Quiz #2  \( \bar{x} = 4.0 \)
\( \text{S.D.} = 3.7 \)

Exam I, Feb. 6, 2014 (next Thursday)
- No office hours Feb. 5
- See Adriana if have questions at last moment

Exam I from previous years will be posted on course website—
blank exams + answer keys—TODAY

Chapter 2 problems recommended:
# 2, 3, 12, 15, 16, 17—answer to be posted on website—TODAY
2. Poly carbonates

- Carbonate linkages along the backbone

- Tradename: Lexan
- Developed by Bayer & GfK in 1953
- Engineering plastic
  - High transparency
  - High impact resistance (toughness)
- CDs, DVDs, eyeglasses, automotive parts (instrument parts, windshield coating etc.), astronaut & football helmets
- No longer baby bottles b/c of hydrolytic degradation to bisphenol A (implicated in cancer)

Out too reactive

- CDs, DVDs, eyeglasses, automotive parts (instrument parts, windshield coating etc.), astronaut & football helmets
- No longer baby bottles b/c of hydrolytic degradation to bisphenol A (implicated in cancer)

Mech involves transesterification

8k41 specialty, expensive live

But industrially too expensive live

Bi(4-nitrophenyl) carbonate

1,1'-carbonyldimidazole
A couple of recent/ongoing advances in polycarbonates:

1. Fundamental studies of molecular structure-property relationships

![Chemical structure](image)

75% $^{13}C = F$

Preferred chain packing and bundling leads to gating of Ar ring flips.

$->D_{high}$ impact strength

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See (et al.):

D. Stuecker, A. K. Mehta,
B. Chen, K.C. Woolay, J. Schaefer
"Local order in polycarbonate glasses by $^{13}C$ and $^{19}F$ Rotational-echo double-resonance NMR",
2006, 44, 2760-2775.

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2. Natural product-based polycarbonates

- derived from renewable resources
- potential engineering materials/bioengineering materials
- degradation (hydrolytically) regenerates the natural product-based monomers + CO$_2$

  "Polycarbonates from the Polyhydroxy Natural Product Quinic Acid", Biomacromolecules 2011, 12, 2512-2517.
Polycarbonates from the Polyhydroxy Natural Product Quinic Acid

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ABSTRACT: Strategies for the preparation of polycarbonates, derived from natural polyhydroxy monomeric repeat units, were developed for bioinspired polycarbonates based on quinic acid. The design and synthesis of regioselectively tert-butyldimethylsilyloxy-(TBSO)-protected 1,4- and 1,5-diol monomers of quinic acid were followed by optimization of their copolymerizations with phenols, generated in situ from trichloromethyl chlorofromate, 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 degree of polymerization of ca. 24, with polydispersities ranging from 2.0 to 3.3, as measured by SEC using tetrahydrofuran as the eluent and with poly(styrenesulfonic acid) standards. Partially because of the presence of the bicyclic backbone, both 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 degradations, 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 1,4-regioisomer possessing lower reactivity and giving higher Tg values, in comparison with the 1,5-regioisomer. Yield was found to have a 10-20 °C increase in Tg 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 Tg 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, based on carbohydrates or fatty acids to diminish the dependence on petroleum products and also to enhance degradability to reduce environmental accumulation of waste.1 An important application of degradable polymers is in "biomimicry" (e.g., suture, orthopedic devices, tissue engineering devices, etc.), where incorporation of biocompatibility and biodegradability is imperative. For this purpose, the polymers used are typically of cotton,2 which undergo hydrolysis to afford products containing hydroxyl groups or carbonates,3 especially aliphatic carbonates that undergo hydrolytic degradation to give carbon dioxide and alcohols.4,5 Beyond these criteria, biodegradable polymeric materials in orthopedic tissue engineering also must possess thermal and mechanical properties that mimic the joint and the degradation to the native cartilage.6 Application polycarbonates, especially those based on biodegradable compounds, may lead to bioinspired degradation products in vivo. Therefore, we have investigated the synthesis of polycarbonates built from a natural monomer, quinic acid, to afford a unique family of bioinspired, degradable, engineering polymers: poly(quinic acid carbonate)s. Quinic acid is found in coffee beans and other plants7 and is known for its growth-promoting properties,8 in converted to tryptophan and nicotamide9 by microorganisms of the gastrointestinal tract,10 and is also a chiral starting material for pharmaceuticals.11,12 Quinic acid was selected as the starting material because of easy access to a bicyclic, diol monomer by known lactonization and selective alkylation,13 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.

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

[a] (a) Anthracene, benzenes/DMAP, reflux, 16 h. (b) TBS-Cl, DMAP, NBS, DMP, RT, 12 h. (c) Diphenylphosphine, pyridine, RT, 48 h.

2. EXPERIMENTAL SECTION

2.1. Materials. Quinic acid 1 (Alfa Aesar, 98%), trichloromethyl chloroformate, boron trifluoride diethyl etherate, and anhydrous potassium carbonate were obtained from commercial suppliers. All other chemicals were of reagent grade and used without further purification. 

2.2. General Procedure of the Copolymerization between Diol Monomers 2 and 3 and Trichloromethyl Chlorofromate. Trichloromethyl chlorofromate 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 chlorofromate 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 3% solutions 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 solid (400 mg, 75%).

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Polyamides

(a) aliphatic polyamides

e.g. Nylon 6,6 (see ppt slides from earlier lecture)

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\begin{align*}
H\left(\text{NH}-(\text{CH}_2)_6-\text{NH}\right)\left(-\text{CH}_2\text{CH}_2\text{NH}_2\right)_n \Rightarrow n\text{ HO}-\text{HO} + \text{HO}-\text{HO} \\
\Delta, -2n-1\text{ H}_2\text{O}
\end{align*}
\]

\[T_m = 265^\circ C\]

- Good chain-chain packing for crystallization + reinforcement

- Intra- and intermolecular hydrogen bonds

- H-bonds strengthen intra- and inter-chain attractions

- Pseudo x-links (supramolecularly)

- \(T_m = 60^\circ C\)

\[\text{cf.} \quad H\left(O-\left(\text{CH}_2\right)_6-O\right)\left(-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2\right)_n \]

- Good chain-chain packing + crystallization

- Lack of H-bonding

\[\text{Rigidity, } T_m + T_g\]
(b) polyaramides

meta-substituted Ar rings

- no aliphatic groups
- rigid, stable Ar rings
- H bonds via amides

- rigidity
- \( T_m + T_g \)
- T decomp.

- Tradename: Kevlar
  (DuPont, 1965)

- similar properties to Nomex but para-substituted Ar rings give enhanced chain-chain packing, alignment, liquid crystalline properties & higher strength

- uses: bullet-proof vests, fabrics in armored vehicles, etc.

- Tradename: Nomex
  (DuPont, 1960s)

- fireproof: doesn't melt, burn or transmit heat
- \( T_{decomp} > 500^\circ C \)

- used as fiber: woven into over gloves, clothing for fire fighters, etc.