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Note

A new synthetic route to 2,3,6-tri-*O*-allylamylose

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Biodegradable, block copolymers containing amylose oligomeric blocks as the biodegradable unit have been synthesized[1] by first preparing fully substituted amylose acetate, hydrolyzing it to a hydroxyl-terminated amylose triacetate oligomer, capping the oligomer with a diisocyanate, and treating the capped prepolymer with functionally terminated, non-amylose polymers [*e.g.*, poly(propylene glycol)]. It is necessary that the amylose oligomer be fully substituted during the chain-extension step, to avoid branching and cross-linking. However, the hydroxyl-blocking group must be readily removable, in order to generate the amylose block in the copolymer. In previous work, the acetyl group was used to prepare amylose[1] and cellulose[2] block-copolymers, as it is readily removed by base. However, if a polyester block is incorporated into the copolymer, the ester interunit linkages are cleaved during removal at the acetyl group.

The stability of allyl ethers under acidic conditions (hydrolysis step → amylose oligomer), their ease of isomerization, and the lability of the resulting 1-propenyl ethers under acid conditions suggested the use of allyl ethers as the protecting groups for the amylose hydroxyl groups during the preparation of amylose–polyester block copolymers.

Allylstarch having a low degree of substitution (d.s.) was prepared by Tomecko and Adams[3] by the direct reaction of starch with allyl bromide in the presence of 10% aqueous NaOH. They attributed the low d.s. values to two competing reactions, as follows.

$$H_2C{=}CH\text{-}CH_2Br + NaOH \rightarrow H_2C{=}CH\text{-}CH_2OH + NaBr$$
$$H_2C{=}CH\text{-}CH_2OH + BrCH_2\text{-}CH{=}CH_2 + NaOH \rightarrow$$
$$H_2C{=}CH\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH{=}CH_2 + NaBr + H_2O$$

Yanovsky[4] studied the hydrolysis of allyl bromide and chloride by NaOH, and found lower degrees of hydrolysis at high (45–50%) concentrations of NaOH. Using 50% aqueous NaOH, he obtained allylstarch with a maximum d.s. of 2.4. Using similar conditions, Yoshimura[5] obtained a d.s. value of 1.67.

Corey and Chaykovsky described[6] the preparation of the methylsulfinyl

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carbanion and its utilization in the Wittig reaction[7,8], and Hakomori[9] reported that the permethylation of glycolipids and polysaccharides is catalyzed by the methylsulfinyl carbanion. We now describe the reaction of amylose with the methylsulfinyl carbanion in dimethyl sulfoxide, to form the alkoxide of amylose, followed by reaction with allyl bromide, to afford tri-*O*-allylamylose, the starting material for the synthesis of amylose–polyester, block copolymers.

EXPERIMENTAL

Materials. — Avebe amylose ISD-224 was kindly supplied by National Starch Co. Allyl bromide was purchased from Fisher Scientific Co., and sodium hydride from Ventron Corp.

General methods. — The Hübl procedure[10] was employed to titrate the double bonds in the allylamylose, and permit calculation of the d.s. ^{1}H-N.m.r. spectra were recorded with a Varian HA-100 n.m.r. spectrometer operating at 100 MHz in the field-sweep mode, for solutions at a concentration of 20% (w/v) in *N*,*N*-dimethylformamide-d_7 containing 2% (w/v) of tetramethylsilane as the internal standard and to provide a lock signal. ^{13}C-N.m.r. spectra were recorded with a JEOL FX-60 pulsed, Fourier-transform, n.m.r. spectrometer equipped with a Texas Instrument 12k Computer and a variable-temperature probe. Spectra were recorded at 15.01 MHz under conditions of broad-band decoupling at 59.75 MHz. Spectra were measured at a concentration of 20% (w/v) in *N*,*N*-dimethylformamide-d_7 for the tri-*O*-allylamylose, and in dimethyl sulfoxide-d_6 for amylose. The solvents provided the deuterium lock, and spectra are reported in p.p.m. downfield from Me_4Si. Infrared spectra were recorded with a Perkin–Elmer 337 IR Grating spectrometer

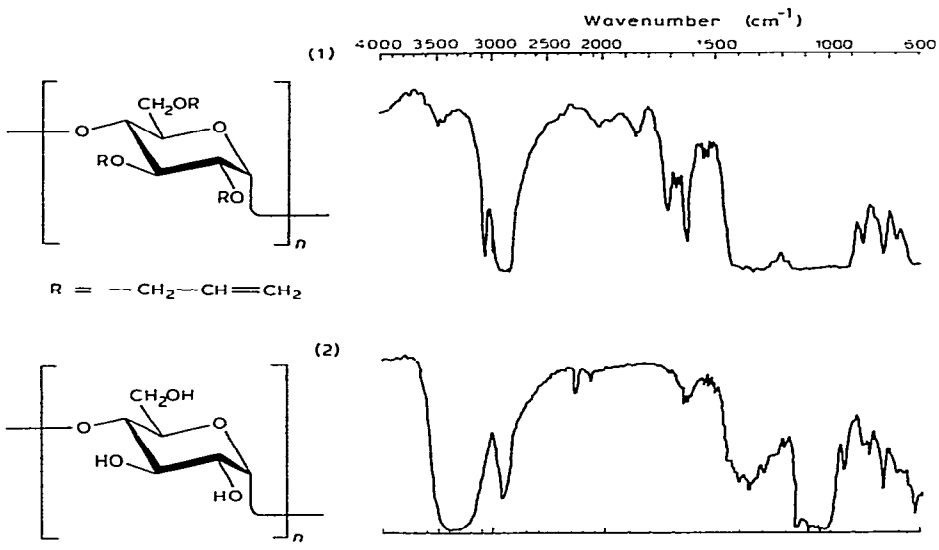

Fig. 1. Infrared spectra of 2,3,6-tri-*O*-allylamylose (1) and amylose (2).

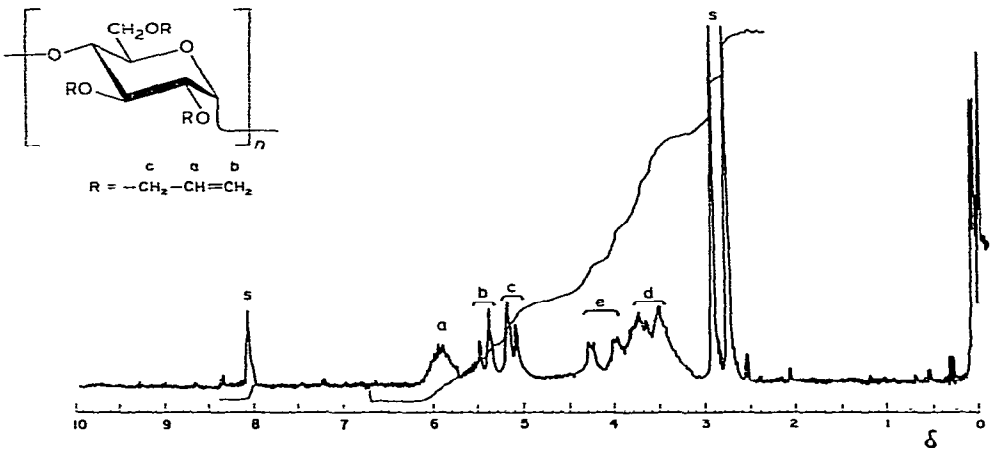

Fig. 2. ^{1}H-N.m.r. spectrum of 2,3,6-tri-*O*-allylamylose in *N*,*N*-dimethylformamide-d_7 at room temperature.

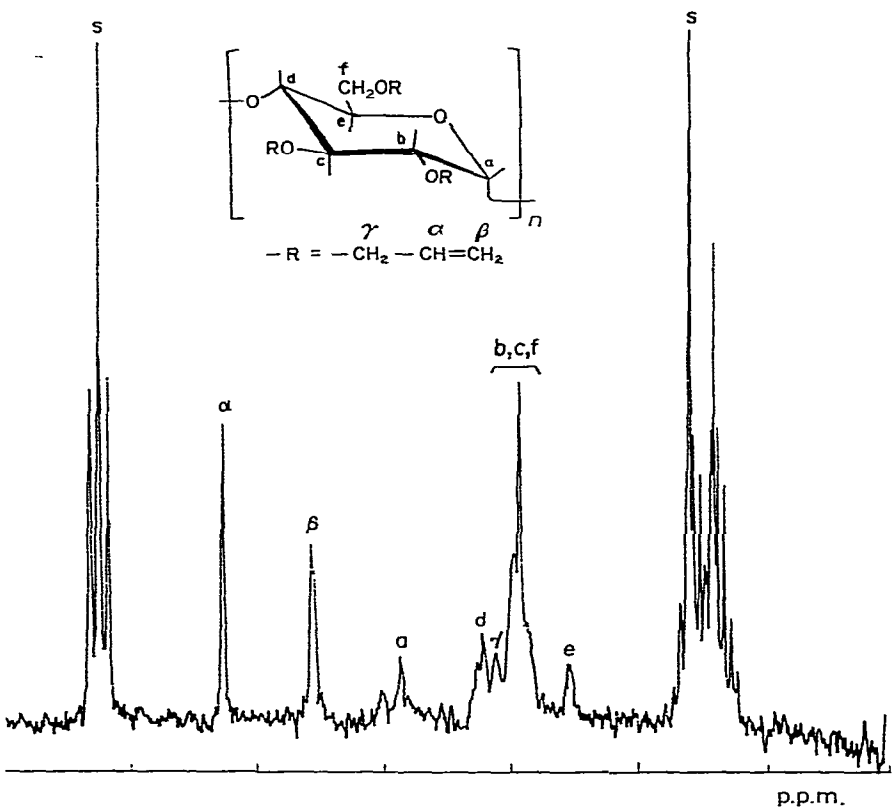

Fig. 3. ^{13}C-N.m.r. spectrum of 2,3,6-tri-*O*-allylamylose.

at room temperature by using a film of amylose cast from Me_2SO or a film of the substituted amylose cast from $HCONMe_2$. The scanning range and rate were respectively 4000–600 cm^{-1} and 25 min/scan.

Methylsulfinyl carbanion. — This was prepared by the method of Chaykovsky and Corey[7]. A mixture of powdered NaH (1.33 g) with dry Me_2SO (40 mL) was gradually heated to 65–70° under nitrogen, with stirring, and maintained at this temperature until the evolution of hydrogen was complete (~0.75 h).

Amylose alkoxide. — Dried amylose (3 g, 1.85 mmol), dissolved under nitrogen in dry Me_2SO (50 mL), was added to a 250-mL flask fitted with a magnetic stirrer and containing the methylsulfinyl carbanion solution. The mixture was stirred under nitrogen for 2.5 h at room temperature.

Allylamylose. — Allyl bromide (20 g, 5.55 mmol) was added to the amylose alkoxide solution, and the mixture was agitated for 20 min under nitrogen. The resulting solution was diluted with distilled water, and the precipitate collected, and washed with chloroform (to remove unreacted allyl bromide). The solid was filtered off, successively washed with ether–petroleum ether and several portions of water (to remove traces of Me_2SO), and dried for 48 h at 80° under high vacuum in a vacuum desiccator prepurged with nitrogen: yield, 38 g, 70%; for its i.r. spectrum, see Fig. 1; p.m.r. spectrum, Fig. 2; and ^{13}C-n.m.r. spectrum, Fig. 3.

RESULTS AND DISCUSSION

Values of d.s. as determined by iodine titration are listed in Table I for three reaction-products prepared by the present method. These data indicated complete substitution of the hydroxyl groups of the amylose, and were supported by the infrared-spectral data. Representative spectra, namely, the i.r. spectra of sample 1 and amylose, are shown in Fig. 1. The absence of the broad, strongly absorbing, hydroxyl peak from the spectrum of sample 1 [which is clearly evident in the spectrum of amylose (3500 cm^{-1})], and the appearance of absorption peaks at 3050, 1700, and 1640 cm^{-1}, attributable to olefinic stretching and C–H bending, demonstrated that the hydroxyl groups on the amylose chain were fully substituted.

The ^1H-n.m.r. spectrum provided additional confirmation. In Fig. 2, the signals at a (δ 5.9), b (δ 5.5), and c (δ 5.1) are due to the protons of the allyl group:

TABLE I

VALUES OF DEGREE OF SUBSTITUTION

Sample no.	*Iodine value*	*D.s.*
1	274.5	3.08
2	278.8	3.10
3	267.6	2.95

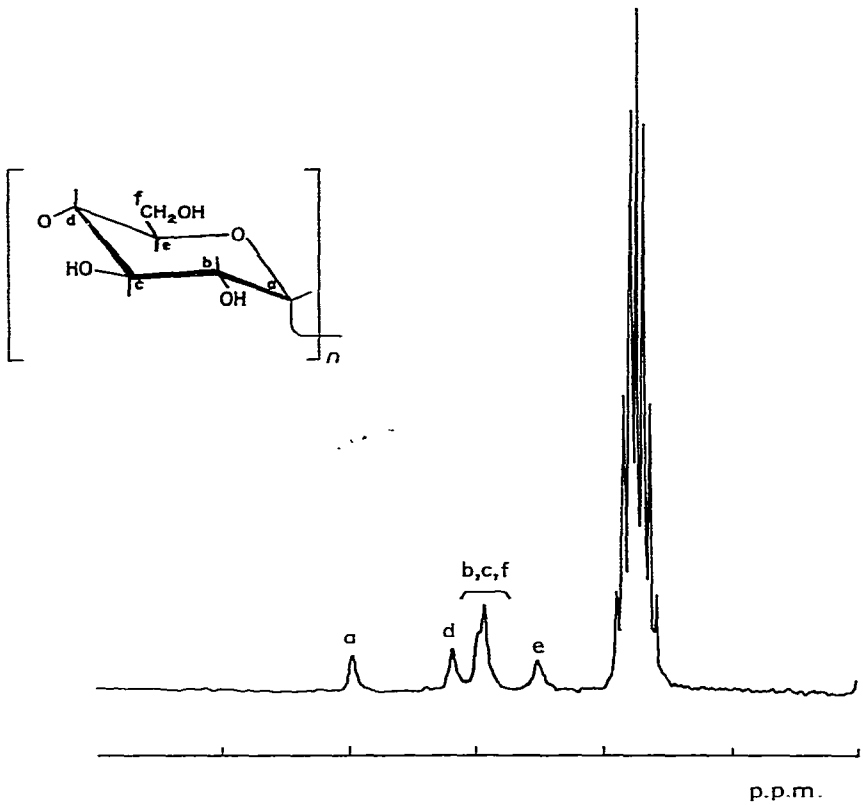

Fig. 4. ^{13}C-N.m.r. spectrum of amylose.

those in the δ 3.2–4.5 region (d and e) are amylose ring-protons, and no OH proton signals are evident.

The ^{13}C-n.m.r. spectra of amylose and reaction product 1 are respectively shown in Figs. 4 and 3. Comparison of these spectra shows that the signals of the glucopyranose carbon atoms are at the same chemical-shift in both the substituted and unsubstituted compounds. The signals of the allyl group carbon atoms are clearly present in Fig. 3. It is apparent that there was no chemical attack on the amylose chain-structure during the series of reactions used to prepare the allylamylose.

These analytical and spectral data confirm that the synthetic procedure described here provides a convenient, high-yield route to 2,3,6-tri-*O*-allylamylose.

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