References and Notes

(1) Jenekhe, S. A. *Nature (London)* **1986**, *322*, 345.

(2) Jenekhe, S. A. *Macromolecules* **1986**, *19*, 2663.

(3) Jenekhe, S. A. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1986**, *17*, 74.

(4) In ref 2 and 3 it is claimed that polymer **3** is blue with a λ_{max} of 692 nm and a bandgap of 810 nm (1.53 eV). The pure polymer is actually off white with λ_{max} of 332 nm (ϵ = 23 400) and a hint of absorption in the 700–800-nm region of (ϵ = 31.4, cf. Figure 2), indicating a small degree of unsaturation. *However, both pure and impure polymers show qualitatively the same electornic spectroscopy behavior when brominated (the former less dramatically so than the latter).*

(5) Kobayashi, M.; Colaneri, N.; Boysel, M.; Wudl, F.; Heeger, A. H. *J. Chem. Phys.* **1985**, *82*, 5717.

(6) Anal. Calcd. for $C_{53}H_{36}S_8$ (**2**, *n* = 3.5) [H(C_4H_2S)(C_4H_2S)–(CHC_6H_5)–(C_4H_2S)(C_4H_2S)–(CHC_6H_5)–(C_4H_2S)(C_4H_2S)–(CHC_6H_5)–(C_4H_2S)(C_4H_2S)H]: C, 68.50; H, 3.90; S, 27.60. Found: C, 68.45; H, 3.78; S, 27.31. Anal. Calcd. for $C_{53}H_{36}Br_{11.3}S_8$ (**2**, gas–solid reaction): C, 34.73; H, 2.02; Br, 49.29; S, 14.01. Found: C, 34.94; H, 2.40; Br, 48.80; S, 9.77. Anal. Calcd. for $C_{49}H_{30}Br_3O_3S_7$ (**2A**, *n* = 2.5, gas–solution reaction): C, 52.05; H, 2.65; Br, 21.24; S, 19.82. Found: C, 51.83; H, 2.63; Br, 21.42; S, 19.79. Anal. Calcd. for $C_{53}H_{40}Br_5N_3S_8$ (**2A**, *n* = 2.5, gas–solid followed by evacuation, followed by gaseous hydrazine): C, 46.28; H, 2.91; Br, 29.11; N, 3.05; S, 19.79. Found: C, 46.64; H, 2.74; Br, 29.26; N, 2.84; S, 18.52. Anal. Calcd. for $C_{26}H_{18}Br_3S_3$: C, 46.93; H, 2.69; Br, 36.00; S, 14.39. Found: C, 46.38; H, 2.45; Br, 36.30; S, 14.09. Anal. Calcd. for $C_{30}H_{26}Br_{2.2}S_4$: C, 48.65; H, 3.52; Br, 24.32; S, 17.29. Found: C, 48.48; H, 3.06; Br, 23.74; S, 15.70 (residue, 9%).

(7) Patil, A. O., unpublished results.

(8) A referee requested we propose structures for the bromination products of **5** and **6**. Based on the elemental analysis, the structure of bromine-treated **6** is very likely just $[6^{\bullet+}][Br_3^-]$. In the absence of more studies, we do not want to speculate about possible structures of $[5][Br_{2.2}][H_2O]$.

(9) Kertesz and Lee (Kertesz, M.; Lee, Y. S. *J. Phys. Chem.* **1987**, *91*, 2690) have calculated a bandgap of 1.13 eV for polymer **2A**.

(10) Buchwalter and Viehbeck (Buchwalter, S. L.; Viehbeck, A. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1987**, *28*, 211; Buchwalter, S. L. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 2897) have suggested that long-wavelength absorptions in similarly prepared furan analogue polymers are due to partial dehydrogenation of the backbone.

A. O. Patil and F. Wudl*

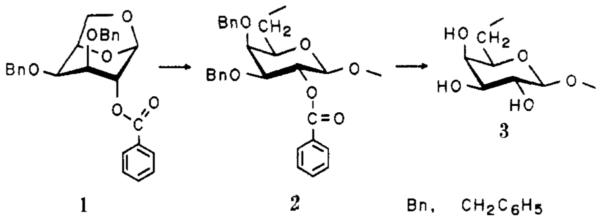
Institute for Polymers and Organic Solids
Department of Physics, University of California
Santa Barbara, California 93106

Received June 9, 1987

Sterically Controlled Ring-Opening Polymerization of a 1,6-Anhydro-β-D-galactopyranose Derivative by Neighboring Group Participation. (1→6)-β-D-Galactopyranan

Neighboring group participation serves to control the stereochemistry of glycosidation reactions.[1] Glycopyranosyl halides with an acetyl or benzoyl group at position 2 are efficient glycosyl donors in the synthesis of β-linked oligosaccharides of the gluco and galacto series. In this paper, polymerization of 1,6-anhydro-2-*O*-benzoyl-3,4-di-*O*-benzyl-β-D-galactopyranose (**1**)[2] followed by deprotection was carried out according to Scheme I and a β-(1→6)-linked D-galactopyranan **3** of $\overline{DP}_n$ = 7 was obtained. The structure determination of **3** was made in comparison with model (1→6)-β-D-galactooligosaccharides[2-6] which were prepared via stepwise and blockwise glycosidation methods to study the interaction with homogeneous myeloma monoclonal antibodies.[7]

Scheme I
Synthesis of β-(1→6)-Linked Galactopyranan Oligosaccharide 3



A variety of linear stereoregular polysaccharides have been synthesized via ring-opening polymerization of anhydro sugar derivatives of different configuration, ring size, and substituent.[8] Polymerization of 1,6-anhydro sugar derivatives proceeds with inversion presumably via a trialkyloxonium ion intermediate.[9] Only one anhydro sugar, 1,6-anhydro-2,3-di-*O*-benzyl-4-deoxy-β-L-*ribo*-hexopyranose, has polymerized with retention of configuration.[10,11] A more general method for the polymerization of anhydro sugars with retention of configuration could lead to the chemical synthesis of biologically relevant polysaccharides that are not presently accessible. The present method using neighboring group participation is suggested for that purpose. Previously, an increase of the β-form content in the polymerization of a bicyclic acetal (4-bromo-6,8-dioxabicyclo[3.2.1]octane) was explained in terms of bromonium ion participation.[12] Exclusive cis-opening polymerization has been attained in the present investigation by means of neighboring benzoyl group participation.

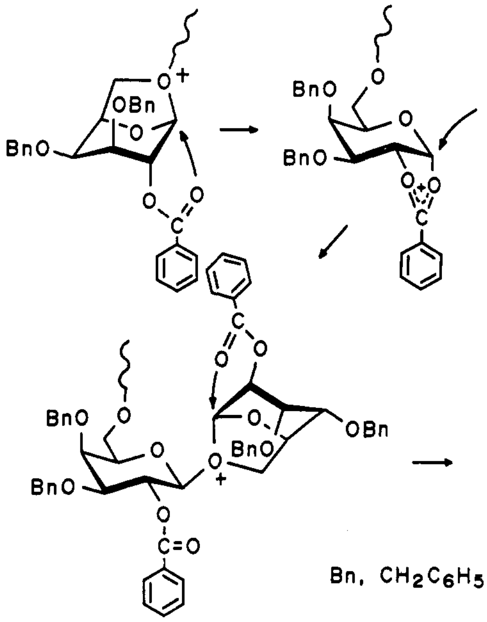
The polymerization of **1** was carried out at 0 °C using 10 mol % of phosphorus pentafluoride in dichloromethane ([**1**] = 1.5 mol/L) for 48 h and a white powdery polymer was isolated in a 66% yield by reprecipitation and chromatography. The number-average molecular weight estimated by GPC was 2.6×10^3 ($\overline{DP}_n$ = 6); $[\alpha]_D^{25}$, +26.8° (*c* 1.0, chloroform); lit.[3] $[\alpha]_D^{25}$, +25.8° for allyl β-glycoside of a tetrameric galactopyranose derivative. The polymerization of **1** was much more sluggish than that of the corresponding tribenzylated analogue (1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-galactopyranose)[13,14] and required a higher polymerization temperature and a larger amount of initiator. The molecular weight of the polymer was lower than those of the polymers obtained from the tribenzyl analogue.

Both debenzylation and debenzoylation of the polymer **2** were simultaneously performed with sodium in liquid ammonia and a free polysaccharide **3** was obtained quantitatively as a hygroscopic powder. It was soluble in water, partially soluble in dimethyl sulfoxide, and insoluble in other common organic solvents.

The optical rotation and ^{13}C NMR data of **3** were consistent with β-(1→6)-linked galactopyranan structure in comparison with those of the model oligosaccharides; $[\alpha]_D^{25}$, +26.9° (*c* 1.0, water); lit.[4] $[\alpha]_D^{20}$, +20° (*c* 1.2, water) for (1→6)-β-D-galactotriose. The six major peaks in the ^{13}C NMR spectrum (D_2O, 5%; internal reference, methanol, 49.0 ppm; 50 MHz) were assigned to the central β-D-galactopyranosyl units: C-1, δ 103.38; C-2, 70.80; C-3, 72.69; C-4, 68.69; C-5, 73.78, C-6, 69.29. These chemical shifts were in agreement with the reported data of methyl (1→6)-β-galactohexaose (C-1, δ 103.46; C-2, 70.77; C-3, 72.66; C-4, 68.70; C-5, 73.79; C-6, 69.23).[6] Corroborating evidence of β-linkage was the coupling constant, $J_{C-1,H-1}$ = 162.6 Hz, which was assigned to the coupling between the anomeric carbon and axial hydrogen.[10,11,15] There were several smaller resonances assignable to the terminal units. However, no signal whose chemical shift was close to that

0024-9297/88/2221-0542$01.50/0

Scheme II
Neighboring Group Participation in the Ring-Opening Polymerization of 1,6-Anhydro-2-*O*-benzoyl-3,4-di-*O*-benzyl-*β*-D-galactopyranose (1)



of (1→6)-*α*-D-galactopyranan[13,14] was detected,. The area ratio of the central C-1 and nonreducing C-1 signals gave a $\overline{\mathrm{DP}}_n$ value of 7.

Scheme II illustrates the proposed mechanism of neighboring group participation in the polymerization of 1. The trialkyloxonium ion is transiently formed at the growing terminal unit,[9] but it is immediately attacked by the carbonyl oxygen of the neighboring benzoyl subistituent with inversion of the C-1 configuration to form a dioxacarbenium ion (or benzoyloxonium ion). As a result, the incoming monomer can attack the reaction center exclusively from the opposite side of the dioxacarbenium ion, that is, the *β*-side of the pyranose ring, and the trialkyloxonium ion is regenerated. The relatively stable dioxacarbenium ion is responsible for the lower reactivity of 1 compared to the tribenzylated analogue.

References and Notes

(1) Paulsen, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 155–173.
(2) Srivastava, V. K.; Sondheimer, S. J.; Schuerch, C. *Carbohydr. Res.* **1980**, *86*, 203–214.
(3) Srivastava, V. K.; Schuerch, C. *Carbohydr. Res.* **1982**, *106*, 217–224.
(4) Bhattacharjee, A. K.; Zissis, E.; Glaudemans, C. P. J. *Carbohydr. Res.* **1981**, *89*, 249–254.
(5) Kováč, P. *Carbohydr. Res.* **1985**, *144*, C12–C14.
(6) Kováč, P. *Carbohydr. Res.* **1986**, *153*, 237–251.
(7) Glaudemans, C. P. J.; Zissis, E.; Jolley, M. E. *Carbohydr. Res.* **1974**, *40*, 129–135.
(8) Schuerch, C. *Adv. Carbohydr. Chem. Biochem.* **1981**, *39*, 157–212.
(9) Zachoval, J.; Schuerch, C. *J. Am. Chem. Soc.* **1969**, *91*, 1165–1169.
(10) Okada, M.; Sumitomo, H.; Sumi, A.; Sugimoto, T. *Macromolecules* **1984**, *17*, 2451–2453.
(11) Okada, M.; Sumitomo, H.; Sumi, A. *Carbohydr. Res.* **1985**, *143*, 275–281.
(12) Okada, M.; Sumitomo, H.; Sumi, A. *Macromolecules* **1982**, *15*, 1238–1242.
(13) Uryu, T.; Libert, H.; Zachoval, J.; Schuerch, C. *Macromolecules* **1970**, *3*, 345–349.
(14) Uryu, T.; Schuerch, C. *Macromolecules* **1971**, *4*, 342–345.
(15) Bock, K.; Pedersen, C. *J. Chem. Soc., Perkin Trans. 2* **1974**, 293–297.

Kazukiyo Kobayashi,* Haruo Ichikawa, and Hiroshi Sumitomo

Faculty of Agriculture, Nagoya University
Chikusa, Nagoya 464, Japan

Conrad Schuerch*

Department of Chemistry
College of Environmental Science and Forestry
State University of New York
Syracuse, New York 13210

Received October 8, 1987

Pressure-Induced Phases in a Thermotropic Polyester

Thermotropic liquid-crystalline polymers (LCPs) are currently being intensively investigated because their ordered fluid phases are precursors to high-performance polymeric solids (fibers, films, and injection-molded articles). In an effort to broaden the range of materials that might exhibit liquid crystallinity, we have examined the role of pressure on a copolyester of 20% hydroxybenzoic acid, 40% isophthalic acid, and 40% hydroquinone, "HIQ-20", whose composition lies just inside of the mesophase range. This work was motivated by observations that low molar mass (isotropic) liquids may be transformed into mesophases at elevated pressures.[1] Pressure-induced liquid crystallinity is simply a consequence of the reduced molar volume (relative to the isotropic state) that characterizes fluids having long-range orientational order. Chandrasekhar et al.[2] have reviewed this phenomenon in low molar mass liquid crystals. Pressure effects in LCPs have also been investigated.[3]

As anticipated, we find that at elevated pressure, the previously reported mesophase of HIQ-20 persists over a wider temperature range, but also, a second high-temperature mesophase is induced at elevated pressure. Additionally, we observe that cooling the mesophase into the solid state under moderate pressures (≥300 bar) yields a morphology that differs dramatically from that found in the solid cooled at ambient pressure. This observation is particularly noteworthy because the pressure required for forming the new solid morphology is comparable to or less than pressures employed in conventional processing techniques.

A rheological investigation and brief description of the synthesis of HIQ copolyesters at various HBA compositions has been recently reported by Kiss.[4] We confirmed by hot-stage optical microscopy and DSC that HIQ-20 exhibits a mesomorphic phase consisting of a melting transition (crystalline to mesomorphic) at 324 °C and a clearing transition (mesomorphic to isotropic) at 342 °C. The high-pressure differential thermal analysis (DTA) thermograms and the pressure–volume–temperature (P–V–T) relations were obtained with a Instron capillary rheometer modified to operate at a maximum temperature of 380 °C and a maximum pressure of 6000 bar (0.6 GPa). A detailed description of this apparatus, which was also used to prepare HIQ-20 specimens annealed and solidified at various pressures, has been given previously.[5]

The X-ray 2θ-scans of HIQ-20 specimens prepared at different pressures show significant differences, indicating that the structure in the solid state changes with the pressure applied during annealing and cooling. At atmospheric pressure the normally observed crystalline phase

0024-9297/88/2221-0543$01.50/0