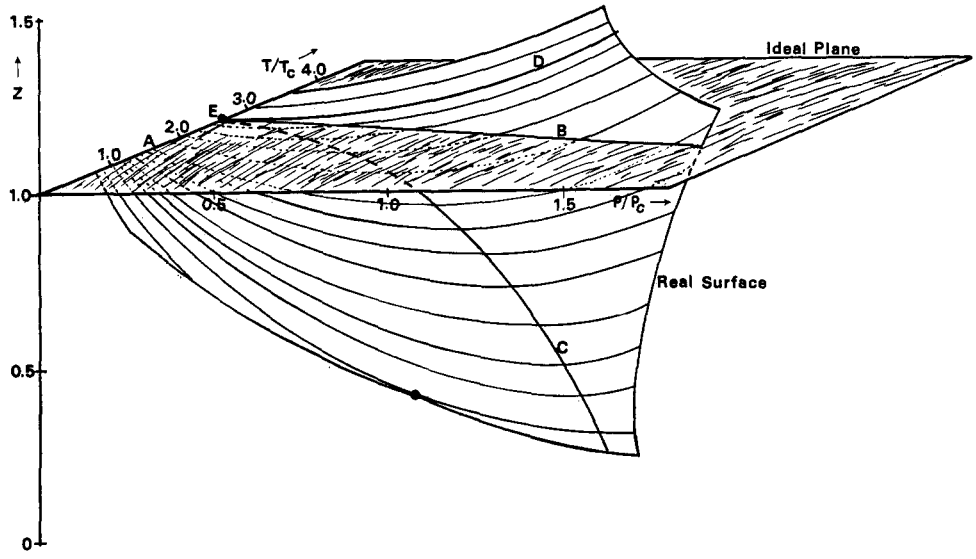

Figure 1. Compressibility factor (Z), reduced temperature, reduced density surface for a real gas, constructed from data given in ref 4.

coefficient is zero in the limit of infinite molecular weight. That is, the temperature T_Θ defined by

$$A_2(T_\Theta, \infty) = 0 \quad (13)$$

(2) A Θ *point* of a polymer solution at a given pressure is any point on the locus

$$A_2(T, \infty) + 2A_3(T, \infty)\phi + 3A_4(T, \infty)\phi^2 + \ldots = 0 \quad (14)$$

that is, the locus of minima in isothermal osmotic pressure plots (π/ϕ *vs.* ϕ) for the limit of infinite molecular weight. The only Θ point which occurs at the Θ temperature is then the point E (*cf.* Figure 1) at which $\phi = 0$ and eq 13 and 14 both apply.

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Polymerization of 1,6-Anhydro-2,3,5-tri-*O*-benzyl-α-D-galactofuranose

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Polysaccharides and their derivatives have been of great interest to chemists over the past century because of their abundance in nature as well as their possible important applications in biological, immunological, and medical fields.[1] However, the chemical synthesis of a limited number of high molecular weight stereoregular polysaccharides[2-5] has only recently been successfully carried out. Stereoregular [1→6]-α-D-glycopyranans have been synthesized by cationic polymerization of 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-glycopyranoses[2-5] followed by debenzylation with sodium in liquid ammonia. In order to extend the scope of the synthetic method to a new ring system and explore the possibility of chemical synthesis of a stereoregular [1→6]-glycofuranan, we have attempted to polymerize 1,6-anhydro-2,3,5-tri-*O*-benzyl-α-D-galactofuranose.

The monomer, 1,6-anhydro-2,3,5-tri-*O*-benzyl-α-D-galactofuranose, was prepared by conventional benzylation of 1,6-anhydro-2,3,5-tri-*O*-acetyl-α-D-galactofuranose[6] (mp 79–80°, $[\alpha]^{25}D$ 144.9° [*c* 1, $CHCl_3$]). The latter was obtained by pyrolysis of D-galactose under reduced pressure (~15 mm), followed by separation of levogalactosan and acetylation. The crude monomer mixture from benzylation was carefully steam distilled, dried, and purified by passing through a neutral alumina column. The structure of the syrupy monomer ($[\alpha]^{25}D$ +60.7° [*c* 0.6, $CHCl_3$]) was confirmed by nmr, ir, tlc, and carbon and hydrogen analysis. (*Anal.* Calcd: C, 75.00; H, 6.48. Found: C, 74.93; H 6.58.) The nmr spectrum of the monomer had a singlet at δ 7.33 (15 H, aromatic protons), a doublet at 5.32 (1 H, J = 4.3 cps, anomeric proton) and multiplets in the region of 4.66–3.71 (12 H). The infrared spectrum of the monomer showed no evidence of hydroxyl groups.

Polymerizations of 1,6-anhydro-2,3,5-tri-*O*-benzyl-α-D-galactofuranose were carried out in anhydrous methylene chloride using a high-vacuum technique.[3] Phosphorus pentafluoride and boron trifluoride etherate were used as catalysts. The results are shown in Table I.

Phosphorus pentafluoride did not cause polymerization at −78°, and most of the monomer was recovered unchanged. However, as the temperature of polymerization was increased from −78 to −30°, the yield of polymer (no. 2 and 3) increased. No significant difference in specific rotation between polymers 2 and 3 was observed, since the product from No. 2 might be contaminated with a small amount of monomer. When the polymerization was carried out at 0°, the specific rotation of the product became positive. Boron trifluoride etherate, a Lewis acid catalyst which caused stereospecific polymerization in the 1,6-anhydroglycopyranan series at temperatures from −20 to 25°, failed to polymerize the monomer at 0°.

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TABLE I
POLYMERIZATION OF 1,6-ANHYDRO-2,3,5-TRI-*O*-BENZYL-α-D-GALACTOFURANOSE

No.	Monomer wt, g	Mol % PF_5	Solvent CH_2Cl_2, ml	Time, hr	Temp, °C	Polymer yield, %	Recovered unreacted material, %	Polymer $[\alpha]^{25}D$,[a] deg	Soluble fraction in supernatant, $[\alpha]^{25}D$,[a] deg	$\bar{M}_n$[b]
1	0.435	13.0	0.50	48	−78	Trace	91		+57.3	
2	0.516	19.6	1.00	95.5	−60	15	85	−9.1	+44.9	755
3	0.332	32.4	0.50	125.5	−30	53	45	−17.0	+20.5	1145
4	0.462	22.7	0.50	125	0	57.7	36.7	+7.7	+33.1	1130
5	0.464	21.6[c]	0.50	143	0		98		+57.4	

[a] Determined in chloroform at 25°. [b] Determined by Mechrolab vapor pressure osmometer, Model 301A. [c] BF_3–Et_2O used as catalyst instead of PF_5.

The experimental results in Table I indicate an increasing rate of polymerization with rise in temperature. At low temperatures (−60 and −30°) the polymerization of 1,6-anhydro-2,3,5-tri-*O*-benzyl-α-D-galactofuranose seems to favor stereospecific attack to give largely β-linked product. Stereospecific attack of the monomer at C-1 (*via* an oxonium ion mechanism)[3,7] followed by cleavage of the 1,6 C–O linkage at the anomeric carbon could give the β-linked furanosyl polymer, whereas the stereospecific cleavage of the 1,4 C–O bond presumably would give a polymer of α linkages and seven-membered rings. If the carbonium ion mechanism[7,8] were operative in the polymerization, a polymer with mixed configuration, both α and β, would be obtained. This appears to be the case at 0°, and presumably the propagating center and its gegenion are sufficiently separated that the gegenion has little influence on the stereochemistry of polymerization.

On the basis of these data, 1,6-anhydro-2,3,5-tri-*O*-benzyl-α-D-galactofuranose seems to be relatively unreactive in polymerization, as might be expected from its molecular structure. The monomer is a tribenzyl ether of 2,8-dioxabicyclo[3.2.1]-octane which contains the ring structures of a substituted tetrahydrofuran, 1,3-dioxane and oxacycloheptane. It has been shown that substituted tetrahydrofurans[9] and 1,3-dioxane[10] do not undergo cationic polymerization due to lack of structural strain. Furthermore, when the anhydro galactofuranose assumes an almost strainless chair conformation of the 1,3-dioxane ring the C-5 substituent can adopt the equatorial position. Therefore, in converting the monomer to polymer, no considerable energy gain could be obtained from conformational changes or the release of structural strain. These factors are believed to be essential for the polymerization of tribenzyl ethers of 1,6-anhydroglycopyranoses. 6,8-Dioxabicyclo[3.2.1]octane,[11] a compound which has a skeleton identical with that of the 1,6-anhydroglycopyranoses, polymerizes sluggishly due to lack of ring strain and energy gain from conformational change.

These results suggest that monomers with similar ring systems such as 1,6-anhydro-2,3,5-tri-*O*-benzyl-β-D-gluco- and -mannofuranose may not polymerize as smoothly as the corresponding pyranose derivatives to give high molecular weight stereoregular glycofuranans. However, both 1,6-anhydro-2,3,5-tri-*O*-benzyl-β-D-gluco- and -mannofuranose possess unstable C-5 axial substituents and may, therefore, polymerize more favorably than 1,6-anhydro-2,3,5-tri-*O*-benzyl-α-D-galactofuranose.

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