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SYNTHETIC POLYMERS AS ANALOGS OF POLYSACCHARIDES

FINAL REPORT

EDWIN J. VANDENBERG AND RICHARD S. JUVET, JR.

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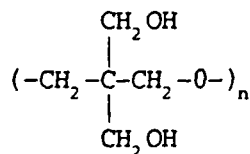
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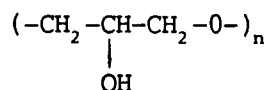
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<p>This report is the final one on ARO Grant No. MIPR-117-87. This work was also supported and administered under NSF Grant No. DMR-8412792.</p> <p>The major thrust of this program was to make and characterize hydrophilic hydroxy polyethers which are interesting analogues of the important naturally occurring polysaccharides. The work, as described below, centered largely around the synthesis, properties and mechanism aspects of poly[3,3-bis(hydroxymethyl)oxetane], (PBHMO) and poly(3-hydroxyoxetane) (PHO). Two U.S. patents were filed and two publications were prepared.</p> <p style="text-align: right;">(continued on reverse)</p>			
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Poly[(3,3-hydroxymethyl)oxetane] (PBHMO),



PBHMO was prepared in high molecular weight by polymerizing the trimethylsilylether of 3,3-bis(hydroxymethyl)oxetane with the $i\text{-Bu}_3\text{Al}-0.7 \text{H}_2\text{O}$ cationic catalyst at low temperature, followed by hydrolysis. PBHMO is crystalline, very high melting (314°C) and highly insoluble, much like its analog, cellulose. It is soluble in 75% H_2SO_4 at 30°C, being 65% converted to the acid sulfate ester; these conditions are useful for viscosity measurement, since the degradation rate is low and at least an order of magnitude less than cellulose in this solvent. PBHMO can be prepared as oriented films and fibers using the lower melting diacetate (179°C) which can be melt or solution (CHCl_3) fabricated and then the oriented forms saponified to oriented PBHMO. BHMO can be directly polymerized to low molecular weight, perhaps somewhat branched, PBHMO (η_{inh} 0.1) with trifluoromethanesulfonic acid catalyst at room temperature. Poly(3-methyl-3-hydroxymethyloxetane) (PMHMO), prepared in high molecular weight (η_{inh} up to 3.8) by the same method used for PBHMO, is more soluble and lower melting (165°C) than PBHMO, appears to be atactic and can be compression molded at 195°C to a tough, clear film which is readily oriented. Copolymers of BHMO with MHMO are crystalline over the entire composition range with a linear variation of T_m with composition, a new example of isomorphism in the polymer area.

Poly(3-hydroxyoxetane) (PHO),



The spontaneous polymer from 3-hydroxyoxetane (HO) reported in the literature without adequate characterization is linear, low molecular weight, water-soluble, atactic, PHO of high crystallinity with $-\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$ end units. The highly crystalline nature of this atactic polymer may be related to the crystalline nature of atactic poly(vinyl alcohol) since PHO can be considered a copolymer of vinyl alcohol and formaldehyde. Spontaneous PHO apparently is formed in a cationic polymerization by the carboxylic acids produced by the air oxidation of HO on standing at room temperature for several months. A mechanism is proposed for this cationic polymerization. High molecular weight, water-soluble, linear, atactic, and highly crystalline PHO (mp = 155°C) was made by polymerizing the trimethylsilyl ether of HO with the $i\text{-Bu}_3\text{Al}-0.7 \text{H}_2\text{O}$ cationic catalyst followed by hydrolysis. Two $^1\text{H-NMR}$ methods for measuring the tacticity of PHO were developed based on finding two different types of methylene units at 400 MHz with the methine protons decoupled. High molecular weight, linear PHO with enhanced isotacticity (80%) has been obtained in low yield as a water-insoluble fraction with $T_m = 223^\circ\text{C}$. The low molecular weight PHO prepared previously by the base-catalyzed, rearrangement polymerization of glycidol is highly branched.

Other Areas

A new high yield procedure for making a bicyclic orthoester from BHMO diacetate using a tin catalyst was discovered. The first coordination copolymerization of tetrahydrofuran was found.

Participating Scientific Personnel

Dr. Edwin J. Vandenberg, project director and principal investigator.
Dr. Richard S. Juvet, Jr., co-principal investigator.
Dr. Jeffrey C. Mullis, post-doctoral research associate.
Tom Miller, graduate student.
Basu Barua, graduate student.
R. A. Nieman, NMR specialist.

Publications submitted to Journal of Polymer Science, Chemistry Edition

"Poly[3,3-bis(hydroxymethyl)oxetane]--An Analog of Cellulose: Synthesis, Characterization and Properties," E. J. Vandenberg, J. C. Mullis, and R. S. Juvet, Jr.

"Poly(3-hydroxyoxetane)--An Analog of Poly(vinyl alcohol): Synthesis, Characterization and Properties," E. J. Vandenberg, J. C. Mullis, R. S. Juvet, Jr., T. Miller and R. A. Nieman.

U. S. Patent Applications

High Molecular Weight Polymers and Copolymers of 3-Hydroxyoxetane and Derivatives thereof. Pending.

Poly[3-(Substituted)-3(Hydroxymethyl)Oxetane] and Method of Preparing Same. Pending.

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