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Semicrystalline Dihydroxyacetone Copolymers Derived from Glycerol

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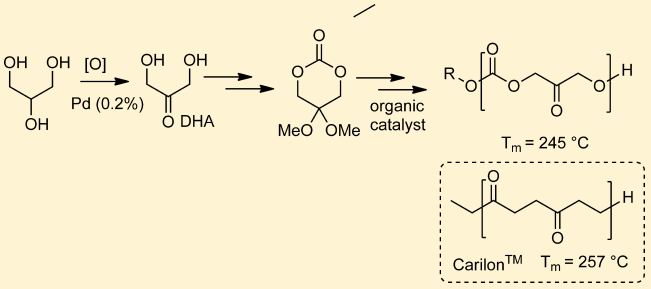
Supporting Information

ABSTRACT: The ring-opening polymerization of glycerol-derived six-membered cyclic dimethylacetal dihydroxyacetone carbonate (MeO_2DHAC) have been studied both in solution and bulk conditions with organic catalysts. The guanidine 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) was the most active catalyst in solution, whereas the thiourea/sparteine catalytic system displayed the most predictable kinetics. Ring-opening polymerization of MeO_2DHAC or copolymerization with ε-caprolactone (CL) in the melt occurred readily with TBD as catalyst to afford random copolymers. Acetal deprotection afforded the polycarbonate poly(dihydroxyactone carbonate) (p(DHAC)) or poly(carbonate ester) copolymers p(DHAC-*r*-CL). The polycarbonate p(DHAC) is a high-melting thermoplastic with a melting point of 246 °C. The p(DHAC-*r*-CL) copolymers all displayed semicrystalline behavior as evidenced by DSC and WAXS analysis with T_g and T_m changing as a function of comonomer composition. These new materials could have potential use in biomedical applications or as biomass-derived thermoplastics.



INTRODUCTION

The development of petroleum-based plastics has proven one of the crowning achievements of the 20th century. As a consequence of their extraordinary versatility and performance relative to their cost, synthetic materials are ubiquitous in modern societies. Petrochemical feedstocks for plastics (ethylene, propylene, α-olefins, terephthalic acid) are inexpensive and available on large scale due to the vast scale of petroleum refining. Over 60 years of development has provided production processes that are unrivaled in terms of their energy efficiency and scale. The global demand for these materials is not likely to abate; nevertheless, the environmental impact of petroleum, gas, and coal-based economies highlights the need for alternative and more varied sources of fuels, chemicals, and synthetic materials to provide the energy, products, and technologies that improve our lives while preserving the environment for future generations.[1]

As biorefineries begin to contribute to our energy portfolio, biofeedstocks will become more readily available. To the extent that biomass-derived plastics can be obtained from renewable resources and the resultant materials can biodegrade or be recycled in a more environmentally sustainable manner, biomass-derived plastics provide a sustainable alternative to the materials of modern societies.[2,3] However, for biomass-derived plastics to gain wide acceptance, they must exhibit performance and cost that are competitive with existing petroleum-derived plastics. Moreover, careful and validated life-cycle metrics will need to be incorporated into material design to ensure that new materials are not only economically competitive but also environmentally more sustainable as well.[2]

We initiated a research program to identify and synthesize new classes of thermoplastics from readily available biofeedstocks. In pioneering work, Putnam reported a new class of poly(dihydroxyacetone carbonates) (pDHAC) derived from dihydroxyacetone (DHA) that was identified as a promising class of biomaterials.[4−7] We were attracted to these polycarbonates due to their structural similarity to the petroleum-derived alternating copolymer of ethylene and carbon monoxide (Carilon, Figure 1).[8−10] Alternating ethylene/CO copolymers exhibit glass transition temperatures of T_g ∼ 15 °C and melting points of 220 °C (CO/ethylene/propylene, 50/44/6).[9,10] We posited that the structurally related polycarbonates might exhibit similar properties and thus provide a class of high-melting thermoplastics derived from biomass feedstocks (Figure 1).

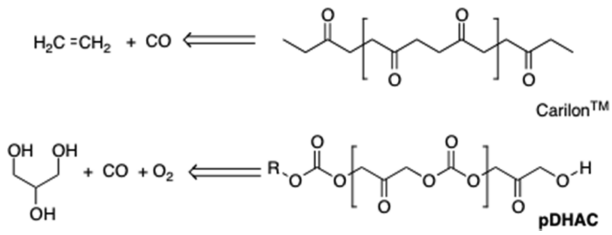


Figure 1. Retrosynthesis of Carilon and poly(dihydroxyacetone carbonate).

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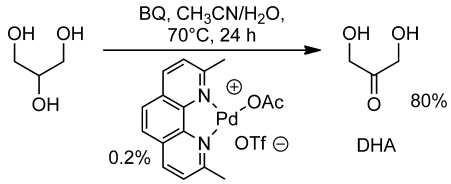
Previous studies reveal that pDHAC some interesting physical properties, particularly for biomedical applications.[4] Putnam reported that the pDHAC homopolymer exhibits a glass transition temperature of T_g = 60−68 °C, a compressive Youngs modulus of 0.5 GPa, and a compressive yield stress of 50 MPa, similar to that of cancellous bone. It is insoluble in common solvents and was reported to decompose thermally at temperatures of 278 °C.[5] No clear evidence of crystallinity was reported, but we anticipated that this material might melt at temperatures close to its decomposition temperature, as reported for E/CO copolymers.[9,11] This motivated us to study the effect on modulating the physical and thermal properties of pDHAC using caprolactone (CL) as soft comonomer, targeting new semicrystalline copolymers derived from renewable feedstock.

Poly(dihydroxyacetone carbonate) (p(DHAC) was previously generated from dihydroxyacetone, a microbially produced commodity used in cosmetics (sunless tanning agents) and the fine chemical industry.[12] We sought a strategy for generating these polymers from glycerol, a readily available byproduct from biodiesel manufacturing (Figure 1).[13−17] Glycerol is an attractive feedstock for the synthesis of value-added chemicals and materials; the use of glycerol as a feedstock for renewable polymeric materials[18,19] would offer new possibilities for replacing current materials derived from petroleum. These considerations stimulated our efforts to develop new catalytic processes for the selective oxidation of glycerol to dihydroxyacetone[20] and the catalytic synthesis of cyclic dihydroxyacetone carbonates from the corresponding 1,3-diols.[21] Herein, we report our investigations on the synthesis and characterization of poly(dihydroxyacetone carbonate) and its copolymers with ε-caprolactone.

RESULTS AND DISCUSSION

We recently reported the selective catalytic oxidation of glycerol[12,22−24] to dihydroxyacetone with Pd neocuproine catalysts (neocuproine = 2,9-dimethyl-1,10-phenanthroline).[20,25−27] This mild and highly selective catalytic procedure provides an expedient route to dihydroxyacetone, the key synthon for the synthesis of pDHAC. Utilizing a modification of our previously published procedure,[20] the preparative oxidation of glycerol to dihydroxyacetone was carried out on a 20 g scale with $[(neocuproine)Pd(OAc)]_2(OTf)_2$[28] (0.2 mol % Pd) in CH_3CN/H_2O 9:1 at 70 °C for 24 h to afford an 80% yield of dihydroxyacetone (eq 1).



(1)

Attempts to generate the unprotected dihydroxyacetone carbonate (DHAC, Figure 2) directly from dihydroxyacetone utilizing disphosgene or the catalytic oxidative carbonylation have so far proved unsuccessful; the surprisingly simple cyclic carbonate DHAC is predicted theoretically to be 22.2 kJ/mol less stable than its isomer glycolide,[29] but this cyclic carbonate has eluded our efforts to date to generate it in pure form. Dihydroxyacetone was converted to the more readily handled dimethylacetal (MeO_2DHA) following a literature procedure.[4]

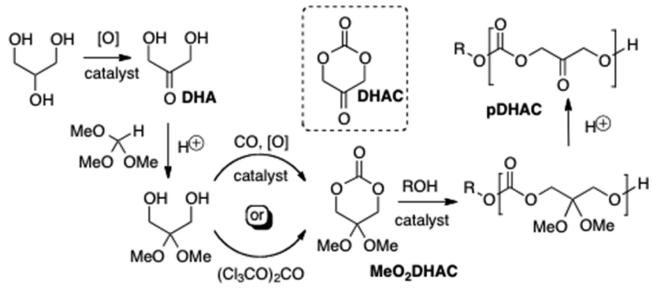
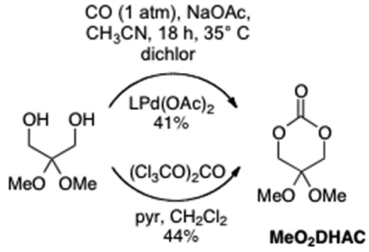


Figure 2. Catalytic transformations of glycerol to poly(dihydroxyacetone carbonate).

The synthesis of polymerizable six-membered carbonates from 1,3-diols is typically carried out with triphosgene.[30,31] While this procedure is convenient and proceeds in high yield on a laboratory scale,[32,33] an alternate method[34] that could avoid phosgene-type reagents would be desirable. To this end, we recently reported a catalytic oxidative carbonylation of 1,3-diols to cyclic carbonates with neocuproine $Pd(OAc)_2$ catalysts (eq 2).[21] The oxidative carbonylation[35] of MeO_2DHA afforded



(2)

the cyclic carbonate MeO_2DHAC in 41% isolated yield.[21] This catalytic process provides an attractive alternative to strategies utilizing triphosgene; part of our motivation in developing these oxidative carbonylations was to develop more environmentally benign strategies for the synthesis of polycarbonates, such as poly(dihydroxyacetone carbonate).

Ring-Opening Polymerization of MeO_2DHAC: Solution. A series of organic catalysts[36,37] were investigated for the ring-opening polymerization of MeO_2DHAC. Initial efforts were focused on the organocatalytic polymerization of MeO_2DHAC in solution (Figure 3), as we[32,33,38−41] and

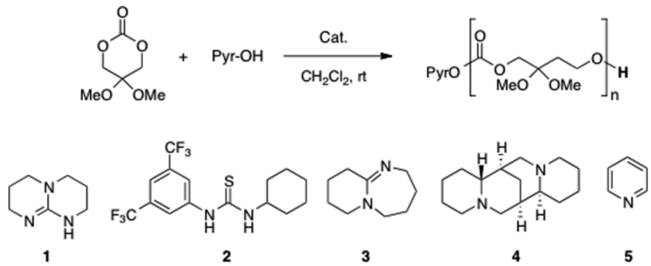


Figure 3. Ring-opening of MeO_2DHAC with different organocatalysts.

others[42,43] had previously shown that these catalysts are both active and selective for the ring-opening polymerization of functionalized and unfunctionalized cyclic carbonates.

Four different catalytic systems were screened (Figure 3 and Table 1). 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD, **1**) was by far the most active catalyst (Table 1, entry 1), reaching nearly full conversion (95%) in only 5.5 min with a polydispersity of 1.55. The thiourea/1,8-diazabicyclo[5.4.0]undec-7-ene (TU **2**/

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Table 1. Solution Polymerization of MeO_2DHAC

entry	catalyst	$[M]_0/[I]_0$	time	conv[a] (%)	M_n(theor) (Da)	M_n(NMR)[b] (Da)	M_n(GPC)[c] (Da)	M_w/M_n[c]
1	**1**	50	5.5 min	95	7700	6300	2900	1.55
2	**3** + **2**	50	70 min	91	7500	7500	4100	1.24
3	**3** + **2**	200	33 min	90	29 000	31 000	18 000	1.20
4	**4** + **2**	50	7 h	67	5800	5800	2800	1.18
5	**4** + **2**	50	22 h	93	8200	8200	4900	1.14
6	**4** + **2**	200	25 h	91	32 000	28 000	9000	1.11
7	**5**+ **2**	100	3.5 h	0				

[a]Conversion was measured by ^{1}H NMR analysis of aliquot taken from the crude reaction mixture. [b]Number-average molecular weight (M_n) determined by ^{1}H NMR integration against pyrenebutanol end group. [c]M_n and M_w/M_n determined by GPC (THF) using PS calibration.

DBU **3**) catalytic system (entry 2) was slower, reaching 91% conversion in 70 min, but displayed a narrower polydispersity (1.24). The TU **2**/(−)-sparteine **4** catalyst was the most selective, providing the greatest control of molecular weight and the narrowest polydispersities (M_w/M_n = 1.11−1.18) (entries 3−5). TU/Pyr (entry 6) was shown to be inactive as catalyst for the polymerization of MeO_2DHAC. The kinetics of ring-opening was investigated for the TU[32]/DBU and TU/(−)-sparteine catalyst systems. In the case of the TU/DBU catalyst system, the ring-opening polymerization is first order in monomer at low conversion, but deviation from simple first-order behavior is observed at high conversion. DBU was also observed to initiate polymerization of MeO_2DHAC in the absence of alcohol initiator and TU, which suggests that DBU may act directly as a nucleophile to induce ROP via a zwitterionic mechanism.[44,45] The nucleophilic behavior of DBU may also lead to transesterification events of the polymer, leading to broader polydispersities. In contrast, the kinetics with a TU/(−)-sparteine catalytic system were more predictable, displaying first-order kinetics and linear evolution of molecular weight with conversion, even at high monomer conversions (Figure 4). For initial monomer concentrations of $[M]_0$ = 1 M and $[M]_0/[I]_0 \approx 110$, the overall first-order rate constant k_{obs} was determined to be $(3.3 \pm 1.3) \times 10^{-3}$ s^{-1} at 20 °C for TU/sparteine. This is about 2 orders of magnitude less than the initial k_{obs} estimated for the TU/DBU catalyst under similar conditions.

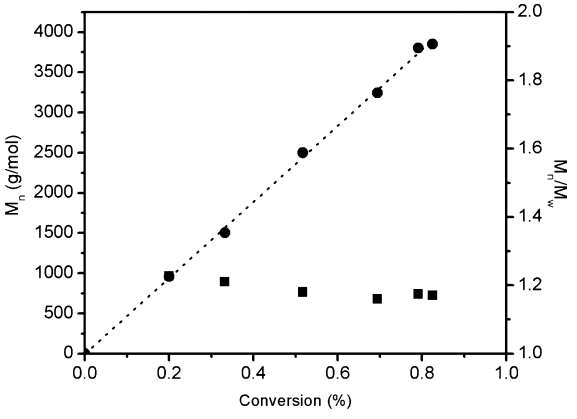

Figure 4. Molecular weight and M_w/M_n vs conversion plots for $[M]_0/[I]_0$ = 110 (averaged over all three runs) and $[M]_0$ = 1 M (in CH_2Cl_2), using 5 mol % TU/(−)/sparteine as catalyst.

Under all conditions employed, we observed a maximum monomer conversion of 90−95%. This suggests that the polymerization approaches equilibrium within the time scale of our kinetic studies. The equilibrium monomer concentration was estimated by letting the reaction equilibrate under a variety of initial monomer concentrations and using several relatively fast ROP catalysts. We obtained an average equilibrium monomer concentration of 0.10 ± 0.01 M at 20 °C (Supporting Information). This is of similar magnitude to equilibrium monomer concentrations reported by Matsuo et al. for trimethylene carbonate and 2,2-disubstituted trimethylene carbonate monomers structurally similar to MeO_2DHAC.[46]

Melt Polymerization. The organocatalytic ring-opening polymerization of MeO_2DHAC occurs readily in solution but can also be carried out in the absence of solvent in the melt (Figure 5 and Table 2). We have previously described melt polymerization of cyclic lactones and carbonates using organocatalytic systems.[33,47,48] Putnam reported the melt polymerization of MeO_2DHAC with tin octanoate;[4,5] Guillaume also recently reported the ring-opening polymerization of MeO_2DHAC with a variety of metal and organocatalysts.[42,43]

These studies showed that TBD was by far the most active catalyst of the organocatalysts investigated for melt polymerization of MeO_2DHAC, which is also in line with our above results on solution polymerization. The ring-opening polymerization of MeO_2DHAC and copolymerization with ε-caprolactone (CL) in the melt in the presence of 1−2.5 mol % TBD at 90−100 °C proceeded smoothly, reaching high monomer conversions within 2−3 h (Figure 5 and Table 2) to generate polycarbonates with number-average molecular weights ranging from 10 000 to 23 000 Da. Analysis of the MeO_2DHAC/CL copolymer sequences by ^{13}C NMR spectroscopy is consistent with random copolymers[5] (Figure S9, Supporting Information) whose compositions correlate closely with the ratio of monomers in the feed. All copolymers displayed monomodal GPC curves with M_w/M_n ranging from 1.4 to 2.2.

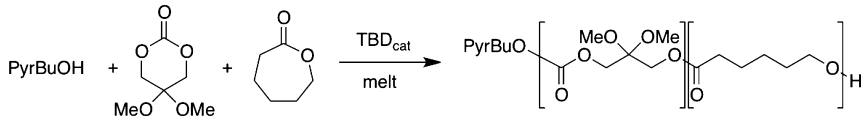

Figure 5. Bulk synthesis of MeOPC/ε-CL copolymers in using TBD as catalyst.

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Table 2. Melt Copolymerizations of MeO_2DHAC and CL with TBD

entry	CL (%)	cond (°C/h)	% conv[a] (MeO_2DHAC/CL)	comp[b] (MeO_2DHAC/CL)	M_n[c] (Da)	M_w/M_n[c]	T_m[d] (°C)
1	0	90/2	98	100/0	10 600	2.24	234
2	10	90/2	99/99	90/10	11 400	2.14	216
3	20	90/2	99/99	78/22	11 800	2.17	189
4	30	90/2	99/99	67/33	9 700	1.97	153
6	45	90/2	99/99	54/46	15 700	2.08	59
7	50	100/2	97/90	48/52	15 300	1.80	43, 65
8	70	90/2	99/99	30/70	16 400	2.03	48
9	81	100/2	99/99	19/81	12 700	1.98	24
10	89	100/2	99/99	12/88	15 700	1.98	27, 34
11	100	90/2	99	0/100	23 800	2.00	56

[a]Conversion was measured by ^{1}H NMR analysis of aliquot taken from the crude reaction mixture. [b]Composition was determined by ^{1}H NMR ($CDCl_3$) integration of the purified samples. [c]Number-average molecular weight (M_n) and polydispersity index (M_w/M_n) was determined by gel permeation chromatography (GPC) using THF as an eluent. [d]Determined by DSC on the acetal-deprotected polymers; see Supporting Information for details.

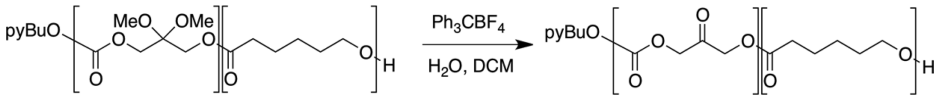

Figure 6. Ketal deprotection of the copolymers using procedure by Tian and co-workers.[49]

Ketal Deprotection and Thermal Properties of Copolymers. The removal of the ketal protecting groups[4,5] was carried out using a slight modification of the procedure reported by Tian and co-workers,[49] where trityl tetrafluoroborate Ph_3CBF_4 (1 equiv) and water (1 equiv) dissolved in dichloromethane solution was added to the polyketals at room temperature (Figure 6).

This procedure resulted in the complete deprotection to afford the p(DHAC) homopolymers and copolymers, as evidenced by ^{1}H and ^{13}C NMR spectroscopy (Figures S6 and S8). Although precipitation was observed in the case of p(DHAC) and copolymers enriched in DHAC, this did not preclude complete deprotection. Comparison of the GPC traces (Figure S10) of the protected and deprotected 12% CL copolymers (both of which are soluble in THF) revealed miminal degradation of the polymers, with slight broadening of the polydispersity (Table S2). A small shoulder was noted in the GPC curve of the deprotected copolymer, which may be indicative of some branching by ketalization between polymer chains; further studies are ongoing to optimize the deprotection procedure. The poly(dihydroxyacetone carbonate) polymers ranged from brittle powders (high DHAC content) to sticky solids (higher CL content). Copolymers with high compositions of DHAC were insoluble in organic solvents.[5,6]

The p(DHAC) homopolymer is semicrystalline, as shown by differential scanning calorimetry (DSC) and wide-angle X-ray (WAXS) analysis (Figure S30). The DSC thermogram of p(DHAC) (Figure 7) reveals a melting peak of 246 °C (ΔH_f = 48 J/g), very similar to that of the ethylene/CO alternating copolymer (T_m = 257 °C).[9,11,50] While the glass transition temperature of p(DHAC) of T_g = 68 °C[51] is higher than that of the alternating ethylene/CO copolymer (T_g = 15 °C), the similarity of the melting points confirms our original hypothesis that the similarities of the structures of the poly(dihydroxyacetone carbonate)s to those of the ethylene/CO copolymers would lead to similar thermal properties.

The DSC thermograms of p(DHAC) reveal an exotherm that occurs soon after the melting peak, consistent with thermal degradation. This was confirmed by thermogravimetric analysis

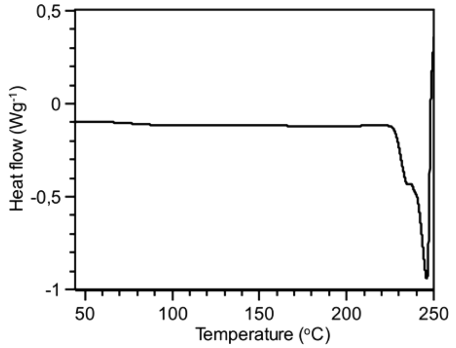

Figure 7. DSC of pDHAC (entry 1, Table 2).

(TGA). Under a nitrogen atmosphere the p(DHAC) homopolymer begins to lose weight at ~216 °C and shows a maximum rate of weight loss at ~280 °C (Figure 8). This is

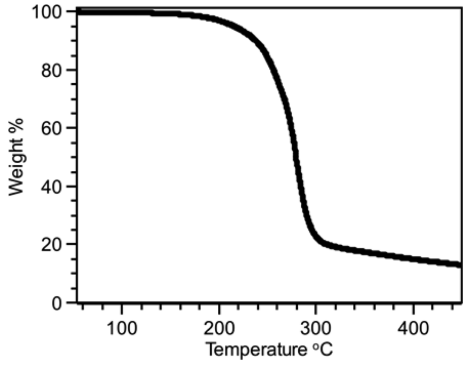

Figure 8. TGA of pDHAC.

consistent with reports by Putman, who reported a decomposition temperature T_d = 273 °C.[5] This behavior is similar to that exhibited by the E/CO copolymers, which show decomposition temperatures just above the melting points between 290 and 370 °C,[9−11] depending on the amount of residual Pd catalyst residues in the polymer.[50]

High melting thermoplastics that decompose at temperatures close to their melting points are challenging to process in the melt. For the E/CO copolymers, the melt-processability can be improved by making ethylene/propylene/CO terpolymers; compositions contain 6% propylene exhibit lower melting points of 220 °C.[9] We investigated a similar strategy by generating a variety of p(DHAC-*r*-CL) copolymers (Table S1).[5] The p(DHAC-*r*-CL) copolymers containing 22 mol % CL exhibit a lower glass transition temperatures (T_g = 17 °C) and a lower melting temperature (T_m = 189 °C, Figure 9), implicating that the properties of these materials can be tuned by appropriate choice of comonomer composition.

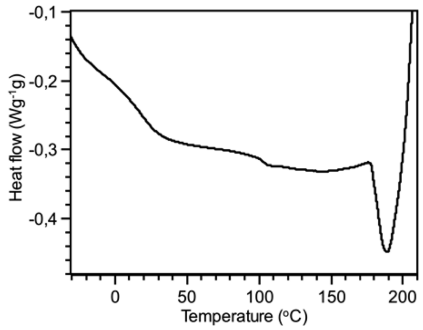

Figure 9. DSC of p(DHAC(0.78)-*r*-CL(0.22)) copolymer.

Analysis of the thermal properties of the deprotected p(DHAC-*r*-CL) copolymers reveals that they are semicrystalline over a range of DHAC/CL compositions (Figure 10). Similar behavior has been observed for other caprolactone copolymers[52−55] and implies that the two monomers cocrystallize.[56]

CONCLUSION

We have developed a new synthetic strategy for the synthesis of high melting polycarbonates from glycerol, a readily available feedstock. Chemoselective catalytic oxidation of glycerol affords dihydroxyacetone, which can be converted to the cyclic carbonate MeO_2DHAC. Ring-opening polymerization of MeO_2DHAC and acetal deprotection provide a route to poly(dihydroxyacetone carbonate), a material previously utilized by Putnam and co-workers for drug delivery[57] and tissue engineering[58] applications. We have shown that this material is also a high melting thermoplastic with thermal properties comparable to the structurally related ethylene/carbon monoxide alternating copolymers. The polycarbonate homopolymers p(DHAC) thermally decompose at temperatures just above their melting points; random copolymers with caprolactone melt at lower temperatures that depend on the composition of the copolymers. This synthetic method provides a strategy for the generation of new classes of performance plastics derived from biomass.

EXPERIMENTAL SECTION

Materials and Methods. All reagents were obtained from commercial sources and used as received unless otherwise noted. 2,2-Dimethoxypropanediol (5 g, 36.8 mmol) as prepared according to the report by Zelikin and Putnam.[4] ε-Caprolactone was dried by twice stirring over calcium hydride (24 h) and distilling *in vacuo* at 50 °C. 1-(3,5-Bis(trifluoromethyl)phenyl)-3-cyclohexyl-2-thiourea (TU), **1**, was synthesized as previously reported.[32] Dichloromethane was dried over calcium hydride and distilled *in vacuo*. (−)-Sparteine was dried and stored over molecular sieves (4 Å). Oven-dried glassware and stir bars were used for all synthetic procedures. ^{1}H (^{13}C) nuclear magnetic resonance (NMR) spectra were recorded at room temperature on a Varian 300 (75), 400 (100), or 500 (125) MHz spectrometer, with shifts reported in parts per million downfield from tetramethylsilane and referenced to the residual solvent peak. Gel permeation chromatography (GPC) was performed in inhibitor-free tetrahydrofuran using a Waters chromatograph equipped with four 5 μm Waters columns connected in series with an increasing pore size and a Waters 410 differential refractometer, calibrated with polystyrene standards. Differential scanning calorimetry (DSC) was performed on a TA Instruments Q100 DSC using a heating and cooling rate of 10 °C/min and a nitrogen flow rate of 50 mL/min. Glass transition temperatures and melting points were determined on the second heating scan at a heating rate of 10 °C/min, if not otherwise specified. Thermogravimetric measurements (TGA) were made using a PerkinElmer TGA7 thermogravimetric analyzer with nitrogen gas sample purge flow at a heating rate of 10 °C/min. Decomposition temperatures are reported as the temperature at which 5% and 50% of the polymer degraded. Wide-angle X-ray scattering (WAXS) measurements were carried out at room temperature using a PANalytical X'Pert PRO X-ray diffraction system using sealed-tube Cu Kα (1.542 Å) radiation. [(Neocuproine)-Pd(OAc)]$_2$(OTf)$_2$ was prepared according to previously described experimental procedure.[27]

Large Scale Oxidation of Glycerol. Glycerol (20 g, 0.22 mol) and 1,4-benzoquinone (25 g, 0.231 mol) were dissolved in an acetonitrile/water mixture (9:1, 200 mL). [(Neocuproine)Pd-(OAc)]$_2$(OTf)$_2$ (0.110 g, 0.10 mmol) was added under stirring, and the reaction mixture was heated at 70 °C for 24 h. Then, after cooling to room temperature, the reaction mixture was concentrated on a rotary evaporator, and the residue was purified by column chromatography using first ethyl acetate until eluting solution turned colorless/faint yellow and then ethyl acetate/methanol (2:1) to fully elute the product. The fractions containing the product (R_f = 0.2 in EtOAc) were collected and concentrated *in vacuo* to about 100 mL volume. This solution was filtered through basic aluminum oxide and concentrated *in vacuo*, yielding dihydroxyacetone as a pale yellow oil (16.0 g, 80% yield). The ^{1}H NMR(D_2O) spectra were in

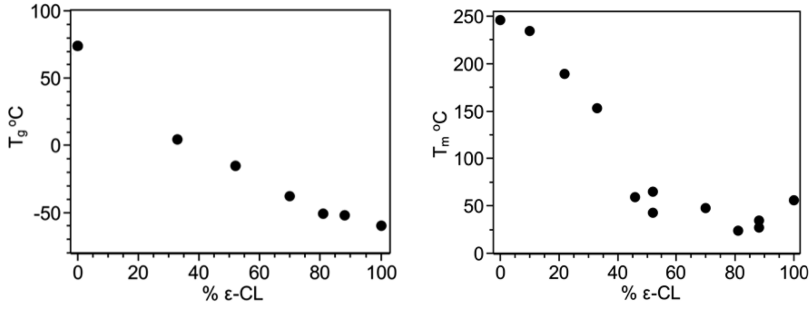

Figure 10. Observed (left) glass transition temperatures (T_g) and melting points (T_m) of p(DHAC-*r*-CL) copolymers as a function of mol % of ε-caprolactone.

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correspondence with previous reported dihydroxyacetone monomer/dimer equilibrium.[59]

Synthesis of Dihydroxyacetone Dimetylacetal Carbonate (MeO_2DHAC). MeO_2DHAC was prepared both by the oxidative carbonylation of 2,2-dimethoxypropanediol (0.69 g, 6.6 mmol)[21] and by a slight modification of the procedure reported with triphosgene,[4] as follows: A Schlenk flask was charged with a stir bar and 2,2-dimethoxypropanediol (5 g, 36.8 mmol). Pyridine (18 mL, 17.6 g, 223 mmol) and dichloromethane (100 mL) were added to the flask. Addition took place in this order so that all pyridine was washed out of the addition funnel before triphosgene was added. The resulting solution was placed in a bath at −78 °C, and to this cooled stirring solution was added a solution of triphosgene (5.5 g, 18.5 mmol) in dichloromethane (75 mL) using an addition funnel. The resulting solution was gradually warmed to room temperature and stirred overnight. The mixture was then concentrated *in vacuo*, yielding a green residue. This residue was directly loaded onto a plug of silica gel as a dichloromethane solution and eluted with ethyl acetate. The fractions containing the product were collected and concentrated *in vacuo,* yielding a yellow oil which was recrystallized from ethanol/hexanes affording MeO_2DHAC as a white solid (2.6 g, 44% yield). The recrystallized product was further purified by vacuum sublimation, prior to use as monomer in polymerization reactions. Dihydroxyacetone dimethylacetal carbonate (MeO_2DHAC): ^{1}H NMR ($CDCl_3$) δ = 4.21 (4H, s, $-CH_2C[(OCH_3)_2]CH_2$), 3.27 (6H, s, $-CH_2C[(OCH_3)_2]CH_2$).

Representative Procedure for Solution Polymerization of MeO_2DHAC (Figure 3 and Table 1). In a glovebox, 1-pyrenebutanol initiator (3.8 mg, 0.0139 mmol), thiourea catalyst **1** (12.8 mg, 0.0347 mmol), and sparteine **3** (8.1 mg, 0.0347 mmol) were added to a vial and dissolved in dichloromethane (0.35 mL). A stirring bar was added to the vial. MeO_2DHAC (112 mg, 0.62 mmol) was added to another vial and dissolved in dichloromethane (0.35 mL), and this solution was transferred to a stirred catalyst/initiator solution. The polymerization was quenched after 7 h by addition of benzoic acid (10 mg). Afterward, the volatiles were removed *in vacuo*; a ^{1}H NMR spectrum of the crude reaction mixture was obtained to measure monomer conversion (70%), and the polymer was purified by dialysis against methanol for 24 h. The polymer inside the dialysis bag was collected and dried *in vacuo*. The purified polymer was analyzed by ^{1}H NMR ($CDCl_3$) to measure degree of polymerization DP (23) by integration against the pyrene end group. GPC (THF) was used to measure PDI (1.181). Poly(dihydroxyacetone dimethylacetal carbonate) (poly(MeO_2DHAC)) (using 1-pyrenebutanol as initiator): ^{1}H NMR ($CDCl_3$) δ = 8.29−7.84 (9H, m, pyrene), 4.21 (4*n*H, s, $-CH_2C[(OCH_3)_2]CH_2-$, pol), 3.62 (2H, s, pyrene-$(CH_2)_3CH_2O-$), 3.60 (2H, s, poly−OCH_2OH), 3.27 (6*n*H, s, $-CH_2C[(OCH_3)_2]CH_2-$, pol), 1.95 (2H, m, pyrene-$CH_2CH_2(CH_2)_2-$), 1.86 (2H, m, pyrene-$(CH_2)_2CH_2CH_2-$).

Representative Procedure for Melt Copolymerization (Entry 7, Table 2). In a glovebox, a vial was charged with a stirring bar, 1-pyrenebutanol (4.2 mg, 0.015 mmol), TBD (21 mg, 0.15 mmol, 5 mol %), dihydroxyacetone dimethylacetal carbonate (MeO_2DHAC) (500 mg, 3.086 mmol), and ε-caprolactone (CL) (353 mg, 3.096 mmol). The vial was sealed and placed in an oil bath at 100 °C and stirred for 2 h. After cooling to room temperature, the reaction was quenched with a solution of 30 mg of acetic acid in anhydrous dichloromethane (2 mL). A homogeneous solution formed and was allowed to stir for 10 min. A crude aliquot was taken to measure conversion by ^{1}H NMR($CDCl_3$) (conversion MeO_2DHAC ≥97%, CL ≥90%). The remaining crude polymer solution was purified by dialysis over methanol (700 mL, changed twice over 12 h). The polymer inside the bag was extracted with dichloromethane and concentrated *in vacuo*, yielding (477 mg, 56% yield) of polymer. Analysis of the purified polymer by ^{1}H NMR($CDCl_3$) integration was used to measure relative composition of pMeO_2DHAC-*r*-CL (48:52). Sequence analysis was done by ^{13}C NMR ($CDCl_3$) (Figure S9). The average molecular chain length (M_n) (15 300 g mol^{-1}) and polydispersity (M_w/M_n) (1.8) were determined by GPC (THF). Poly(dihydroxyacetone dimethylacetal carbonate-*co*-ε-caprolactone) (poly(MeO_2DHAC (48%)-*co*-CL-(52%)): (using 1-pyrenebutanol as initiator): ^{1}H NMR ($CDCl_3$) δ = 8.29−7.84 (9H, m, pyrene), 4.38−3.94 (4*n*H(DHAC) + 2*n*H(CL), m, $-CH_2C[(OCH_3)_2]CH_2-$ and $-OCH_2(CH_2)_4C(O)-$, polymer), 3.79 (2H, s, pyrene-$(CH_2)_3CH_2-$), 3.55 (2H, s, $-CH_2OH$), 3.48 (2H, s, pyrene-$CH_2(CH_2)_3-$), 3.42−3.07 (6*n*H(DHAC), m, $-CH_2C[(OCH_3)_2]CH_2-$, polymer), 2.43−2.25 (2*n*H (CL), $-OCHH_2(CH_2)_3CH_2C(O)-$, polymer), 1.88−1.56 (4*n*H (CL), $-OCHH_2$ $(CH_2)_2CH_2CH_2C(O)-$, polymer), 1.46−1.31 (2*n*H (CL), $-O(CH_2)_3CH_2CH_2C(O)-$, polymer) (Figure S5) ^{13}C NMR ($CDCl_3$) δ = 173−174 ($-O(CH_2)_5C(O)-$), 154−155 ($-CH_2C(OMe)_2CH_2OC(O)-$), 98−99 ($-CH_2C(OMe)_2CH_2OC(O)-$), 68−69 ($-OCH_2(CH_2)_4C(O)-$), 63−65 ($-CH_2C(OMe)_2CH_2OC(O)-$), 59−60 ($-OCH_2(CH_2)_4C(O)-$), 49 ($-CH_2C(OCH_3)_2CH_2OC(O)-$), 34 ($-OCH_2CH_2(CH_2)_3C(O)-$), 29 ($-O(CH_2)_4CH_2C(O)-$), 25 ($-O(CH_2)_2CH_2(CH_2)_2C(O)-$), 24 ($-O(CH_2)_3CH_2CH_2C(O)-$) (Figure S7).

Representative Procedure for Ketal Deprotection of Polymers (Table S2). To a stirring solution of pMeO_2DHAC (48%)-*r*-pCL (52%) copolymer (entry 5, Table S1) (477 mg, 1.67 mmol DHAC units) in CH_2Cl_2 (33 mL) was added Ph_3CBF_4 (275 mg, 0.83 mmol, 0.5 equiv per MeO_2DHAC repeat unit). Thereafter, water (30 mg, 1.67 mmol, 1 equiv to MeO_2DHAC repeat unit) was added, and the homogeneous solution was allowed to stir at room temperature overnight. After reaction, the solvent was removed *in vacuo*, and the crude polymer was purified by precipitation in methanol. The precipitated polymer was collected and dried *in vacuo*. Poly(dihydroxyacetone carbonate) (poly(DHAC)): ^{1}H NMR (DMSO-d_6) δ = 4.97 (4*n*H, s, poly-CO_3CH_2CO). Poly(dihydroxyacetone carbonate-*co*-ε-caprolactone) (poly(DHAC(48%)-*co*-CL(52%)) (using 1-pyrenebutanol as initiator): ^{1}H NMR ($CDCl_3$): δ = 8.20−7.87 (9H, m, pyrene), 4.97−4.70 (4*n*H (DHAC), m, $-CH_2C(O)CH_2OC(O)-$, polymer), 4.32−4.03 (2*n*H (CL) + 4*n*H (DHAC), m, $-CH_2C[(OCH_3)_2]CH_2-$ and $-OCH_2(CH_2)_4C(O)-$, polymer), 3.36−3.27 (6*n*H (DHAC), m, $CH_2C[(OCH_3)_2]CH_2-$, polymer), 2.53−2.28 (2*n*H (CL), $-OCHH_2(CH_2)_3CH_2C(O)-$, polymer), 1.81−1.61 (4*n*H (CL), $-OCHH_2$ $(CH_2)_2CH_2CH_2C(O)-$, polymer), 1.55−1.35(2*n*H (CL), $-O(CH_2)_3CH_2CH_2C(O)-$, polymer) (Figure S6). ^{13}C NMR ($CDCl_3$): δ = 199 ($-CH_2C(O)CH_2OC(O)-$), 173 ($-O(CH_2)_5C(O)-$), 155 ($-CH_2C(O)CH_2OC(O)-$), 66−70 (($-CH_2C(O)CH_2OC(O)-$ and $-OCH_2(CH_2)_4C(O)-$), 34 $OCH_2CH_2(CH_2)_3C(O)-$), 28 ($-O(CH_2)_4CH_2C(O)-$), 25 ($-O(CH_2)_2CH_2(CH_2)_2C(O)-$), 24 ($-O(CH_2)_3CH_2CH_2C(O)-$) (Figure S8).

■ ASSOCIATED CONTENT

Supporting Information

Kinetic plots of solution polymerization, equilibrium monomer concentration, ^{1}H and ^{13}C NMR of polymers, DSC and TGA of copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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