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Advancing the Development of Highly-Functionalizable Glucose-Based Polycarbonates by Tuning of the Glass Transition Temperature

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Supporting Information

ABSTRACT: Fundamental studies that gain an understanding of the tunability of physical properties of natural product-based polymers are vital for optimizing their performance in extensive applications. Variation of glass transition temperature (T_g) was studied as a function of the side chain structure and molar mass for linear poly(glucose carbonate)s. A remarkable range of T_g values, from 38 to 125 °C, was accomplished with six different alkyloxycarbonyl side chains. The impact of molar mass on T_g was investigated for two series of polymers and discrete oligomers synthesized and fractionated with precise control over the degrees of polymerization. The T_g was found to be greatly influenced by a synergistic effect of the flexibility and bulkiness of the repeating unit side chain, as well as the chain end relative free volume. This work represents an important advance in the development of glucose-based polycarbonates, as materials that possess high degrees of functionalizability to be capable of exhibiting diversified physicochemical and thermal properties by simple side chain modification.

Natural product-based degradable polymers obtained from renewable resources are desirable alternatives to petrochemicals for future macromolecular materials.[1−5] Development of sugar-based monomers and polymers is particularly intriguing and has been a growing area for decades due to their biocompatibility, degradability, structural diversity, and functionalization potential that enables fine-tuning of their physical proprieties.[6−9] The drive to promote the application of such materials in various fields prompted the development of a wide range of well-controlled polymers as well as the investigation of their fundamental properties.

The ability to modulate the physical properties of synthetic polymers is highly desirable, as they affect the behavior and performance of these materials in practical applications. The relationship between the T_g and polymer structures has been attracting enduring fundamental and practical research interest;[10−13] however, such studies have not yet been explored for sugar-based renewable polycarbonates. Previous research has demonstrated relatively high T_g for sugar-based polycarbonates,[14−17] arising from their inherently rigid backbone containing cyclic glucose building blocks, which potentially limits the variety of applications of these durable materials. Therefore, tailoring and broadening the T_g range of sugar-based polycarbonate materials would further enable their usage in fields such as stretchable and self-healing materials,[18] drug delivery vehicles,[19] and soft implants/scaffolds.[20]

Variation of T_g has been extensively studied for traditional linear polymers and dendrimers, where T_g is shown to correlate with certain parameters, including molar mass,[21,22] chemical composition of the backbone,[23] steric hindrance of substituents,[24] side chain flexibility,[25] chain-end composition,[26] intermolecular interaction between polymer chains,[27] cross-linking density,[28] and dispersity.[29] Under the guidance of polymer physics, various methods have been utilized in tailoring T_g. Mandelkern and co-workers studied the influence of side chain length on the T_g of poly(*n*-alkyl methacrylates).[30] More recently, Muñoz-Guerra, Galbis and co-workers reported the dependence of T_g on the compositions and functionality of a series of degradable linear polyesters and copolyesters from bicyclic acetalized monosaccharide monomers.[31,32] Coates, DiStasio and co-workers provided chemical and physical insights into how substituent effects influence the T_g of biorenewable polyesters.[11] Although the strategies for tuning T_g have been continuously explored, there has been a lack of molecular engineering directed toward the investigation of T_g on renewable glucose-based polycarbonates.

The synthesis of novel glucose-based polymers allows the structure to be tailored at the monomer level for a specific property and expands the scope of available structures beyond those found in Nature. In earlier studies, we have demonstrated the versatility of glucose carbonate monomers and polymers with modifications of the pendent hydroxyl groups on the 2,3-*O* positions.[33,34] In this work, we report variation of T_g for poly(glucose carbonate)s by systematically changing the alkyloxycarbonyl side chains of their constituent monomers. The dependency of T_g on molar mass was investigated within two polymer systems, both showing an exciting $\surd$-shaped plot of T_g vs log M_n.

To evaluate the effects of side chain structure, six substituent alkyl groups, ethyl, *n*-butyl, *n*-hexyl, isobutyl, neopentyl, and

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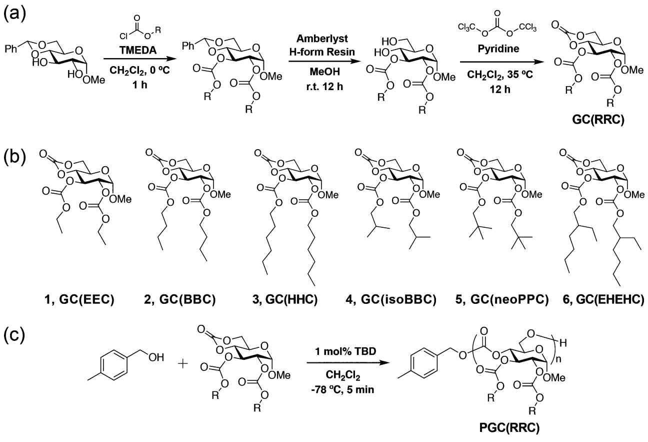
Scheme 1. (a) Synthesis of Bicyclic Glucose Carbonate Monomers GC(RRC); (b) Structures of Alkyloxycarbonyl Protected Glucose Carbonate Monomers; (c) Synthesis of the Polymers PGC(RRC)



2-ethylhexyl, were studied. These side chains were installed into the glucose carbonate monomers via carbonate linkages following previously reported synthetic methods,[15] to introduce full hydrolytic degradability of the resulting polymers (Scheme 1).[35] The monomers GC(RRC) exhibited ^{13}C NMR spectroscopic signals at ca.147 ppm, demonstrating the successful ring closing with the presence of the cyclic carbonate (Figures S1−S5). Six well-defined homopolymers PGC(RRC) were then produced through organocatalytic ring-opening polymerization (ROP) (Scheme 1c), and the products were structurally confirmed by ^{1}H NMR spectroscopy (Figures S6−S11), ^{13}C NMR spectroscopy (Figure 1c), Fourier-transform infrared spectroscopy (FT-IR) (Figure S12), and matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) (Figure S13). The sharpness of proton resonance peaks reflected the restricted configurations of the glucose cyclic structure, as well as the regioselectivity of the polymerization during propagation steps. Only one peak corresponding to the backbone carbonate resonance at 153.9 ppm was observed from each ^{13}C NMR spectrum (Figure 1c), further suggesting the regioregularity of PGC(RRC). Nearly equal molar masses (M_n = 15−16 kDa) and narrow dispersities ($Đ$ = 1.04−1.06) were achieved for all six PGC(RRC), as determined by size exclusion chromatography (SEC) (Figure 1b, Table S1), ensuring the comparability of their thermal properties would rely upon the differences in side chain composition with little effect from differences in molar mass. The well-defined structures of these homopolymers with 4-methylbenzyl alcohol end-group functionality were also demonstrated by MALDI-TOF MS (Figure S13), which revealed populations with spacing numbers in accordance with the expected repeating unit values (i.e., 364.1m/z for PGC(EEC), 420.2 m/z for GC(BBC) and GC(isoBBC), 476.2 m/z for GC(HHC), 448.2 m/z for GC(neoPPC), and 532.3 m/z for GC(EHEHC)). High thermal decomposition temperatures at 330−345 °C, as measured by thermogravimetric analysis (TGA) (Figure S14), indicated the thermal stability of these glucose-based polycarbonates.

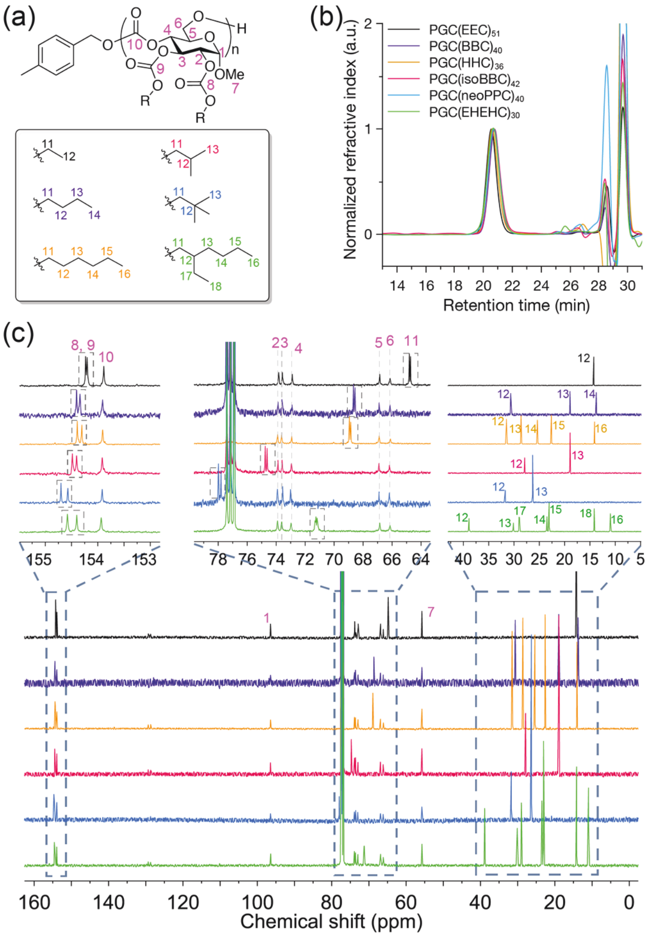


Figure 1. (a) Structures of PGC(RRC), (b) SEC chromatograms (THF as eluent, 1.0 mL·min^{-1}), and (c) ^{13}C NMR (126 MHz, CDCl$_3$) spectra of PGC(RRC).

On increasing the side chain length from ethyl to n-butyl to n-hexyl, with an elongation of only two methylene groups each step, the T_g remarkably decreased from 120 to 68 to 46 °C, as determined by differential scanning calorimetry (DSC) (Figure 2). A further decrease in T_g to 38 °C was observed for PGC(EHEHC)$_{30}$, possibly due to the increased free volume created by the free rotation of the additional branched ethyl

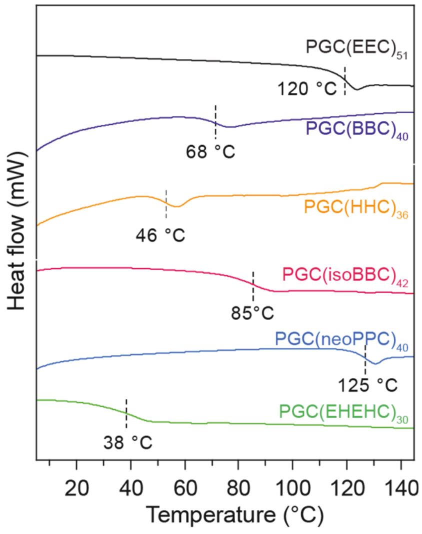


Figure 2. DSC thermograms of PGC(RRC) (M_n = 15−16 kDa, $Đ$ ≤ 1.06).

group.[36] However, an increase of the T_g to 85 °C was found for the branched isobutyl group modified PGC(isoBBC)$_{42}$, ranking between the ethyl and *n*-butyl groups, suggesting combined effects of the chain length and branching.[25] The highest T_g of 125 °C was observed for PGC(neoPPC)$_{40}$, which can be explained by the presence of the quaternary carbon that brings in dramatic steric hindrance and rigidity.

The effect of molar mass on T_g was also investigated for two series of discrete oligomers and polymers, PGC(neoPPC) and PGC(EHEHC), which possessed the highest and lowest T_g, respectively. It is known that the T_g of linear polymers generally increases with increasing molar mass, which is often explained by the free volume ratio of polymer chain ends that facilitate the flexibility of a polymer chain considerably.[37] In the low molar mass range, this variation is especially pronounced, due to the prominent decrease of the ratio of chain ends with the increasing repeating units. In this system, the glucose carbonate monomers with the fused bicyclic structure were postulated to exhibit higher T_g than the corresponding ring-opened unimers, attributing to the combined effects from chain ends and structural rigidity. To examine this hypothesis and probe the dependency of T_g on molar mass, polymers ($DP_n > 6$, $Đ < 1.10$) and oligomers were synthesized following the ROP procedure, by varying the monomer-to-initiator ratio. Unlike the polymer analogues, the oligomer mixture with $DP_n < 6$ is not optimal for understanding the intrinsic properties of each component.[38] Therefore, preparative SEC was used for efficient separation of the oligomer mixtures from one ROP reaction into their constituent species.

Oligo/polyGC(neoPPC)s were prepared with different monomer-to-initiator ratios from 2 to 20. Low dispersities of all batches were observed for the polymeric products by SEC analysis (Figure 3a, solid lines, Table S2), while multiple peaks were found when feed ratios were set at 2 and 3, corresponding to the mixtures of oligomers with different molar mass distributions (Figure S15). These oligomer mixtures were then fractionated by preparative SEC (chloroform as eluent), affording pure discrete oligomers as verified by analytical SEC chromatograms (Figure 3a, dashed lines). MALDI-TOF MS spectra also reinforced their purity unambiguously, with *m*/*z* values corresponding to the expected structures, and separation of ca. 448.2 *m*/*z* correlating with the GC(neoPPC) repeating unit. ^{1}H NMR spectroscopic analysis of the discrete oligomers provided insights into subtle structural changes as the size of the oligomer increased (Figure S16). With progression from the unimer to tetramer of GC(neoPPC), relative intensities of the glucose proton resonances (3.75−5.40 ppm region) increased when compared with the chain-end proton resonances at 2.35, 7.17, and 7.28 ppm, with integration numbers closely correlating to the oligomer DP_n.

The T_g of each discrete oligomer ($DP_n < 5$) and polymer ($DP_n > 6$) of GC(neoPPC) were then measured using DSC from 0 to 150 °C at 10 °C/min, and a variation over 100 °C was observed. With the evolution from unimer to polymer ($DP_n = 40$), the free volume ratio of the chain ends decreased, leading to a rising trend of T_g from 13 to 125 °C. Interestingly, the GC(neoPPC) monomer behaved as an outlier of the trend line, with a T_g value of 57 °C, which is higher than the corresponding monocyclic ring-opened unimer and dimer with a methylbenzyl chain end. The fact that T_g strikingly decreased by 44 °C once the ring-opening occurred supported our hypothesis concerning the impact of the rigid fused bicyclic structure of the monomer. A special $\sqrt{}$-shaped plot was shown for T_g vs log M_n (Figure 3d), and a linear correlation was found for T_g *vs* M_n^{-1}, which is explained by the Flory−Fox theory,[39] with the exception of the monomer (Figure 3e). Although precise identification of the T_g plateau point was difficult within the given molar mass range in Figure 3d, the intercept in Figure 3e suggested that the T_g value extrapolated to infinite molar mass is expected to be close to 125 °C ($DP_n = 40$), where the effect of chain ends is insignificant.

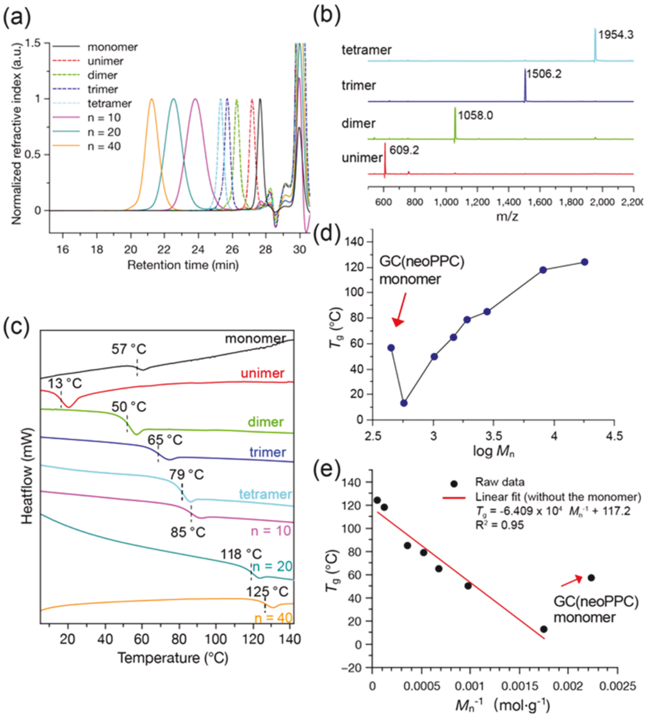


Figure 3. Characterizations of oligo/polyGC(neoPPC). (a) SEC chromatograms, with dashed lines indicating discrete oligomers isolated by preparative SEC, (b) MALDI-TOF MS spectra of the discrete oligomers (with K^+ as the adduct ion), (c) DSC thermograms of monomer, oligomers, and polymers, and plots of (d) T_g vs log M_n, and (e) T_g *vs* M_n^{-1}.

To verify the generality of this trend in the glucose-based polycarbonate system, the study was extended to a PGC(EHEHC) series, which exhibited the lowest T_g among the six polymer analogues. Oligo/polyGC(EHEHC) was prepared in the same manner as for PGC(neoPPC) and structurally confirmed by SEC (Figure 4a, Figure S17), ^{1}H NMR spectroscopy (Figure S18), and MALDI-TOF MS (Figure S19). Similar trends of T_g progression from monomer to oligomer to polymer were also discovered. The bicyclic monomer with flexible side groups displayed low T_g at −10 °C, which decreased to −25 °C for the monocyclic ring-opened unimer and increased gradually up to 38 °C with the chain elongation to $DP_n = 30$ (Figure 4b). The plots of T_g vs log M_n and M_n^{-1} (Figure S20) indicated the plateau of T_g at *ca.* 38 °C for PGC(EHEHC). Combining together the results of PGC(neoPPC) and PGC(EHEHC), the general thermal property trends have been validated for poly(glucose carbonate)s (Figure S21).

In summary, variation of glass transition temperature of poly(glucose carbonate)s has been successfully achieved via control over the side chain structure and molar mass. A wide T_g range from 38 to 125 °C was achieved by varying the

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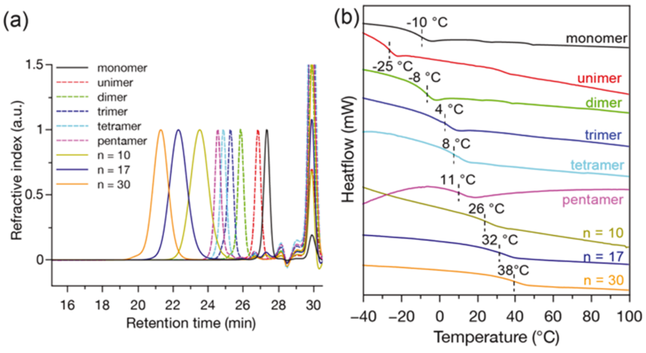

Figure 4. (a) SEC chromatograms (dash lines: discrete oligomers isolated from preparative SEC), and (b) DSC thermograms of oligo/polyGC(EHEHC) of different molar mass.

alkyloxycarbonyl protecting groups, of which the trend was rationalized by free volume evolution with the comprehensive effects derived from side-chain steric hindrance and flexibility. The two polymers at both ends of the trend were further evaluated to understand the relationship of T_g with molar mass. T_g variations with molar mass, among wide ranges of 13−125 °C and −25−38 °C for PGC(neoPPC) and PGC(EHEHC), respectively, are both well fitted to the Flory−Fox theory. It is especially interesting to note the enormous decrease of T_g from bicyclic monomers to monocyclic ring-opened unimers in both situations, which strongly demonstrated the rigidity loss with ring opening of the six-membered glucose carbonate ring. Future studies will be directed toward the utilization of these sustainable glucose-based polycarbonates with a high degree of functional adaptability and physical property tunability toward extensive applications.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b10675.

Experimental procedures, figures, tables, and additional data (PDF)

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Notes

The authors declare no competing financial interest.

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