Characterization of Polymers. The ^{13}C NMR spectra were recorded in the Fourier-transform-proton-noise-decoupled mode with a Varian XL-100-15 spectrometer. The ^{13}C NMR spectra of substituted glucopyranans were measured at ambient temperature in chloroform-*d* or benzene-d_6 with tetramethylsilane (Me_4Si) as the internal standard. The chemical shifts are expressed in ppm downfield of the internal Me_4Si absorption. The ^{13}C spectra of unsubstituted glucopyranans were recorded at 70 °C in dimethyl-d_6 sulfoxide, which also served as internal standard. Chemical shifts are expressed in ppm relative to the central absorption of dimethyl-d_6 sulfoxide (δ 39.5). A 60° pulse, 6151-Hz spectral width, 0.666-s acquisition time, and 8192 data points were used for all ^{13}C NMR spectra.

Optical rotations were determined in chloroform for benzylated or bromobenzylated polymers and in 1 N NaOH for free polysaccharides at 23 °C in a Perkin-Elmer Model 141 polarimeter with a jacketed 1-dm cell. Optical rotations for free polysaccharides were measured after allowing approximately 1 h for complete dissolution.

Molecular weight distributions of the substituted polymers were analyzed by gel permeation chromatography in tetrahydrofuran. A Glenco septumless injector (Model SV-3), a Glenco pump (Model HPLPS-1), a Waters differential refractometer (Model R-401), and five 30-cm-long stainless steel columns packed with micro-styragel (Waters, 1×10^5, 1×10^4, 1×10^3, 5×10^2, and 1×10^2 Å) were used. The flow rate was 2.0 mL/min. Calibration curves were obtained by using polystyrene standards (Waters). Viscosities were measured in chloroform with a Cannon-Ubbelohde viscometer at 25 °C. The absolute number-average molecular weights of the substituted polymers were determined in chloroform at 25 °C with a Mechrolab Model 301 vapor-phase osmometer.

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References and Notes

(1) Barretto-Bergter, E.; Gorin, P. H. J. "Advances in Carbohydrate Chemistry and Biochemistry"; Tipson, E. S., Horton, D., Eds.; Academic Press: New York, 1983; Vol. 41, pp 67–103.

(2) Walker, G. J.; Hare, M. D. *Carbohydr. Res.* **1977**, *58*, 415.

(3) Ebisu, S.; Misaki, A.; Kato, K.; Kotani, S. *Carbohydr. Res.* **1974**, *38*, 374.

(4) Schuerch, C. "Advances in Carbohydrate Chemistry and Biochemistry"; Tipson, E. S., Horton, D., Eds.; Academic Press: New York, 1982; Vol. 39, pp 157–212.

(5) Varma, A. J.; Schuerch, C. *J. Org. Chem.* **1981**, *46*, 700.

(6) Kong, F.; Schuerch, C. *Carbohydr. Res.* **1983**, *112*, 141.

(7) Ito, H.; Eby, R.; Kramer, S.; Schuerch, C. *Carbohydr. Res.* **1980**, *86*, 193.

(8) Good, F.; Schuerch, C. *Carbohydr. Res.* **1984**, *125*, 165.

(9) Good, F. J., Jr. *Org. Magn. Reson.*, accepted for publication.

(10) Ito, H.; Schuerch, C. *Macromolecules* **1981**, *14*, 246.

(11) Kong, F.; Schuerch, C. *Macromolecules* **1984**, *17*, 983.

(12) Uryu, T.; Yamanouchi, J.; Kato, T.; Higuchi, S.; Matsuzaki, K. *J. Am. Chem. Soc.* **1983**, *105*, 6865.

(13) Uryu, T.; Kitano, K.; Ito, K.; Yamanouchi, J.; Matsuzaki, K. *Macromolecules* **1981**, *14*, 1.

(14) Higashimura, T.; Sawamoto, M. "Abstracts", IUPAC, 6th International Symposium on Cationic Polymerization and Related Processes, Ghent, Belgium, 1983, pp 15–18.

(15) Hoffman, G. C.; Simson, B. W.; Timell, T. *Carbohydr. Res.* **1971**, *20*, 185.

(16) Zachoval, J.; Schuerch, C. *J. Am. Chem. Soc.* **1969**, *91*, 1165.

(17) Uryu, T.; Schuerch, C. *Macromolecules* **1971**, *4*, 342.

(18) Jeanes, A.; Haynes, W. C.; Wilham, C. A.; Rankin, J. C.; Melvin, E. H.; Austin, M. J.; McCluskey, J. E.; Fisher, B. E.; Tsuchiya, H. T.; Rist, C. E. *J. Am. Chem. Soc.* **1954**, *76*, 5041.

(19) Colson, P.; Jennings, H. J.; Smith, I. C. P. *J. Am. Chem. Soc.* **1974**, *96*, 8081.

(20) Vogel, A. I. "A Text-book of Practical Organic Chemistry", 3rd ed.; Longman: London, 1956; pp 815–16.

(21) Dauben, H. J.; Honnen, L. R.; Harmon, K. M. *J. Org. Chem.* **1960**, *25*, 1442.

(22) Ruckel, E. R.; Schuerch, C. *J. Org. Chem.* **1966**, *31*, 2233.

(23) Ruckel, E. R.; Schuerch, C. *J. Am. Chem. Soc.* **1966**, *88*, 2605.

(24) Fengel, D.; Wegener, G., presented at the Spring Meeting of the Cellulose, Paper, and Textile Division, American Chemical Society, Appleton, WI, May 17–19, 1978, paper no. 17.

Ring-Opening Polymerization of 1,4-Anhydro-2,3,6-tri-*O*-benzyl-α-D-glucopyranose and 1,4-Anhydro-2,3,6-tri-*O*-benzyl-β-D-galactopyranose

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ABSTRACT: Ring-opening polymerization of 1,4-anhydro-2,3,6-tri-*O*-benzyl-α-D-glucopyranose (ABGLU) (=1,5-anhydro-2,3,6-tri-*O*-benzyl-β-D-glucofuranose) by phosphorus pentafluoride catalyst gave new stereoregular polysaccharide derivatives, 2,3,6-tri-*O*-benzyl-(1→5)-α-D-glucofuranans with $[\alpha]_D$ value of +82° and number-average molecular weights of 8.5×10^3 ($\overline{DP}_n = 20$). Natural cellulose and amylose, (1→4)-β-D-glucopyranan and (1→4)-α-D-glucopyranan, respectively, were used to determine the structure of the synthetic glucan by means of ^{13}C NMR spectroscopy and optical rotation. Cationic catalysts other than phosphorus pentafluoride provided poly(ABGLUs) with mixed structures depending on the polymerization conditions. The ring-opening polymerization of 1,4-anhydro-2,3,6-tri-*O*-benzyl-β-D-galactopyranose (ABGAL) (=1,5-anhydro-2,3,6-tri-*O*-benzyl-α-D-galactofuranose) yielded polymers with mixed structures consisting, under all polymerization conditions employed, mainly of (1→5)-β-D-galactofuranosidic units. The structure of poly(ABGALs) was influenced by relatively minor changes in polymerization conditions. The mechanism of the ring-opening polymerization of ABGLU and ABGAL is discussed.

In addition to the successful synthesis of dextran-type polysaccharides from several D-aldohexoses,[1,2] a cellulose-type polysaccharide, (1→4)-β-D-ribopyranan, has been prepared with D-ribose as the starting monosaccharide.[3] Although it has been revealed that the ring-opening polymerization of 1,6-anhydro sugars is an excellent method for obtaining stereoregular (1→6)-α-D-glycopyranans, the application of the same method to 1,4-anhydro sugars has not always provided a cellulose-type polysaccharide, i.e., a (1→4)-β-D-glycopyranan. Previously, 1,4-anhydro-α-D-

Table I
Ring-Opening Polymerization of 1,4-Anhydro-2,3,6-tri-*O*-benzyl-α-D-glucopyranose by Lewis Acid Catalysts[a]

no.	catalyst	mol % to monomer	temp, °C	time, h	yield, %	$[\alpha]^{25}_{\mathrm{D}}$,[b] deg	$10^{-3}\overline{M}_n$
1	PF_5	3	−20	96	44.5	+82.2	8.5
2[c]	PF_5	5	−40	263	73.5	+70.0	5.8
3	PF_5	10	−60	94	46.8	+71.2	6.1
4	PF_5	10	−78	116	58.3	+82.4	8.5
5	$SbCl_5$	5	0	142	15.5	+54.2	6.2
6	$SbCl_5$	5	−20	159	55.7	+59.2	3.0
7	$SbCl_5$	5	−40	140	40.0	+70.9	9.0
8[c]	$SbCl_5$	5	−40	264	37.0	+62.6	4.9
9	$SbCl_5$	5	−78	43	44.4	+76.8	10.9
10	$BF_3{\cdot}O(C_2H_5)_2$	5	−20	115	63.6	+69.4	9.0
11	$BF_3{\cdot}O(C_2H_5)_2$	5	−78	241	6.2	+35.0	9.7
12	$SnCl_4$	7	−78	136	0		

[a] Monomer (0.2 g) was polymerized at a 100% w/v monomer concentration. Solvent, CH_2Cl_2. [b] Measured in $CHCl_3$ (*c* 1%). [c] Monomer concentration 50% w/v. Solvent, toluene.

ribopyranose derivatives have been polymerized into (1→4)-β-D-ribopyranan, but a 1,4-anhydro-α-D-xylopyranose derivative did not give the cellulose-type polysaccharide, but a new synthetic polysaccharide, (1→5)-α-D-xylofuranan.[4]

Furthermore, the polycondensation of unsubstituted[5] and substituted D-glucoses[6] failed to provide a stereoregular cellulose with high molecular weight. Kops and Schuerch first investigated the cationic ring-opening polymerization of 1,4-anhydro-2,3,6-tri-*O*-methyl-β-D-galactopyranose, revealing that the polymer obtained has fairly high molecular weight but low stereoregularity.[7]

Micheel and co-workers attempted the stereospecific ring-opening polymerization of 1,4-anhydro-2,3,6-tri-*O*-benzyl-α-D-glucopyranose with the aim of synthesizing cellulose.[8,9] They reported that the polymers obtained were composed of mixed structures of mainly (1→4)-β-linked (cellulose type) and (1→4)-α-linked (amylose type) D-glucopyranosidic units, though the molecular weight was low. Since 1,4-anhydro-α-D-glucopyranose, which can equally be regarded as 1,5-anhydro-β-D-glucofuranose, has two ring-opening modes of 1,4- or 1,5-ring scission, there are four possible structural units in the polymer obtained, which are caused by the ring-opening modes and the α- and β-configurations. Thus, Micheel and co-workers revealed that it was possible to control the bond to be cleaved. However, Kops and Schuerch found that in the polymerization of the 1,4-anhydrogalactopyranose the structure of the polymer obtained consisted mainly of (1→5)-linked units. Furthermore, 2,7-dioxabicyclo[2.2.1]heptane, which is considered to be a model compound of the 1,4-anhydro sugar, has been polymerized by cationic catalysts to give a polymer with a backbone structure consisting of five-membered rings.[10]

We have reported that the selective ring-opening polymerization of 1,4-anhydroglycopyranose derivatives depends on the kind of monosaccharide, the O-substituents, and the polymerization conditions, especially the kind of catalyst.[3,11]

In this study, we have investigated the possibility of synthesizing (1→4)-β-D-glucopyranan (cellulose) and (1→4)-α-D-galactopyranan through the selective ring-opening polymerization of 1,4-anhydro-2,3,6-tri-*O*-benzyl-α-D-gluco- and -β-D-galactopyranoses, respectively. The structures of synthetic polyglucose derivatives are elucidated by comparing their ^{13}C NMR spectra with those of benzylated natural cellulose and amylose.

Results and Discussion

Ring-Opening Polymerization of 1,4-Anhydro-2,3,6-tri-*O*-benzyl-α-D-glucopyranose (ABGLU). ABGLU was polymerized by various cationic catalysts at low temperatures from 0 to −78 °C. The results of polymerizations are summarized in Table I. When the polymerization was carried out with phosphorus pentafluoride as catalyst in methylene chloride, poly(1,4-anhydro-2,3,6-tri-*O*-benzyl-D-glucopyranoses) [poly(ABGLUs)] with high positive specific rotations of +71° to 82° were obtained in 44–58% yield (nos. 1, 3, and 4). The specific rotation of poly(ABGLUs) prepared by $SbCl_5$ catalyst increased from +54° to +77° as the temperature of polymerization was decreased from 0 to −78 °C (nos. 5–9). Although the polymerization with boron trifluoride etherate as the catalyst gave the polymer only in low yield, increasing temperature resulted in the formation of polymer in 64% yield. Stannic chloride did not produce any polymer at −78 °C in a longer period, perhaps due to too low temperature. With a change to a less polar solvent, toluene, lower specific rotations of polymers were obtained (nos. 2 and 8).

Number-average molecular weights of the polymers were in the range of 3.0×10^3 ($\overline{DP}_n = 8$) to 11×10^3 ($\overline{DP}_n = 25$) under the various experimental conditions shown in Table I. The highest molecular weight was obtained with antimony pentachloride at −78 °C. Since, in the cationic polymerization of di-*O*-benzylated 1,4-anhydropentoses, it was found that polymers with very large molecular weights were achieved with such moderate Lewis acids as boron trifluoride etherate and stannic chloride,[4,11] the low molecular weight of the glucan derivatives may be attributable to the presence of the 6-benzyloxymethyl group in ABGLU and to impurities in the monomer.

When ABGLU was also polymerized by catalysts other than complexing Lewis acids, results were somewhat different, as shown in Table II. Polymerizations with $((C_2H_5)_3O)BF_4$, CF_3SO_3H, and $(CF_3SO_2)_2O$ as catalyst afforded poly(ABGLUs) with lower positive specific rotations than those of the polymers catalyzed by PF_5 and $SbCl_5$. The triethyloxonium tetrafluoroborate catalyst produced the poly(ABGLU) with the lowest positive $[\alpha]_{\mathrm{D}}$ +22.5°, in agreement with Micheel and Brodde.[9] Coordination catalysts based on $Al(i\text{-}Bu)_3$ did not produce any polymer from ABGLU, although it was recently found that they are good catalysts for the ring-opening polymerization of oxacyclobutane derivatives with low polymerizability.[12]

Structure of Poly(ABGLU). There are four possible structural units in the poly(D-glucose) prepared by the ring-opening polymerization of 1,4-anhydro-2,3,6-tri-*O*-benzyl-α-D-glucopyranose, namely, the (1→4)-β- ((1→4)-β-P) (1) and (1→4)-α-D-glucopyranosidic ((1→4)-α-P) (2) units and the (1→5)-β- ((1→5)-β-F) (3) and (1→5)-α-D-glucofuranosidic ((1→5)-α-F) (4) units (Figure 1). The structure of the synthetic glucan was determined by ^{13}C NMR spectroscopy and optical rotation. Since there are no available ^{13}C NMR spectra of benzylated cellulose and

Table II
Ring-Opening Polymerization of 1,4-Anhydro-2,3,6-tri-*O*-benzyl-α-D-glucopyranose by Various Catalysts[a]

no.	catalyst	mol % to monomer	temp, °C	time, h	yield, %	$[\alpha]^{25}_{D}$,[b] deg	$10^{-3}\bar{M}_n$
13[c]	$((C_2H_5)_3O)BF_4$	10	−20 0	90 112	24.0	+66.6	13.0
14	$((C_2H_5)_3O)BF_4$	10	−78↓	94↓	55.7	+22.5	3.7
15	CF_3SO_3H	2	−40	96	75.9	+40.0	8.7
16[d]	$(CF_3SO_2)_2O$	5	0	138	44.1	+33.4	2.4
17	$(CF_3SO_2)_2O$	2	−78	70	10.0	+30.8	2.5
18[e]	$(i\text{-}Bu)_3Al\text{–}H_2O$ (1:0.5)		−78	112	0		
19[e]	$(i\text{-}Bu)_3Al\text{–}H_2O\text{–}Acac$ (1:0.4:0.8)		+30	190	0		

[a] Monomer (0.2 g) was polymerized at a 100% w/v monomer concentration. Solvent, CH_2Cl_2. [b] Measured in $CHCl_3$ (*c* 1%). [c] Monomer concentration 50% w/v. [d] Monomer concentration 50% w/v. Solvent, toluene. [e] Monomer concentration 40% w/v. Solvent, toluene. Concentration of initiator ($(i\text{-}Bu)_3Al$ basis), 0.07 mol/L.

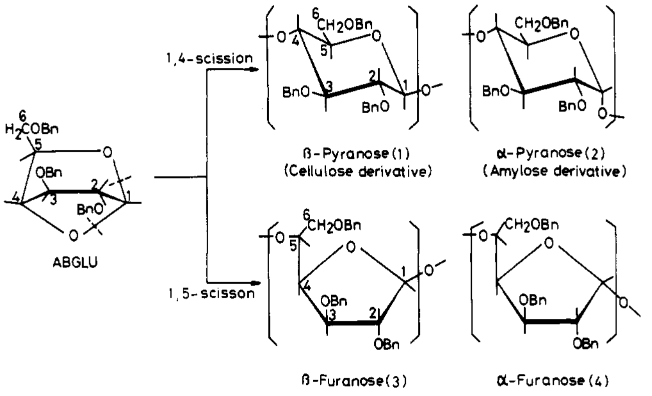


Figure 1. Ring-opening modes of 1,4-anhydro-2,3,6-tri-*O*-benzyl-α-D-glucopyranose.

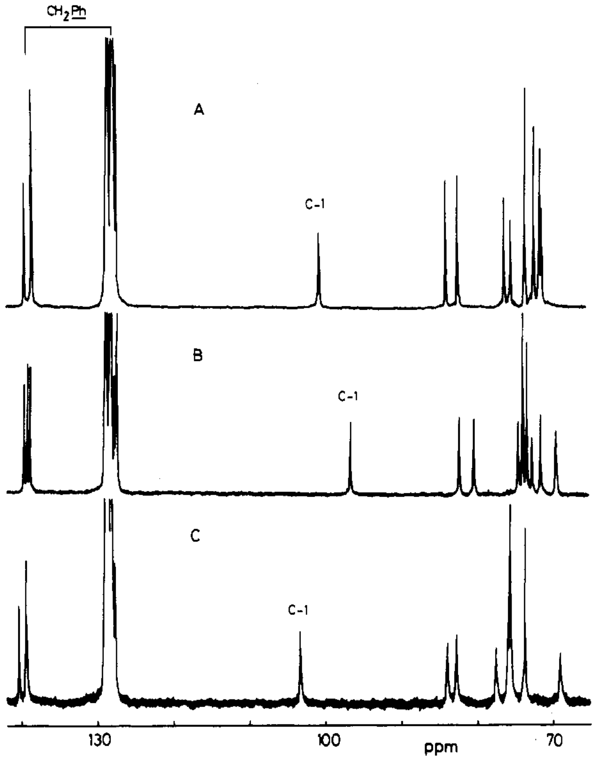


Figure 2. ^{13}C NMR spectra of (A) 2,3,6-tri-*O*-benzyl-(1→5)-α-D-glucofuranan prepared by PF_5 ($[\alpha]_D$ +82.4°), (B) benzylated amylose ($[\alpha]_D$ +78.0°), and (C) benzylated cellulose ($[\alpha]_D$ +16.1°) (CD_2Cl_2 as solvent).

amylose, the natural polysaccharides were benzylated.

^{13}C NMR spectra of synthetic and natural benzylated glucans are shown in Figure 2. In the spectrum 2A of poly(ABGLU) having $[\alpha]_D$ +82.4° (no. 4 in Table I), individual carbon absorptions due to the sugar moiety appear as single peaks, indicating that the polymer has high stereoregularity. Taking into account the high positive specific rotation, one may conclude that this poly(ABGLU) is 2,3,6-tri-*O*-benzyl-(1→5)-α-D-glucofuranan (4) or 2,3,6-tri-*O*-benzyl-(1→4)-α-D-glucopyranan (2).

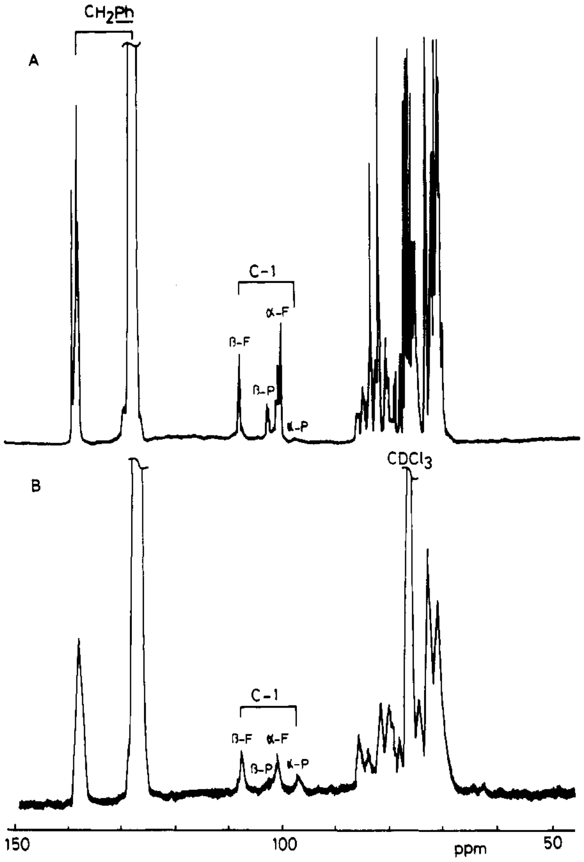


Figure 3. ^{13}C NMR spectra of poly(1,4-anhydro-2,3,6-tri-*O*-benzyl-D-glucopyranose) prepared by (A) CF_3SO_3H ($[\alpha]_D$ +40.0°) and (B) $((C_2H_5)_3O)BF_4$ ($[\alpha]_D$ +22.5°) (Me_4Si as reference zero).

In order to determine the structure of the synthetic glucan, ^{13}C NMR spectrum of the poly(ABGLU) was compared with that of a natural benzylated amylose which is 2,3,6-tri-*O*-benzyl-(1→4)-α-D-glucopyranan. Spectrum 2B of benzylated amylose having $[\alpha]_D$ +78° is completely different from spectrum 2A of the synthetic benzylated glucan. For instance, the C-1 absorptions of the benzylated amylose and of the synthetic benzylated glucan appear at 96.7 and 101.1 ppm, respectively. Since the synthetic glucan with high positive specific rotation is a glucan derivative, the structure of which is different from amylose, it was concluded that the stereoregular polymer is 2,3,6-tri-*O*-benzyl-(1→5)-α-D-glucofuranan. The NMR spectrum 2C of the benzylated cellulose with $[\alpha]_D$ +16.1°, that is, 2,3,6-tri-*O*-benzyl-(1→4)-β-D-glucopyranan, is also different from the spectrum of the synthetic one.

Table III
Structure of Poly(1,4-anhydro-2,3,6-tri-*O*-benzyl-D-glucopyranoses) Prepared under Different Conditions

	polymerization conditions			polymer structure,[a] %			
no.	catalyst	temp, °C	$[\alpha]^{25}_{D}$, deg	(1→5)-α-F	(1→5)-β-F	(1→4)-α-P	(1→4)-β-P
1	PF_5	-78	+82.4	100	0	0	0
2	PF_5	-40	+70.0	86	7	4	3
3	$SbCl_5$	-20	+59.2	87	13	0	0
4	CF_3SO_3H	-40	+40.0	53	29	1	17
5	$(CF_3SO_2)_2O$	0	+33.4	21	11	32	36
6	$((C_2H_5)_3O)BF_4$	0 → -78	+22.5	31	36	15	18

[a] Determined from the proportion of C-1 absorptions in ^{13}C NMR spectrum of poly(ABGLU).

Table IV
^1H Chemical Shifts and Coupling Constants of 1,4-Anhydro-2,3,6-tri-*O*-benzyl-α-D-glucopyranose (ABGLU) and 1,4-Anhydro-2,3,6-tri-*O*-benzyl-β-D-galactopyranose (ABGAL)[a]

	chemical shift, ppm							
	H-1	H-2	H-3	H-4	H-5	H-6	H-6′	$3CH_2C_6H_5$
ABGLU	5.36 s	3.61 d	3.91 s	4.55 q	4.04 q′	3.75 q	3.80 q	4.34–4.51
ABGAL	5.46 d	3.84 d	3.55 d	4.59 d	3.82 q	3.43 q	3.35 q	4.46–4.62
	coupling constant, Hz							
	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{4,6}$	$J_{4,6'}$	$J_{5,6}$	$J_{5,6'}$	$J_{6,6'}$
ABGLU	0	2.08	5.00	3.85	7.63	4.27	7.63	4.27	10.53
ABGAL	2.29	1.22	0	1.52	0	0	4.96	7.93	9.46

[a] s, singlet; d, doublet; q, quartet; q′, quintet.

Table V
Ring-Opening Polymerization of 1,4-Anhydro-2,3,6-tri-*O*-benzyl-β-D-galactopyranose by Lewis Acid Catalyst[a]

no.	catalyst	mol % to monomer	temp, °C	time, h	yield, %	$[\alpha]^{25}_{D}$,[d] deg	$10^{-3}\bar{M}_n$
1	PF_5	5	0	116	72	+12.8	2.3
2	PF_5	3	-20	165	68	-1.6	3.2
3	PF_5	10	-40	114	74	+5.8	2.6
4[b]	PF_5	5	-40	73	59	+17.3	2.9
5[c]	PF_5	10	-60	69	17	-2.8	3.6
6	PF_5	10	-78	166	58	-2.2	2.9
7	PF_5	3	-78	93	40	-10.7	3.4
8	$SbCl_5$	3	0	140	57	-2.9	2.7
9	$SbCl_5$	3	-20	141	68	+0.2	3.4
10	$SbCl_5$	5	-40	48	27	+6.7	2.5
11	$SbCl_5$	5	-50	70	8	+5.5	2.3
12	$SbCl_5$	3	-78	71	6	+0.6	3.3
13	$BF_3{\cdot}O(C_2H_5)_2$	7	-78	91	0		

[a] Monomer (0.2 g) was polymerized at a 100% w/v monomer concentration. Solvent, CH_2Cl_2. [b] Solvent, toluene. [c] Monomer concentration 50% w/v. [d] Measured in $CHCl_3$ (*c* 1%).

On the other hand, ^{13}C NMR spectra of poly(ABGLUs) with low $[\alpha]_D$ values are shown in Figure 3. Spectrum 3A of the polymer prepared by CF_3SO_3H catalyst indicates that the C-1 absorptions consist of four peaks at 108, 103, 101, and 97 ppm, of which the peak at 97 ppm is very small. As shown in the spectrum 3B of the polymer having $[\alpha]_D$ +22.5°, which was prepared by $((C_2H_5)_3O)BF_4$ catalyst, the intensities of the four peaks are different from those of the polymer having $[\alpha]_D$ +40.0°, although the peaks are broad probably because of low molecular weight of the former polymer. Since the C-1 absorptions of the benzylated cellulose and amylose appear at 103.4 and 96.7 ppm, respectively, the four C-1 peaks at 108, 103, 101, and 97 ppm can be assigned to the (1→5)-β-F, (1→4)-β-P, (1→5)-α-F, and (1→4)-α-P units. For several polymers prepared under different conditions, the four structural units were determined from the ^{13}C NMR spectra (Table III). It was revealed that the polymers prepared by CF_3SO_3H, $(CF_3SO_2)_2O$, and $((C_2H_5)_3O)BF_4$ initiators are composed of high proportions of (1→4)-D-glucopyranosidic units. For instance, the polymer with $[\alpha]_D$ +33.4° which was prepared with $(CF_3SO_2)_2O$ as initiator consisted of 32% (1→4)-α-P and 36% (1→4)-β-P units, although the molecular weight was very low. Micheel and co-workers reported that the $((C_2H_5)_3O)BF_4$ initiator afforded a polymer composed of (1→4)-D-glucopyranosidic units,[9] but we could not reproduce their result. The PF_5 and $SbCl_5$ catalysts provided polymers rich in (1→5)-D-glucofuranosidic units.

Ring-Opening Polymerization of 1,4-Anhydro-2,3,6-tri-*O*-benzyl-β-D-galactopyranose (ABGAL). The structure of a new compound ABGAL was analyzed by means of ^1H NMR spectroscopy, as the results are shown in Table IV as well as those of ABGLU. ABGAL was also polymerized by Lewis acid catalysts at low temperatures from 0 to -78 °C, as shown in Table V. When the polymerization was performed with phosphorus pentafluoride catalyst, poly(ABGALs) with $[\alpha]_D$ of -11° to +13° were obtained in 40–72% yield. The change to a less polar solvent, toluene, resulted in the formation of polymer with a little higher positive rotation +17°. Similarly, antimony pentachloride as catalyst also gave poly(ABGALs) with $[\alpha]_D$ of -3° to +7° in fairly high yield (nos. 8–10 in Table V), but the yields are low in the polymerization at lower temperatures (nos. 11 and 12). Polymerization by boron trifluoride etherate at -78 °C did not produce any polymer in 91 h. Table V indicates that the specific rotation of poly(ABGALs) was influenced by relatively minor changes

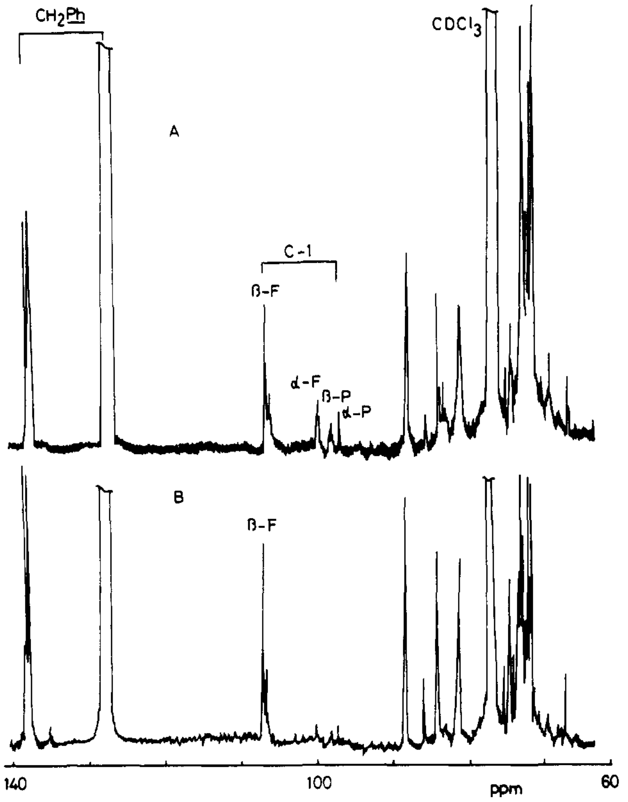


Figure 4. ^{13}C NMR spectra of poly(1,4-anhydro-2,3,6-tri-*O*-benzyl-D-galactopyranose) prepared by PF_5: (A) $[\alpha]_D$ +5.8°, (B) $[\alpha]_D$ −10.7° (Me_4Si as reference zero).

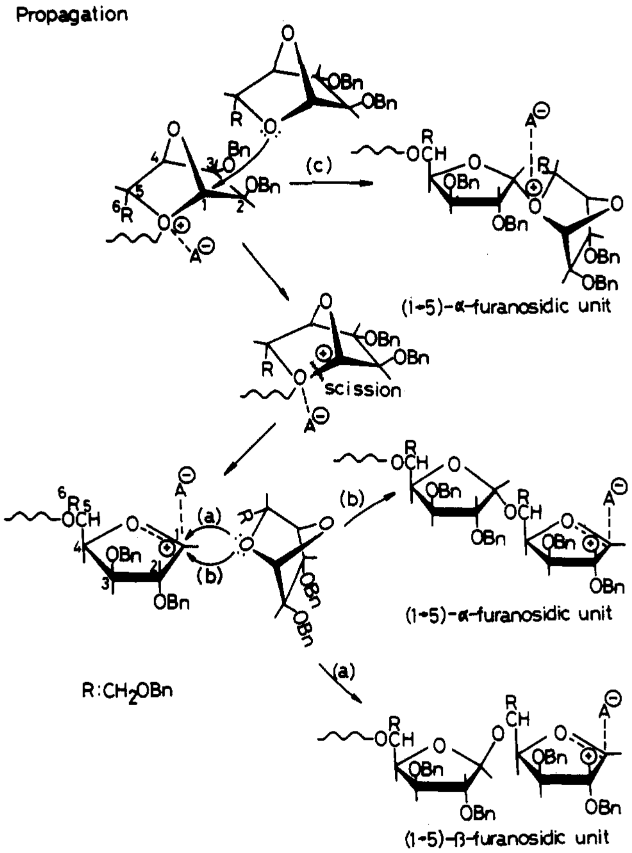
in such polymerization conditions as temperature, time, and solvent as well as the kind of catalyst.

Number-average molecular weights of the poly(ABGALs) were low in the range of 2.3 × 10^3 ($\overline{DP}_n$ = 5) to 3.6 × 10^3 ($\overline{DP}_n$ = 8), which are much lower than those of the polyglucose derivatives prepared under similar conditions. The low molecular weights of poly(ABGALs) may be attributable to the steric hindrance caused by the three bulky benzyl groups in ABGAL, because in the polymerization of tri-*O*-methylated 1,4-anhydro-β-D-galactopyranose fairly high molecular weights ($\overline{DP}_n$ = 30–90) were obtained.[7]

Structure of Poly(ABGAL). ^{13}C NMR spectra of poly(ABGALs) with different specific rotations are shown in Figure 4. Comparing the spectrum 4B of the poly(ABGAL) having $[\alpha]_D$ −10.7° with spectrum 4A of poly(ABGAL) having $[\alpha]_D$ +5.8°, we recognize that the former polymer has very high stereoregularity. The splitting of individual carbon absorptions is considered to be due to the low molecular weight of polymers. Taking into account the negative specific rotation and the mechanism of ring-opening polymerization leading to stereoregular polymer, which will be described later, we concluded that the poly(ABGAL) with $[\alpha]_D$ −10.7° is predominantly 2,3,6-tri-*O*-benzyl-(1→5)-β-D-galactofuranan.

On the other hand, spectrum 4A of the poly(ABGAL) with a positive specific rotation of +5.8° shows that the absorption due to C-1 carbon appears as four peaks. The assignments of the ^{13}C NMR absorptions were based on the optical rotation and a comparison with the chemical shifts of methyl D-galactosides[7,13], assuming that there are minor differences due to etherification and solvent change. For several poly(ABGALs), the increase in proportions of C-1 absorptions at 106.9 and 98.1 ppm caused the increase in the negative specific rotation, while the absorptions at 100.1 and 97.1 ppm contributed to the positive specific rotation. Thus, the C-1 absorptions at 106.9, 100.1, 98.1, and 97.1 ppm were assigned to (1→5)-β-D- and (1→5)-α-D-galactofuranosidic untis, (1→4)-β-D- and (1→4)-α-D-galactopyranosidic units, respectively. For a poly(ABGAL) with $[\alpha]_D$ +5.8°, the proportions of the four structural units were determined from the ^{13}C NMR spectrum to be 65, 20, 7, and 8%, respectively. All the poly(ABGALs) prepared under various conditions had mixed structures consisting mainly of (1→5)-β-D-galactofuranosidic units.

Scheme I



Mechanism of Polymerization. The ring-opening polymerization of AGBLU is considered to proceed via both a trialkyloxonium ion mechanism (S_N2 type) and a carbenium ion mechanism (S_N1 type), as was the case in the ring-opening polymerization mechanism of 1,4-anhydro-2,3-di-*O*-benzyl-α-D-xylopyranose (ABXP).[4]

A stereoregular structure consisting exclusively of (1→5)-α-D-glucofuranosidic units can be attained by a trialkyloxonium ion mechanism, as shown in Scheme I, c. The selective 1,5-ring opening of ABGLU can be interpreted as due to a possibly higher nucleophilicity of the 1,5-linked oxygen than that of the 1,4-linked oxygen, or by the antiperiplanar theory of Deslongchamps et al.,[14] as in the case of the selective 1,5-ring opening polymerization of ABXP.

On the other hand, Scheme I, a and b, indicates that a mixed structure consisting of (1→5)-α- and (1→5)-β-D-glucofuranosidic units can be formed by a carbenium ion mechanism. The mechanism has been described in detail in the polymerization of ABXP.[4] It was revealed that the polymerization of ABGLU by $SbCl_5$ and some other catalysts (Table II) proceeds predominantly via a carbenium ion mechanism.

It seems that in the polymerization of ABGLU the substituents at C-2 and C-3 positions play an important role in chain propagation, as was already observed in the polymerization of 1,4-anhydropentose derivative.

ABGLU is only different from ABXP with respect to the C-5 substituent. The significant question is what the effect will be of the additional C-5 substituent on the chain propagation. The low degree of polymerization ($\overline{DP}_n$ = ~25) of poly(ABGLUs) can be compared with the high DP ($\overline{DP}_n$ = 32–477) of poly(ABXPs). Although it was found that mild catalysts $BF_3{\cdot}OEt_2$ and $SnCl_4$ were good catalysts for producing high yield and high molecular weight poly(ABXPs),[4] they did not produce high molecular weight poly(ABGLUs). Therefore, the C-5 substituent in the ABGLU was found to influence steric hindrance of the chain propagation and to lower the polymerizability of the monomer.

ABGAL is different from ABGLU with respect to the direction of the 1,4-ring; that is, ABGAL has the opposite configuration at C-1 and C-4 compared with ABGLU. Therefore, if the selective 1,5-ring opening polymerization of ABGAL via a trialkyloxonium ion mechanism occurs, a stereoregular structure consisting exclusively of (1→5)-β-D-galactofuranosidic unit will be obtained. The stereoregular structure was almost achieved in the ring-opening polymerization of ABGAL in this study. Since poly(ABGALs) are composed of mainly (1→5)-β-D-galactofuranosidic unit, the chain propagation mechanism of ABGAL is assumed to be similar to that of ABGLU. The degree of polymerization in poly(ABGALs) is lower than that in poly(ABGLUs), implying that the chain propagation of ABGAL polymerization is more influenced by steric hindrance originating from the monomer structure than that of ABGLU.

Experimental Section

Synthesis of 2,3,6-Tri-*O*-benzyl-D-glucose (5). 5 was synthesized by hydrolysis of benzylated starch. To a starch (300 g) solution in 20% sodium hydroxide (aqueous, 3.6 L), benzyl chloride (750 mL) was added and the solution was stirred overnight at 60 °C. The reaction mixture was successively washed with a large quantity of water and methanol several times and dried in vacuo. After the benzylation was repeated, the partially benzylated compound was thoroughly benzylated according to the method of Hakomori.[15] The yield of the yellow benzylated starch was 23%, $[\alpha]^{25}_D$ +78.0° (*c* 1%, $CHCl_3$). To a benzylated starch (180 g) solution in 5 L of dioxane, 600 mL of 50% sulfuric acid (aqueous) was added, and the solution was stirred for 20 h at 95 °C. The solution was neutralized with 30% sodium hydroxide (aqueous), filtered, and evaporated to dryness. The syrup was extracted with chloroform, followed by evaporating to dryness. The dried compound was then extracted with ethanol. After a workup procedure, the compound was separated by mean of silica gel column chromatography, using 3:1 benzene–ethyl acetate. 5 was recrystallized from benzene–petroleum ether: yield, about 50%; mp 106–107 °C (lit.[16] mp 108 °C).

Cellulose was benzylated by using the same method as that of starch, and the benzylated cellulose was used for the NMR measurement, $[\alpha]^{25}_D$ +16.1° (*c* 1%, $CHCl_3$).

1,4-Anhydro-2,3,6-tri-*O*-benzyl-α-D-glucopyranose (ABGLU) (8). ABGLU was synthesized from 5 according to the modification of Micheel and Kreuzer's method.[16] 2,3,6-Tri-*O*-benzyl-α-D-glucopyranosyl chloride (6) was prepared by the reaction of 5 (7 g) with dry hydrogen chloride. 6 was reacted with silver fluoride (12 g) to give 2,3,6-tri-*O*-benzyl-β-D-glucopyranosyl fluoride (7). Potassium *tert*-butoxide (12 g) was added to the 7 solution in toluene. The solution was kept for 1 day at room temperature, filtered, and then evaporated to a dark brown syrup. This syrup was separated by means of silica gel column chromatography, using 10:1 benzene–ethyl acetate, and 8 was obtained as slightly yellow syrup: yield of 8 based on 5, about 30%; $[\alpha]^{20}_D$ −9.7° (*c* 1%, $CHCl_3$) (lit.[8] $[\alpha]^{20}_D$ −9.6° (*c* 1%, $CHCl_3$)).

1,4-Anhydro-2,3,6-tri-*O*-benzyl-β-D-galactopyranose (ABGAL) (13). ABGAL was synthesized from the 2,3,6-tri-*O*-benzyl-D-glucose 5 according to the modification of Kops and Schuerch's method which gave the 1,4-anhydrotri-*O*-methylgalactose.[18] Methyl 2,3,6-tri-*O*-benzyl-D-glucopyranoside (9) was prepared from 5. 5 (15 g) was added to 150 mL of anhydrous methanol containing 1% hydrogen chloride and refluxed overnight in the presence of $CaSO_4$. The solution was neutralized by bubbling anhydrous ammonia. The compound was separated by means of silica gel column chromatography, using 3:1 benzene–ethyl acetate. The yield of the colorless syrup **9** was 84%. Methyl 2,3,6-tri-*O*-benzyl-4-*O*-tosyl-D-glucopyranoside (**10**) was prepared by adding 6.7 g of *p*-toluenesulfonyl chloride to a **9** (13 g) solution in 14 mL of dry pyridine, followed by keeping the solution for 4 days at room temperature. The syrup obtained was separated by means of silica gel column chromatography, using 3:1 benzene–ethyl acetate. The yield of the colorless syrup **10** was 95%. 1,6-Di-*O*-acetyl-2,3-di-*O*-benzyl-4-*O*-tosyl-D-glucopyranose (11) was prepared according to the method for synthesizing the 1,6-anhydrotri-*O*-benzylmannopyranose.[19] A cold solution of sulfuric acid (0.2 mL) in acetic anhydride (8 mL) was added to **10** (11.3 g) in acetic anhydride (32 mL). The mixture was stirred for 75 min at room temperature, then poured into ice water, and stirred overnight. The crude syrup was separated by means of silica gel column chromatography, using 6:1 benzene–ethyl acetate. The yield of the yellow syrup **11** was 84%. 1,4-Anhydro-2,3-di-*O*-benzyl-β-D-galactopyranose (**12**) was prepared by reacting **11** with alkali. To a **11** (9.3 g) solution in chloroform, anhydrous isopropyl alcohol (300 mL) was added, and the solution was cooled in an ice bath. Sodium (0.74 g) in anhydrous isopropyl alcohol (242 mL) was added to the solution. The reaction mixture was stirred for 18 h at room temperature, followed by the addition of a small amount of water. The crude syrup was separated by means of silica gel column chromatography, using 1:1 benzene–ethyl acetate. The yield of the yellow syrup **12** was 50%. 1,4-Anhydro-2,3,6-tri-*O*-benzyl-β-D-galactopyranose (ABGAL) (13) was obtained by benzylation of **12** according to the method of Hakomori.[15] A **12** (1 g) solution in 5 mL of dimethylformamide was added dropwise to a sodium hydride (0.34 g) solution in dimethylformamide and it was reacted for 1 h. Then, a benzyl chloride (0.8 mL) solution in 10 mL of dimethylformamide was dropwise added to the solution and stirred overnight at room temperature. The compound was separated by means of silica gel column chromatography, using 10:1 benzene–ethyl acetate: yield of the clear syrup **13**, 78%; $[\alpha]^{25}_D$ +57.6° (*c* 1%, $CHCl_3$). Anal. Calcd. for $C_{27}H_{28}O_5$: C, 74.98; H, 6.53. Found: C, 75.98; H, 6.52.

Polymerization of ABGLU and ABGAL. High-vacuum technique was used.[2] Monomer was dried in a polymerization ampule by evacuating for several hours and dissolving in dry methylene chloride, followed by distilling the methylene chloride off the monomer solution. $((C_2H_5)_3O)BF_4$ catalyst which was prepared by Meerwein's method[20] was recrystallized from nitrobenzene–diethyl ether mixture. A coordination initiator based on Al(*i*-Bu)$_3$ modified with H_2O and acetylacetone was prepared by Kops' method.[12] Polymerizations were carried out at low temperatures for 43–241 h. Polymers were purified by reprecipitations using chloroform and petroleum benzin and subsequent freeze-drying from benzene.

Measurements. The 400-MHz ^1H and 100-MHz ^{13}C NMR spectra were measured on the solutions in $CDCl_3$ and CD_2Cl_2, respectively, by means of a Jeol GX-400 spectrometer. The peak assignment was performed by the decoupling method.[21] Specific rotations were measured by means of a Perkin-Elmer 241 polarimeter. Molecular weights of polymers were determined by means of a Toyo Soda HLC-802UR gel permeation chromatography using standard polystyrenes as reference and tetrahydrofuran as solvent. For this kind of polymer, the molecular weights determined by the GPC method are known to agree with those by the osmotic method.[22]

References and Notes

(1) Schuerch, C. *Acc. Chem. Res.* **1973**, *6*, 184; *Adv. Carbohydr. Chem. Biochem.* **1981**, *39*, 157.
(2) Uryu, T.; Tachikawa, H.; Ohaku, K.; Terui, K.; Matsuzaki, K. *Makromol. Chem.* **1977**, *178*, 1929.
(3) Uryu, T.; Kitano, K., Ito, K.; Yamanouchi, J.; Matsuzaki, K. *Macromolecules* **1981**, *14*, 1.
(4) Uryu, T.; Yamanouchi, J.; Hayashi, S.; Tamaki, H.; Matsuzaki, K. *Macromolecules* **1983**, *16*, 320.
(5) Klar, J. *Chem.-Ztg.* **1963**, *87*, 731.
(6) Husemann, E.; Müller, G. J. M. *Makromol. Chem.* **1966**, *91*, 212.
(7) Kops, J.; Schuerch, C. *J. Polym. Sci., Part C* **1965**, *No. 11*, 119.

(8) Micheel, F.; Brodde, O.-E.; Reinking, K. *Liebigs Ann. Chem.* **1974,** 124.
(9) Micheel, F.; Brodde, O.-E. *Liebigs Ann. Chem.* **1974,** 702.
(10) Hall, H. K., Jr.; DeBlauwe, F.; Carr, L. J.; Rao, V. S.; Reddy, G. S. *J. Polym. Sci., Polym. Symp.* **1976,** *No. 56,* 101.
(11) Uryu, T.; Yamanouchi, J.; Kato, T.; Higuchi, S.; Matsuzaki, K. *J. Am. Chem. Soc.* **1983,** *105,* 6865.
(12) Kops, J.; Spanggaard, H. *Macromolecules* **1982,** *15,* 1200.
(13) Gorin, P. A. J.; Mazurek, M. *Can. J. Chem.* **1975,** *53,* 1212.
(14) Deslongchamps, P.; Moreau, C.; Frehel, D.; Atlani, P. *Can. J. Chem.* **1972,** *50,* 3402.
(15) Hakomori, S. *J. Biochem. (Tokyo)* **1964,** *55,* 205.
(16) Micheel, F.; Kreutzer, U. *Liebigs Ann. Chem.* **1969,** *722,* 228.
(17) Yamaguchi, H.; Schuerch, C. *Carbohydr. Res.* **1980,** *81,* 192.
(18) Kops, J.; Schuerch, C. *J. Org. Chem.* **1965,** *30,* 3951.
(19) Sondheimer, S. J.; Eby, R.; Schuerch, C. *Carbohydr. Res.* **1978,** *60,* 187.
(20) Micheel, F.; Brodde, O.-E. *Liebigs Ann. Chem.* **1975,** 1107.
(21) Uryu, T.; Hatanaka, K.; Yoshinari, K.; Matsuzaki, K. *J. Polym. Sci., Polym. Chem. Ed.* **1982,** *20,* 3402.
(22) Uryu, T.; Kitano, K.; Tachikawa, H.; Ito, K.; Matsuzaki, K. *Makromol. Chem.* **1978,** *179,* 1773.

Zwitterion Polymerization of 2-Methyl-2-oxazoline and Methacrylic Acid

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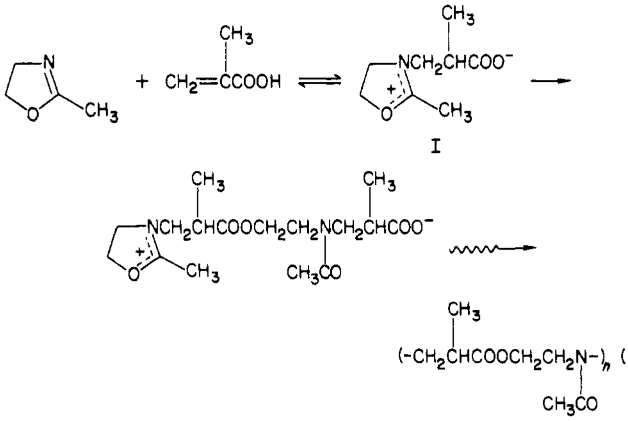
ABSTRACT: The reaction of 2-methyl-2-oxazoline (MeOXO) and methacrylic acid (MAA) has been studied in bulk and solution (acetonitrile) at 60–70 °C. The products were separated by high-performance liquid chromatography and analyzed by ^{1}H and ^{13}C NMR spectroscopy. Contrary to previous reports by Balakrishnan and Periyasamy (*Makromol. Chem., Rapid Commun.* **1980,** *1,* 307) the reaction of MeOXO and MAA does not yield high molecular weight alternating copolymer but only very low molecular weight products. All of the products contain olefinic and acetamido end groups with varying amounts of MeOXO and MAA units in between the end groups. A mechanism is proposed to account for the observed products and to explain the reported results of Balakrishnan and Periyasamy.

Introduction

2-Methyl-2-oxazoline, a nucleophilic type monomer, has been reported to undergo zwitterion polymerization with a number of electrophilic type monomers such as acrylic acid,[1-3] methacrylic acid,[4] acrylamide,[5] 2-hydroxyethyl acrylate,[6] succinic anhydride,[7] ethylenesulfonamide,[8] and 3-hydroxy-1-propanesulfonic acid sultone[9] to yield low molecular weight alternating copolymers. Balakrishnan and Periyasamy[4] studied the 2-methyl-2-oxazoline–methacrylic acid (MeOXO–MAA) system and proposed a reaction mechanism involving the initial formation of genetic zwitterion I followed by propagation through the reaction of I with itself and with larger-sized zwitterions to yield the alternating copolymer II.

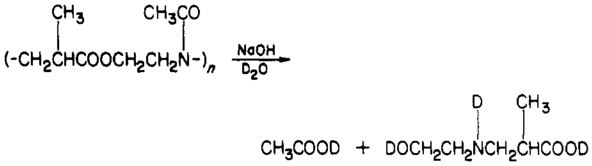

I

(1)

II

Balakrishnan and Periyasamy isolated a pale brown gum by pouring the MeOXO–MAA reaction mixture into diethyl ether followed by drying at 70 °C. ^{1}H NMR spectra of the gum and its alkaline hydrolysate were presented in support of copolymer structure II. However, our interpretation of the published spectral data does not support structure II. The ^{1}H NMR spectrum of the gum was reported as consisting of singlets at 1.95 (α-CH_3) and 2.05 (CH_3CO) ppm and multiplets at 3.6 (CH_2NCH_2 and CH) and 4.3–4.4 (OCH_2) ppm. The singlet at 1.95 ppm, assigned to the α-CH_3 protons of the methacrylate unit, is too far downfield for that type of proton.[10] For example, the α-CH_3 protons of methyl isobutyrate are found at 1.2 ppm.[11] Furthermore, the α-methyl signal for II should be a doublet as it is for methyl isobutyrate. The ^{1}H NMR spectrum reported by Balakrishnan and Periyasamy shows only the 1.9–5 ppm region. The ratio of various signal areas in the reported spectrum also fails to support structure II. The 1.95, 2.05, 3.6, and 4.3–4.4 ppm signals show areas in the approximate ratio 1.1:2.5:2.6:1 instead of 3:3:5:2 as required for structure II and the spectral assignments by Balakrishnan and Periyasamy.

The published ^{1}H NMR spectrum of the hydrolyzed gum also does not support structure II. The gum was hydrolyzed by NaOH in D_2O and should yield equimolar amounts of deuterated acetic and *N*-(2-hydroxyethyl)-3-amino-2-methylpropionic acids based on structure II.


(2)

The ^{1}H NMR of the hydrolysate was reported as consisting of singlets at 1.9 (α-CH_3) and 2.0 (CH_3COOD) ppm, triplets

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