links to strengthen the elastic matrix. To the best of our knowledge, these TPEs are always made from two different monomers and may require purification of the middle block. Motivated by the desire to prepare hard or soft materials, as well as triblock TPEs, from one single monomer and in one pot, we anticipated that *cis/trans* stereoselective polymerization of a selected monomer would provide the desired platform. Here we describe such a monomer, which is a dual cyclic carbonate/olefin. We also demonstrate that these polymers are amenable to cross-linking and thermosets formation.

cis-1,4-Butenediol is a 1,4-diol which may be derived from erythritol,[21] a fermentation product of glucose (Figure 1). The
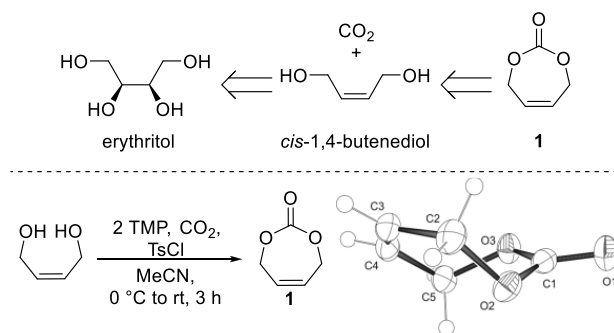

Figure 1. Retrosynthetic approach to 1,4-butenediol from erythritol; synthesis of 4,7-dihydro-1,3-dioxepin-2-one (**1**); ORTEP[23] view of the crystal structure of **1** (displacement ellipsoids at 50% probability level).

corresponding cyclic carbonate, 4,7-dihydro-1,3-dioxepin-2-one (**1**), was readily prepared in one step from CO_2, in 51% crystalline yield, following a procedure reported by our group (Figure 1).[22] CO_2 insertion was achieved using 2 equiv of 2,2,6,6-tetramethylpiperidine (TMP) with cyclization facilitated by 1 equiv of *para*-toluenesulfonate chloride (TsCl). **1** is

Table 1. Polymerization of 1 Using ROTEP and ROMP Catalysis with Divergent *Cis/Trans* Stereoselectivity[a]

entry	[cat.]	$[1]_0:[\text{cat.}]_0:[\text{I}]_0$[b]	temp (°C)	time (min)[c]	conv (%)[d]	cis/trans[e] (m:n)	$M_{n,theo}$ (g mol^{-1})[f]	$M_{n,NMR}$ (g mol^{-1})[g]	$M_{n,SEC}$ [Đ$_M$] (g mol^{-1})[h]
1	TBD	50:1:1	22	1	100	100:0	5820	6500	6400 [1.65]
2	TBD	100:1:1	22	10	100	100:0	11 520	10 800	11 000 [1.62]
3	TBD	150:1:1	22	40	100	100:0	17 220	17 100	18 100 [1.53]
4	Sn(Oct)$_2$[i]	100:0.5:1	60	10	70[j]	100:0	8070	9400	8600 [1.16]
5	Sn(Oct)$_2$[i]	200:0.5:1	60	18	41[j]	100:0	9400	7300	8900 [1.27]
7	**GII**	150:1:0	22	30	100	15:85	17 190	–	22 600 [2.02]
8	**GII**[k]	150:1:0	22	30	100	5:95	17 190	–	22 500 [1.58]
9	**GII**	300:1:0	22	50	100	10:90	34 290	–	34 300 [1.80]
10	**GII**[i]	150:1:0	120	30	100	20:80	17 190	–	23 200 [2.69]

[a]In CH$_2$Cl$_2$ with $[1]_0$ = 1 mol L^{-1} unless stated otherwise. [b]I is 4-MeBnOH. [c]Reaction times not optimized. [d]Calculated by relative integration of the alkene protons in **1** (δ = 5.82 ppm, t (J = 1.8 Hz)) and poly(**1**) (cis δ = 5.80 ppm, t (J = 4.1 Hz), trans δ = 5.90 ppm, t (J = 3.0 Hz)) in the ^{1}H NMR spectrum in CDCl$_3$. [e]Determined by relative integration of alkene protons in the *trans* and *cis* polymer. [f]Calculated as M_r(I)+ (M_r(**1**) × $[1]_0$/$[\text{I}]_0$ × conv/100%); for ROMP: M_r(I) = M_r(CHPh) and $[\text{I}]_0$ = [cat.]$_0$. [g]For ROTEP: calculated by the relative integration of the methylene protons in I (δ = 5.12 ppm, s) and in poly(**1**); undeterminable for ROMP. [h]Calculated by SEC relative to polystyrene standards in CHCl$_3$ or THF eluent, Đ$_M$ = M_w/M_n. [i]No solvent. [j]Reaction quenched as stirring stopped. [k]Reaction carried out under UV light (λ = 365 nm).

a seven-membered cyclic compound with both a carbonate and an alkene functionality, providing opportunities for ring-opening polymerization using metathesis (ROMP) or trans-carbonation (referred to here as ROP) methodologies. We reasoned that ROMP and ROP would both produce a polycarbonate, but could show opposite stereoselectivity toward the configuration of the polymer alkene bonds.

First, various organo- and metal-based catalysts were screened for the ROP of **1** in solution (Table S1). When using 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as the catalyst (Table 1), ROP proceeded rapidly at room temperature with 100% conversion after 10 min, at a monomer/catalyst/initiator ($[1]_0$:[cat.]$_0$:[I]$_0$) feed ratio of 100:1:1 (Table 1, entry 2). The quantitative conversion of the monomer to polymer is consistent with the high ring strain of **1** calculated by DFT (Figure S56). For each of the ROP catalysts tested, the *cis* configuration of the monomer's alkene was maintained in the polymer as evidenced by ^{1}H NMR spectroscopy (Figure 2). Using TBD led to a good correlation between theoretical and experimental M_n values measured by Size-Exclusion Chromatography (SEC), with dispersities (Đ$_M$) of 1.3–1.8 (Tables 1 and S1). ROP could also occur at 60 °C in molten monomer

using Sn(Oct)$_2$ or TBD as the catalyst (Table 1 entry 4 and Table S1 entry 5, respectively). MALDI-ToF spectrometry and ^{1}H NMR spectroscopy confirmed the presence of 4-methyl benzyl alcohol and OH chain ends (Figure S27). Initial rate kinetic studies carried out with TBD indicated first-order kinetics (k_{obs} = 0.117 s^{-1}) with respect to monomer concentration (Figures S30–S31). M_n was found to increase linearly with conversion (Figures S32–S33) with an $M_{n,SEC}$ of 22 100 g mol^{-1} achievable (degree of polymerization (DP) $\approx$ 200, Figure S18).

Next, the ROMP of **1** was carried out (Scheme 1), catalyzed by Grubbs second generation catalyst (**GII**). Quantitative

Scheme 1. Divergent Stereoselective Strategies Used for the ROP of 1

conversion was achieved at 22 °C in solution after 30 min at the $[1]_0$:[**GII**]$_0$ 150:1 ratio. Good control over M_n and Đ$_M$ was observed across the range of loadings tested (Table 1, entries 7−10 and Table S2). An $M_{n,SEC}$ of up to 34 300 g mol^{-1} (DP $\approx$ 300) was achieved after 50 min (Table 1, entry 9). Satisfyingly, **GII** favored the formation of the *trans* isomer with stereo-regularities of up to 95% obtainable in 30 min under UV, as observed by ^{1}H NMR spectroscopy (Figure 2 and Table 1, entry 8). The *trans* selectivity of the reaction was found to be sensitive to time, monomer concentration, and temperature (Table S2). Longer reaction times and high dilution favored formation of the *trans* isomer, with a maximum selectivity of 95% observed after 92 h (Table S2, entry 9). At 120 °C, *trans* selectivity decreased to 88% and 80% when performing reactions in 1,2-tetrachloroethane or neat monomer, respectively (Table S2, entry 6, Table 1, entry 10).

Postpolymerization isomerization was also explored as DFT indicated the *trans* isomer was thermodynamically more stable (Figure S57). Isomerization of the double bond was possible
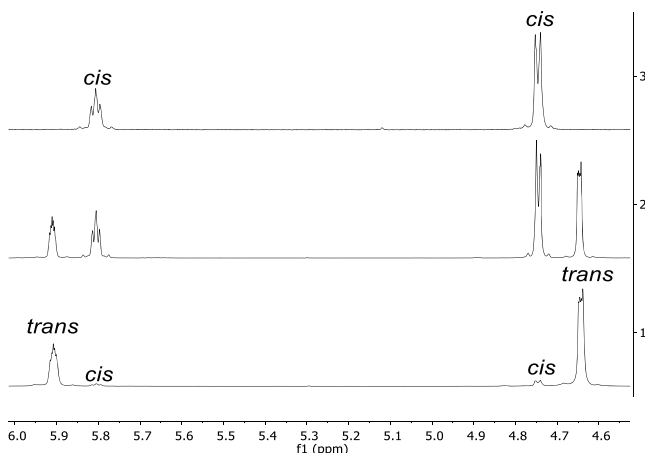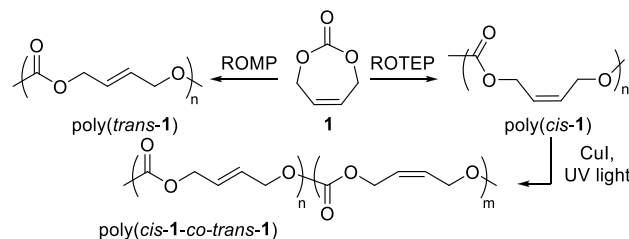

Figure 2. Alkene and methylene regions of the ^{1}H NMR spectra of poly(**1**), demonstrating the divergence of the catalytic strategies used, and the partial isomerization from poly(*cis*-**1**) (top) to poly(*trans*-**1**) (bottom), using CuI under UV light (middle).

under UV light at room temperature, using 1 alkene equivalent of CuI (52% conversion of poly(*cis*-**1**) to *trans* isomer, 68 h) (Figure S10). No degradation of the polymer was observed by SEC (Figure S13) or NMR spectroscopy (Figure S12).

The appearance and solubility of poly(*trans*-**1**) are significantly different from those of poly(*cis*-**1**). At room temperature poly(*trans*-**1**) is a viscoelastic solid, soluble in THF, whereas poly(*cis*-**1**) is a powder, insoluble in THF but soluble in CHCl$_3$ (Figure S8). Thermogravimetric analysis (TGA) indicated that the onset of thermal degradation ($T_{d,onset}$) for both polymers occurred at 152 °C (Table S4, entries 1 and 2). Differential scanning calorimetry (DSC) revealed for the *cis* polymer the presence of a minor glass transition at −24 °C (T_g) and a melting transition at 115 °C (T_m) (Figure S46). For the 5:95 (*cis/trans*) polymer, a major single T_g at −22 °C was observed, attributed to the *cis* regime (Figure 3 and Figure S47). A T_m was not observed. The
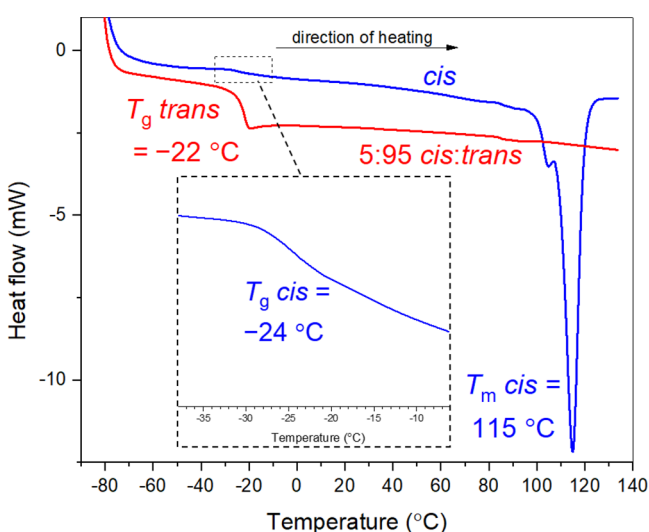

Figure 3. DSC thermograms of poly(*cis*-**1**) (top) and poly(*trans*-**1**) (bottom).

significant difference in crystallinity of the *trans* and *cis* polymers highlights the impact of the double-bond isomerism on material properties.

Cross-linking experiments were conducted to explore the potential of the polymers for thermoset formation and coating applications.[24−26] Trimethylolpropane tris(3-mercapto-propionate) was reacted with poly(*cis*-**1**) and a *cis/trans* (12:88) polymer in the presence of photoinitiator Irgacure 819 at three alkene/thiol $[C=C]_0:[SH]_0$ loadings (1:1, 2:1, 5:1). DSC analysis confirmed the formation of highly cross-linked networks with no T_m or T_g being observed up to 140 °C at ratios of 1:1 and 2:1 (Figures S51−S53). Crystallinity was still observed for a weakly cross-linked 5:1 sample (Figure S50). TGA revealed increasing thermal stability with increasing cross-linking (Table S6, maximum $T_{d,onset}$ = 193 °C).

The synthesis of a *cis-trans-cis* triblock was then attempted, utilizing a sequential ROMP/ROTEP concept originally demonstrated by Hillmyer and co-workers,[27−29] albeit this time with one single monomer, **1** (Scheme 2). *Cis*-butene-1,4-diol was used as a chain transfer agent (CTA) for the ROMP of **1** in a $[1]_0:[GII]_0:[CTA]_0$ ratio of 20:0.005:1 (Table 2, entry 1). THF was used as the solvent to decrease deactivation of the CTA by **GII**,[30] and a $[CTA]_0:[GII]_0$ ratio of 200:1 was

Scheme 2. Sequential ROMP/ROTEP Strategy for the Formation of *Cis-Trans-Cis* Triblock Copolymers

poly(*cis*-**1**-*b*-*trans*-**1**-*b*-*cis*-**1**)
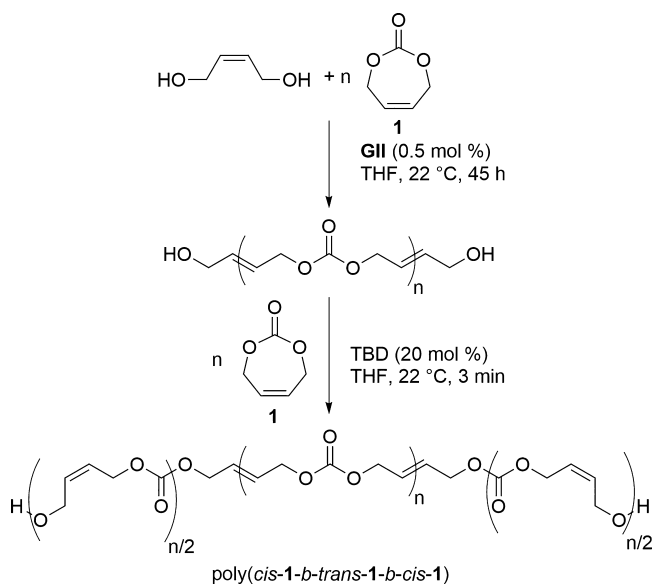
chosen to ensure high incorporation of CTA in the polymer.[31] After 45 h, an aliquot indicated 100% conversion of **1** to poly(**1**) with a *cis/trans* ratio of 7:93 and an $M_{n,SEC}$ ($Đ_M$) of 2100 (2.02) g mol^{-1} (Table 2 entry 1). MALDI-ToF spectrometry revealed the presence of OH chain ends (Figure S31), and ^{1}H NMR spectroscopy confirmed the incorporation of the CTA into the polymer's backbone with the expected 1:20 ratio (Figure S21). TBD and more monomer were then added in a 2:20 ratio with respect to $[CTA]_0$. ^{1}H NMR spectroscopy indicated 100% conversion of monomer after 3 min giving a polymer (**ABA-1**) with a *cis/trans* content of 54:46 and an $M_{n,SEC}$ ($Đ_M$) of 4600 (2.06) g mol^{-1}. ^{1}H DOSY NMR spectroscopy confirmed the presence of only one polymer species, with both *cis* and *trans* regimes, and the sequential increase of molar mass (decrease in diffusion coefficient from 2.06 × 10^{-8} to 1.48 × 10^{-8} s^{-1}, Figures S22 and S24). The experiment was repeated at a $[1]_0:[GII]_0:[CTA]_0$ feed ratio of 40:0.005:1, with additional monomer and TBD (40:1 with respect to $[CTA]_0$). A *cis-trans-cis* ABA triblock (**ABA-2**) of higher M_n ($M_{n,SEC}$ = 8900 g mol^{-1}, $Đ$ = 1.60, *cis/trans* 56:44) was obtained (Table 2, entry 2). ^{13}C{^{1}H} NMR spectroscopy gave some insight into the copolymer chain microstructure, revealing limited transcarbonation reactions and well-defined blocks (Figure S25). This was supported by DSC analysis, which showed phase separation and retention of the crystallinity of the *cis* end-blocks (Figure S55).[18]

In conclusion, we have demonstrated that from novel dual monomer **1**, divergent stereoselective polymerization catalytic strategies can direct polymer properties between a soft amorphous material (T_g −22 °C) and a hard semicrystalline material (T_m 115 °C). These thermoplastics can further be transformed into thermosets via cross-linking of the alkene polymer backbone. A CTA has also been employed to synthesize triblock ABA polymers from this single monomer, with potential applications as thermoplastic elastomers. Our ongoing efforts are now aimed at investigating the effect of composition and molar mass of these triblock copolymers on nanoscales morphologies and mechanical properties. Finally, the carbonate function of these polymers introduces some

Table 2. Synthesis of Poly(*cis*-1-*b*-*trans*-1-*b*-*cis*-1)

entry	n:CTA	*cis/trans*	M_{theo} (g mol^{-1})[b]	$M_{n,NMR}$ (g mol^{-1})[c]	$M_{n, SEC}$[d] (g mol^{-1})[d]	$Đ_M$[d]
1	20:1	54:46 (3:97)	4650 (2370)	3700 (2200)	4600 (2100)	2.06 (2.02)
2	40:1	54:46 (3:97)	9210 (4650)	10 000 (5000)	8900 (4700)	1.60 (1.67)

[a]Sequential procedure outlined in Scheme 2, with $[1]_0$ = 1 mol L^{-1}. Monomer conversion quantitative for each step. Values in brackets were obtained after the ROMP step. [b]Calculated as $M_r(CTA) + (2 \times n \times M_r(1))$. [c]Calculated by the relative integration of the methylene protons in the CTA (δ = 4.19−4.27 ppm) and the polymer (δ = 4.60 − 4.80 ppm). [d]Calculated by SEC relative to polystyrene standards in THF eluent.

opportunities for chemical and biological degradation. We anticipate that understanding the degradability of these materials will facilitate their adoption as sustainable alternatives in various commodity and specialty applications.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.9b06259.

> Experimental and computational procedures, NMR spectra of monomer and polymers, Plot of M_n and $Đ_M$ vs. conversion, polymerization kinetic data, images of SEC traces, MALDI-ToF MS, TGA-MS, DSC traces and DMA data, DFT calculations data and associated digital repository (PDF)
>
> Single-crystal X-ray diffraction data for **1** (CIF)

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Notes

The authors declare no competing financial interest.

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