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Polycarbonates from the Polyhydroxy Natural Product Quinic Acid

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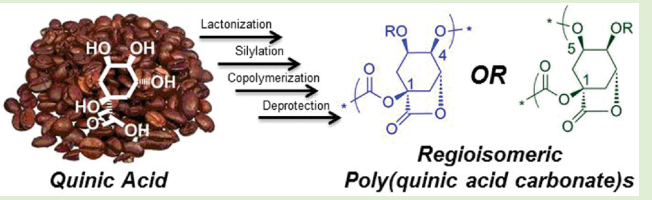
Supporting Information

ABSTRACT: Strategies for the preparation of polycarbonates, derived from natural polyhydroxy monomeric repeat units, were developed for biosourced polycarbonates based on quinic acid. The design and synthesis of regioselectively *tert*-butyldimethylsilyloxy (TBS)-protected 1,4- and 1,5-diol monomers of quinic acid were followed by optimization of their copolymerizations with phosgene, generated in situ from trichloromethyl chloroformate, to yield protected poly(1,4-quinic acid carbonate) and poly(1,5-quinic acid carbonate). The molecular weights reached ca. 7.6 kDa, corresponding to degrees of polymerization of ca. 24, with polydispersities ranging from 2.0 to 3.5, as measured by SEC using tetrahydrofuran as the eluent and with polystyrene calibration standards. Partially because of the presence of the bicyclic backbone, each regioisomeric poly(quinic acid carbonate) exhibited relatively high glass-transition temperatures, 209 °C for poly(1,4-quinic acid carbonate) and 229 °C for poly(1,5-quinic acid carbonate). Removal of the TBS-protecting groups was studied under mild conditions to achieve control over potential competing reactions involving polymer degradation, which could include cleavage of lactones within the repeat units, carbonate linkages, or both between the repeat units. Full deprotection was not achieved without some degree of polymer degradation. The regiochemistry of the monomer showed significant impact on the reactivity during deprotection and also on the thermal properties, with the 1,5-regioisomeric polymer having lower reactivity and giving higher T_g values, in comparison with the 1,4-regioisomer. Each regioisomer underwent a 10−20 °C increase in T_g upon partial removal of the TBS-protecting groups. As the extent of deprotection increased, the solubility decreased. Ultimately, at long deprotection reaction times, the solubility increased and the T_g decreased because of significant degradation of the polymers.



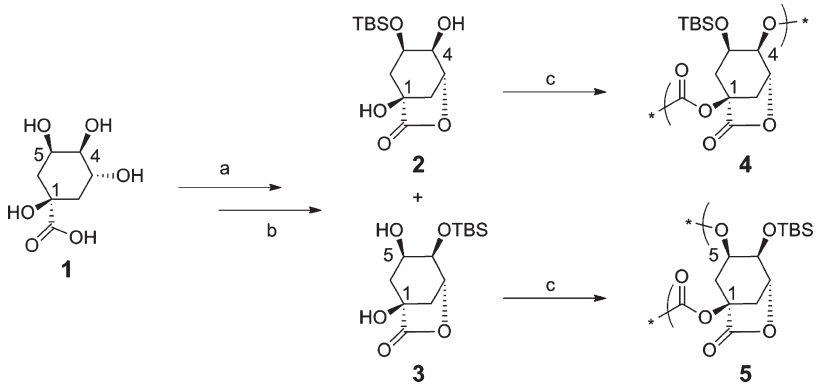
1. INTRODUCTION

Over the past few decades, there has been a significant interest in the preparation of polymers that originate from renewable resources,[1−4] typically based on carbohydrates or fatty acids to diminish the dependence on petroleum products and also that undergo degradation to reduce landfill accumulation of waste.[2] An important application of degradable polymers is in biomedicine (e.g., sutures, orthopedic devices,[3] tissue engineering,[4] drug delivery devices,[5−7] etc.), where incorporation of biocompatibility and biodegradability is imperative. For this purpose, the polymers used are typically of esters,[8,9] which undergo hydrolysis to afford products containing carboxylic acid and alcohol groups or carbonates,[3] especially aliphatic carbonates that undergo hydrolytic degradation to give carbon dioxide and alcohols.[10,11] Beyond these criteria, biodegradable polymeric materials in orthopedic tissue engineering also must possess thermal and mechanical properties and the time of degradation to the needs of the particular application. Polycarbonates, especially those based on bisphenol A, are a foundation material for engineering applications, in general, and we have a keen interest in exploring novel polycarbonates that are derived from renewable resources, may serve as replacements for poly(bisphenol A carbonate), which has been implicated as a toxic and carcinogenic compound,[13−15] and may lead to bioresorbable degradation products.

In this context, we have investigated the synthesis of polycarbonates built from a natural monomer, quinic acid, to afford a unique family of biosourced, degradable, engineering polymers: poly(quinic acid carbonate)s. Quinic acid is found in coffee beans and other plants[16,17] and is known for its growth-promoting properties,[16,18] is converted to tryptophan and nicotamide by microflora of the gastrointestinal tract,[19] and is also a chiral starting material for pharmaceuticals,[20] including Tamiflu. Quinic acid was selected as the starting material because of easy access to a bicyclic diol-monomer by known lactonization and selective silylation,[21,22] which could lead to materials having high-temperature thermal transitions and strong mechanical properties. Surprisingly, despite its interesting biological activity and its chirality, quinic acid has not been reported as a monomer that can undergo polymerization. This Article reports the design, synthesis, and characterization of *tert*-butyldimethylsilyloxy-protected poly(quinic acid carbonate)s and also includes various attempts for removal of the protecting groups.

Received: March 4, 2011
Revised: May 19, 2011
Published: June 06, 2011

Scheme 1. Syntheses of Diol Monomers 2 and 3 and Poly(quinic acid carbonate)s 4 and 5[a]



[a] (a) Amberlyst, benzene/DMF, reflux, 16 h; (b) TBS-CI, DMAP, NEt_3 DMF, RT, 12 h; and (c) diphosgene, pyridine, RT, 48 h.

2. EXPERIMENTAL SECTION

2.1. Instrumentation. The ^{1}H NMR (300 and 500 MHz) and ^{13}C NMR (75 and 125 MHz) spectra were obtained on either a Varian Mercury 300 MHz or an Inova 500 MHz spectrometer using the solvent as internal reference. Glass transition (T_g) temperatures were measured by differential scanning calorimetry on a Mettler Toledo DSC822^e apparatus (Mettler Toledo, Columbus, OH) with a heating rate of 20 °C/min. The T_g was taken as the midpoint of the inflection tangent upon the third heating scan. Thermogravimetric analysis was performed under a N_2 atmosphere using a Mettler Toledo model TGA/SDTA851^e apparatus with a heating rate of 10 °C/min. Gel permeation chromatography (GPC) measurements were conducted on two different systems, both equipped with a Waters Chromatography (Milford, MA) model 1515 isocratic pump, a model 2414 differential refractometer, and a three-column set of Polymer Laboratories (Amherst, MA) Styragel columns (PL_{gel} 5 μm Mixed C, 500 Å, and 10^4 Å, 300 × 7.5 mm columns) for the tetrahydrofuran system or a three-column set of Waters Chromatography Styragel columns (HR 2, HR 4E, and HR4, 300 × 7.8 mm columns) for the dimethylformamide system. The systems were equilibrated at 35 °C in THF or 70 °C in DMF, which served as the polymer solvent and eluent (flow rate set to 1.00 mL/min). Polymer solutions were prepared at a known concentration (ca. 3 mg/mL), and an injection volume of 200 μL was used. Data collection and analyses were performed with Precision Acquire software and Discovery 32 software, respectively (Precision Detectors). The differential refractometer was calibrated with standard polystyrene materials (SRM 706 NIST) for the tetrahydrofuran system and poly(ethylene glycol) for the dimethylformamide system. The infrared measurements were obtained with a Shimadzu IR Prestige, FTIR spectrophotometer equipped with an ATR accessory.

2.1. Materials. Quinic acid **1** (Alfa Aesar, 98%), trichloromethyl chloroformate (Alfa Aesar, 98%), Amberlyst (Sigma Aldrich, 15-ion-exchange resin), dimethylaminopyridine, triethylamine (Sigma Aldrich, >99%), *tert*-butyldimethylsilyl chloride (Alfa Aesar, 97%), and boron trifluoride diethyl etherate (Alfa Aesar, >98%) were used as received. Pyridine was distilled over potassium hydroxide, tetrahydrofuran, and dimethylformamide were dried through columns (J. C. Meyer Solvent Systems). (1*R*,3*R*,4*S*,5*R*)-5-*tert*-Butyldimethylsilyloxy-1,4-dihydroxy-cyclohexane-1,3-carbolactone **2**, (1*R*,3*R*,4*S*,5*R*)-4-*tert*-butyldimethylsilyloxy-1,4-dihydroxy-cyclohexane-1,3-carbolactone **3**, and calcium sulfonate resin were synthesized as previously described.[21−23]

2.2. General Procedure of the Copolymerization between Diol Quinic Acid 2 or 3 and Trichloromethyl Chloroformate. Trichloromethyl chloroformate was added to a cold (0 °C) solution of diol quinic acid in pyridine (600 g/L) under nitrogen three times over ca. 10 min. *Caution! Trichloromethyl chloroformate is highly toxic by inhalation and ingestion; use of respiratory mask is required.* After 48 h at room temperature, a saturated solution of sodium bicarbonate was added until no further emission of carbon dioxide was observed. The residue was diluted with dichloromethane; the organic layer obtained was washed with a 10% solution of hydrochloric acid, then dried with magnesium sulfate, filtered, and concentrated under reduced pressure. The crude polymer was dissolved in dichloromethane, followed by precipitation in cold methanol to afford the desired polymer as a white solid.

Synthesis of ***4***. The general procedure for copolymerization was applied to a solution of diol quinic acid **2** (500 mg, 1.73 mmol) in pyridine (850 μL) and trichloromethyl chloroformate (207 μL, 1.73 mmol) to obtain a white solid (400 mg, 75%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.13 (bs, 1H, H-4), 4.78−4.92 (m, 1H, H-3), 4.07 (bs, 1H, H-5), 2.19−3.17 (m, 4H, H-2, H-6), 0.83−0.92 (m, 9H, $(CH_3)_3CSi$), 0.04−0.09 (m, 6H, $(CH_3)_2Si$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 170.5−170.8 (CO-lactone), 150.0−153.3 (CO-carbonate), 78.1−78.4 (C1), 73.3−73.7 (C3), 70.5−71.7 (C4), 65.6−65.8 (C5), 36.9−37.1 (C6), 33.2−34.0 (C2), 25.4−25.6 ($(CH_3)_3CSi$), 17.7−18.0 ($(CH_3)_3CSi$), $^-$5.3−$^-$5.0 ($(CH_3)_2Si$). IR ν_{max}/cm^{-1}: 3104−2758, 1803, 1746, 1240, 124, 1033, 843, 777. T_g = 209 °C. $(T_d)_{onset}$ = 284 °C; $(T_d)_{50}$ = 384 °C; 284−420 °C, 89% mass loss; 11% mass remaining at 500 °C.

Synthesis of ***5***. The general procedure for copolymerization was applied to a solution of diol quinic acid **3** (500 mg, 1.73 mmol) in pyridine (850 μL) and trichloromethyl chloroformate (207 μL, 1.73 mmol) to obtain a white solid (462 mg, 85%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.76−4.77 (m, 1H, H-5), 4.67 (bs, 1H, H-3), 4.37 (bs, 1H, H-4), 3.00−3.15 (m, 1H, H-2), 2.62−2.69 (m, 1H, H-2), 2.26−2.34 (m, 2H, H-6), 0.83−0.92 (m, 9H, $(CH_3)_3CSi$), 0.04−0.09 (m, 6H, $(CH_3)_2Si$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 170.6−170.7 (CO-lactone), 149.7−152.8 (CO-carbonate), 78.1−78.5 (C1), 76.1−76.4 (C3), 71.9−72.74 (C5), 64.5 (C4), 32.7−33.0 (C2, C6), 25.5 ($(CH_3)_3CSi$), 17.9 ($(CH_3)_3CSi$), −5.1 ($(CH_3)_2Si$). IR ν_{max}/cm^{-1}: 3096−2272, 1803, 1746, 1227, 1060, 832, 776. T_g = 225 °C. $(T_d)_{onset}$ = 302 °C, $(T_d)_{50}$ = 373 °C; 302−416 °C, 92% mass loss; 8% mass remaining at 500 °C.

2.3. General Procedure of the Removal of the TBS-Protecting Group. Boron trifluoride diethyl etherate was added to a solution of protected poly(quinic acid carbonate) in anhydrous tetrahydrofuran at different temperatures. After different durations, Amberlyst H^+ (15 times the mass of protected poly(quinic acid carbonate)) and calcium sulfonate resin (15 times the mass of protected poly(quinic acid carbonate)) were added to the reaction, and the mixture was stirred for 2 h at the same temperature as the reaction occurred. The resins were removed by filtration and rinsed twice with tetrahydrofuran. The filtrate was concentrated under reduced pressure; then, the residue was

triturated with methanol to afford a white precipitate, which was collected by filtration and dried under vacuum pump.

Synthesis of ***6***. The general procedure for the removal of the TBS-protecting group was applied to a solution of polymer **4** (30 mg, 0.1 mmol) in anhydrous tetrahydrofuran (3 mL) and boron trifluoride diethyl etherate (60 μL, 0.5 mmol) to obtain a white solid (18.3 mg, 74%). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 4.96−5.20 (m, 2H, H-3, H-4), 4.02−4.06 (m, 1H, H-5), 2.95−2.97 (m, 1H, H-2), 2.55−2.61 (m, 1H, H-2), 2.09−2.44 (m, 2H, H-6), 0.83−0.87 (m, 3.6H, $(CH_3)_3$CSi), 0.05−0.07 (m, 2.5H, $(CH_3)_2$Si). IR ν_{max}/cm^{-1}: 3226−3050, 3022−2774, 1810, 1760, 1223, 1120, 1026, 839, 775. T_g = 230 °C. $(T_d)_{onset}$ = 334 °C, $(T_d)_{50}$ = 395 °C; 334−430 °C, 93% mass loss; 7% mass remaining at 500 °C

Synthesis of ***7***. The general procedure for the removal of the TBS-protecting group was applied to a solution of polymer **5** (30 mg, 0.1 mmol) in anhydrous tetrahydrofuran (3 mL) and boron trifluoride diethyl etherate (240 μL, 2.0 mmol) to obtain a white solid (18.0 mg, 78%). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 4.95−4.97 (m, 1H, H-5), 4.57−4.62 (m, 1H, H-3), 4.39−4.44 (m, 1H, H-4), 2.89−3.12 (m, 4H, H-2, H6), 0.86−0.87 (m, 2.4H, $(CH_3)_3$CSi), 0.03−0.08 (m, 1.6H, $(CH_3)_2$Si). IR ν_{max}/cm^{-1}: 3351−3084, 3039−2739, 1812, 1759, 1231, 1067, 834, 780. T_g = 250 °C. $(T_d)_{onset}$ = 320 °C, $(T_d)_{50}$ = 397 °C; 320−445 °C, 82% mass loss; 18% mass remaining at 500 °C.

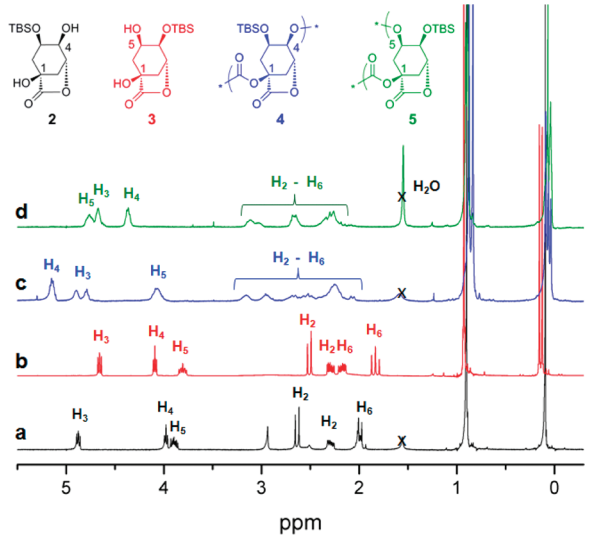


Figure 1. ^{1}H NMR ($CDCl_3$) spectra of diol quinic acid monomers (a) **2** and (b) **3** and poly(quinic acid carbonate)s (c) **4** and (d) **5**.

3. RESULTS AND DISCUSSION

Beginning from quinic acid, **1**, the regioisomeric monomers having 1,4- and 1,5-diols, **2** and **3**, respectively, were prepared by a two-step reaction sequence (Scheme 1).[21,22] Quinic acid **1** underwent lactonization between positions 1 and 3 with 75% yield. The procedure for silylation of lactonized quinic acid described by Garg et al.[22] was then performed with modification of the duration and the temperature (overnight at room temperature, instead of 2 h at −15 °C) to give diol monomers **2** and **3** with 56 and 24% yields, respectively, isolated by column chromatography. The chemical shifts of the protons from the quinic acid moiety (Figure 1a,b) confirmed the structures of diols **2** and **3**, as previously described.[21]

The copolymerizations between diol quinic acid **2** and phosgene generated by different carbonylation agents were tested under a variety of reaction conditions. After screening the copolymerizations of **2** with phosgene in toluene/pyridine, diphosgene in pyridine, triphosgene in pyridine, and carbonyldiimidazole in pyridine, each with and without added solvents, at various temperatures and concentrations over ca. 20 different reactions, it was observed by SEC (using tetrahydrofuran as the eluent and with polystyrene calibration standards) that only trichloromethyl chloroformate (diphosgene) in the presence of pyridine (being the base as well as the solvent) allowed for the formation of polycarbonates.

The temperature, duration, concentration, and number of equivalents of diphosgene were then optimized by an experimental design[24] (matrix 4^3, where 4 is the number of factors and 3 is the number of levels tested for each factor) to identify with only nine experiments the conditions that gave rise to polycarbonates having the largest molecular weights with the highest monomer conversions (Table 1, entries 1−9). The average and the effect of each level, for all factors, were calculated: the concentration (600 g/L) was identified as the most positive factor for this reaction (Figure 2). Using the highest positive levels of each of the factors, the experimental design was validated to give poly(1,4-quinic acid

Table 1. Conditions and Results of the Experimental Design for the Co-Polymerizations between Diol Quinic Acid 2 and Trichloromethyl Chloroformate

entry	concentration (g/L)[a]	duration (h)	equiv[b]	temperature (°C)	M_p (kDa)[c]	conversion (%)[d]	yield[e]
1	400	48	1	25	8.2	99	62
2	400	72	2	50	1.1	47	
3	400	96	3	75	6.1	95	43
4	600	48	2	75	5.1	97	40
5	600	72	3	25	8.0	96	51
6	600	96	1	50	7.2	99	51
7	800	48	3	50	1.8	94	51
8	800	72	1	75	0.7	40	
9	800	96	2	25	1.1	96	13
10	600	48	1	25	9.7	99	75
11	600	0.5	1	25	1.4	10	70
12	600	24	1	25	3.1	90	7

[a] Concentration of **2** in distilled pyridine. [b] Number of equivalents of trichloromethyl chloroformate version **2**. [c] Peak average molecular weight determined by SEC-THF for crude polymers versus polystyrene standards. [d] Determined by ^{1}H NMR spectroscopy by dividing the value of the integration at 5.13 ppm (H4 polymer) and the integration between 4.78 and 4.92 ppm (H3 monomer + polymer). [e] After precipitation in cold methanol.

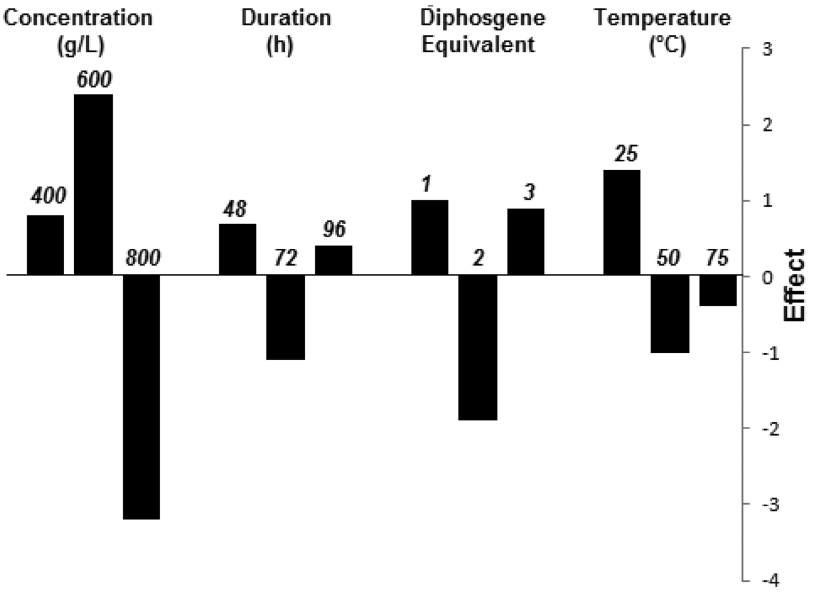


Figure 2. Effect of each factor evaluated during the experimental design.

Table 2. Properties of Protected Poly(quinic acid carbonate)s 4 and 5 Obtained by Co-Polymerization between Trichloromethyl Chloroformate and Diols 2 and 3

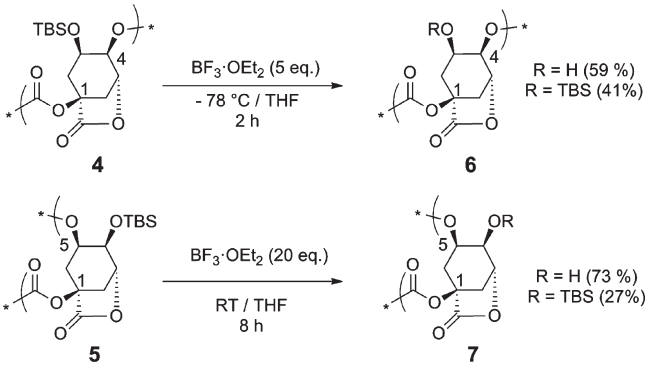
entry	polymer	yield (%)[a]	M_n (kDa)[b]	PDI[b]	T_g (°C)	$(T_d)_{onset}$ (°C)[c]	$(T_d)_{50}$ (°C)[d]
1	4	75	7.5	2.0	209	284	331
2	5	85	7.7	3.5	225	302	373

[a] After precipitation in cold methanol. [b] Determined by SEC-THF for precipitated polymers versus polystyrene standards. [c] Temperature degradation onset observed by TGA. [d] Temperature at 50 wt % loss observed by TGA.

carbonate) **4** with 75% yield after precipitation showing the best results with 99% conversion of the diol quinic acid **2** and a peak average molecular weight of 9.7 kDa (Table 1, entry 10). However, the lack of solubility of the polymer in pyridine (solid formation occurred 30 min after the end of diphosgene addition) was observed, questioning the necessity to perform the polymerization over 48 h. The results of the experiments quenched after 30 min and 24 h (Table 1, entries 11 and 12) showed that even if the mixture became nonhomogeneous the reaction continued to proceed and that the duration was required to allow the growth of the polymer.

The optimized experimental conditions for the polymerization of **2** were then applied to the 1,5-diol quinic acid monomer **3** to afford poly(1,5-quinic acid carbonate) **5**. The copolymerizations of the diol monomers **2** and **3** with phosgene to give polycarbonates **4** and **5** were clearly demonstrated by ^{1}H NMR spectroscopy (Figure 1a vs 1c and Figure 1b vs 1d for the monomers and corresponding polymers, respectively) by observation of the downfield shifts for most protons from the quinic acid moiety and, in particular, the significant downfield shift (1 to 1.2 ppm) of the protons on the carbons involved in the formation of the carbonate linkages; H-4 for **4** and H-5 for **5**. The carbonate linkages were directly observed by the introduction of ^{13}C NMR resonances at ca. 150 ppm, in addition to the lactone ^{13}C signal at ca. 170 ppm. The presence of the carbonate and lactone functionalities was confirmed additionally by

Scheme 2. Partial Removal of the TBS-Protecting Groups of Polycarbonates 4 and 5



two C═O absorbance bands at 1746 and 1803 cm^{-1} in the IR spectra, whereas the monomer exhibited only a single absorbance at 1777 cm^{-1}. Although the molecular weight distribution of **5** was slightly broader than that of **4**, as determined by GPC, the two regioisomeric polycarbonates had similar molecular weights (Table 2, entries 1 and 2), which allowed for direct comparisons of the properties of the materials in relation to the regiochemistry.

The poly(quinic acid)s exhibited thermal properties in agreement with other highly rigid polycarbonate materials. The onset temperatures for thermal decomposition for both polycarbonates (between 284 and 302 °C) were comparable to the typical range of decomposition temperatures of polycarbonates from 200 (polyethylene carbonate) to 350 °C (poly(bisphenol A carbonate)). High glass-transition temperatures (>205 °C) have been observed for these polymers exceeding that of commercial poly(bisphenol A carbonate) by ca. 50 °C. An absence of melting transitions (T_m) or crystallization transitions (T_c), below the thermal decomposition onset temperatures, suggested that the polymers were amorphous. These exceptional thermal characteristics may be due to the presence of the bicyclic backbone in these materials, which introduces rigidity to the polymer similar to the cyclic backbone of poly(cyclohexene

Table 3. Conditions and Results of the TBS Removal of 4 and 5

entry	polymer	equiv[a]	duration (h)	temperature (°C)	removal TBS (%)[b]	M_n (kDa)[c]	PDI[c]	T_g (°C)	$(T_d)_{onset}$ (°C)[d]
1	4	5	1	−78	28	4.4	3.1	214	328
2	4	5	2	−78	59	3.3	2.1	230	334
3	4	5	4	−78	46	4.9	2.1	228	316
4	4	5	6	−78	44	3.8	1.9	212	325
6	4	5	15	RT	90	0.4	2	70	233
7	5	20	1.5	RT	44	8.4	2.9	235	316
8	5	20	3	RT	46	8.8	3.7	238	319
9	5	20	6	RT	55	NS[e]	NS[e]	240	320
10	5	20	8	RT	73	NS[e]	NS[e]	250	320
11	5	20	15	RT	63	NS[e]	NS[e]	244	317[f]
12	5	20	24	RT	49	7.3	2.6	216	310[f]

[a] Number of equivalents of trifluoride diethyl etherate versus 4 or 5. [b] Determined by ^{1}H NMR spectroscopy (DMSO-d_6). [c] Determined by SEC-DMF versus poly(ethylene glycol) for precipitated polymers. [d] Temperature degradation onset observed by TGA. [e] Not soluble in DMF. [f] Observation of a loss of 20% mass between 90 and 180 °C due to loss of water.

carbonate) that shows a 90 °C increase in T_g in compared with its noncyclic analog poly(ethylene carbonate).[12] Moreover, monomer regiochemistry showed a significant impact on the polycarbonate T_g (20 °C difference between **4** and **5**), which suggests that the O-1, O-4 carbonate linkage of **4** is more flexible than its regioisomer, **5**, linked between O-1, O-5.

Removal of the silyl protecting groups was performed under mild conditions to conserve the carbonate and lactone linkages. Although the usual fluoride reagents, including tetrabutylammonium fluoride, hydrofluoric acid with pyridine, and in situ generation of hydrofluoric acid by reaction of potassium fluoride with trimethylsilylchloride, were unsuccessful in selective removal of the protecting groups, surprisingly boron trifluoride diethyl etherate ($BF_3 \cdot Et_2O$)[25] allowed partial removal of the protecting groups without causing degradation of the lactone and carbonate links (Scheme 2). The deprotection of **5** was performed at room temperature with 20 equiv of $BF_3 \cdot Et_2O$, whereas a drastic reduction of molecular weight and coincident effects on the thermal properties was observed when compound **4** underwent the deprotection at room temperature with only 5 equiv of the $BF_3 \cdot Et_2O$ reagent (Table 3, entry 6). To quench the reaction and remove the generated silyl alcohol, we usedd calcium sulfonate resin combined with sulfonic acid resin, as described by Parlow et al. for quenching and purification of desilylating reactions involving tetrabutylammonium fluoride as reagent.[23] The complete deprotection of both of the materials was not achieved, however, without degradation of the polymer, as observed by a decrease in the glass-transition temperatures and the thermal stabilities; the maximum TBS removal observed leading to poly(quinic acid carbonate)s **6** and **7** was 59 and 73%, respectively (Table 3).

Significant changes in properties were observed upon the removal of even a fraction of the TBS-protecting groups. Each regioisomer underwent a 10−20 °C increase in T_g, which can be reasonably attributed to hydrogen-bond network formation. The presence of hydroxyl groups, esters, and carbonates along the backbone, together with maintenance of the rigid bicyclic monomer unit backbone structure, could explain the high glass-transition temperatures observed at 230 and 250 °C for poly(quinic acid carbonate)s **6** and 7, respectively (Table 3, entries 2 and 10). As the extent of deprotection increased, the solubility decreased. Ultimately, at long deprotection reaction times, the solubility increased and the T_g decreased because of significant degradation of the polymers.

4. CONCLUSIONS

Unique and potentially degradable polycarbonates, starting from a renewable resource, quinic acid, have been synthesized by condensation polymerization with phosgene generated in situ from trichloromethyl chloroformate. The conditions of polymerization have been tuned to result in the generation of *tert*-butyldimethylsilyloxy poly(quinic acid carbonate)s having relatively high molar masses (M_n = 7.5−7.7 kDa) and exhibiting simultaneously high glass-transition temperatures (T_g = 209−229 °C) and good resistance to thermal degradation ((T_d)$_{onset}$ = 284−302 °C) compared with previously reported polycarbonates. Obviously, monomer regiochemistry has been identified as a crucial parameter that contributes to the thermal properties of the polymers with a 20 °C difference in T_g between each of the regioisomers and in terms of reactivity during removal of the protecting group with initial degradation observed after 8 h at room temperature when carbonate is linked on O-1, O-5, against <4 h at low temperature when the linkage was created between O-1 and O-4. The study of the TBS removal encountered a competition between deprotection and degradation of the polymer with a limitation at 60−70% of removal of the protecting groups. Even with the limited deprotection, the glass-transition temperatures increased by 10−20 °C (T_g = 230−250 °C), which is beginning to approach the onset of thermal degradation, and the solubility decreased. These physical property changes may result in challenges with processing of the final polycarbonate materials. With further development, it is expected that these polycarbonates may find application as replacements for poly(bisphenol A carbonate), as orthopedic tissue engineering materials, or both because of their rigid bicyclic backbone structure and aliphatic nature that will allow for the breaking down of the polymer to carbon dioxide and polyhydroxy bioresorbable degradation products.

■ ASSOCIATED CONTENT

Supporting Information. ^{1}H, ^{13}C, and 2D (COSY and Hetcor) NMR spectra for the monomers and polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

The Welch Foundation is gratefully acknowledged for support through the W. T. Doherty-Welch Chair in Chemistry, grant no. A-0001.

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