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Note

Some studies on the selective synthesis of sucrose acetates using template and random trityl chloride functionalised macroporous polymers

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The quest to find more efficient synthetic routes in producing sucralose (**9**) has indeed become a competitive aspect of carbohydrate research over the years [1]. Notably a biocatalytic synthesis via a tetrachlororaffinose intermediate [2], a fructosyl transferase-catalysed conversion to a sucralose precursor, sucrose-6-acetate [3], and regioselective deacetylation of sucrose octaacetate by either sequential use of the enzymes, alcalase and AP6 lipase [4], or use of the commercially available proteases or lipases [5], to produce the sucralose precursor, 2,3,3′,4′,6-penta-*O*-acetylsucrose (**7**), are some of the recent developments using enzymatic methods in this field. While designing organic materials which in some way will simulate the selectivity and efficiency displayed by enzymes is an ongoing challenge for the organic chemist, one of the more intricate problems in the design of enzyme analogue systems is the selective introduction of organic functionality and maintenance of their spatial arrangement over a period of time. A highly original application to this problem came from the pioneering work of Wulff and co-workers in using template polymers [6]. In extending the idea to finding concise and efficient synthetic routes for making sucralose, we were interested in using the 2,3,3′,4,4′-penta-*O*-acetyl-1′,6,6′-tri-*O*-vinyltrityl sucrose monomer **3** as a template as-

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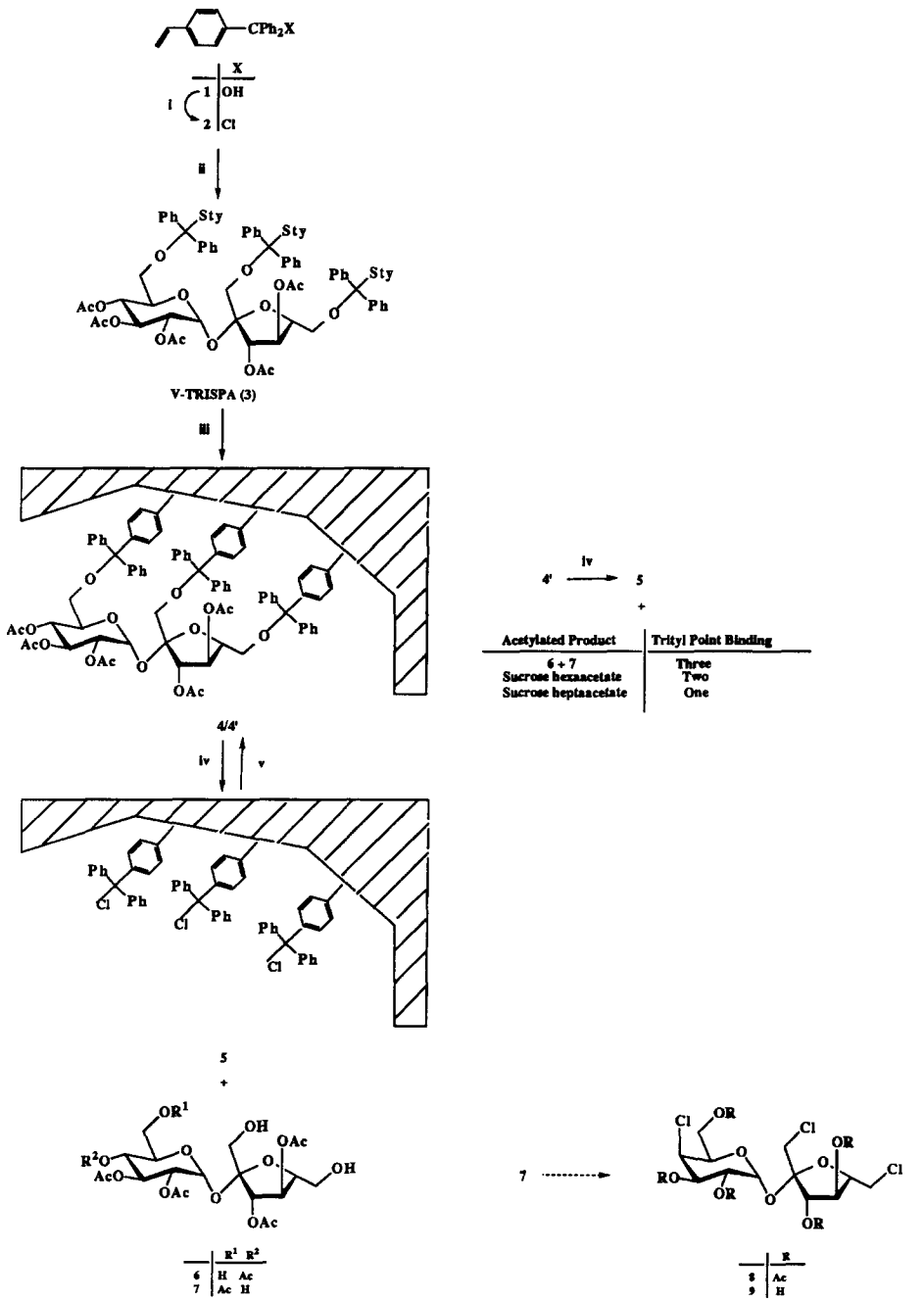


Scheme 1. *Reagents.* (i) $SOCl_2$, 2,4,6-collidine, hydroquinone (catalytic amt.), Me_2NCHO; (ii) **6**, pyridine; (iii) **3**, DVB, styrene, toluene (diluent), polyvinylalcohol (surfactant), water, benzoyl peroxide; (iv) HCl (g), CH_2Cl_2; (v) (a) sucrose, pyridine, (b) Ac_2O, pyridine.

Table 1
Comparative data of template and control polymers having 10% mole trityl chloride loading and 20% mole crosslinkage

	Template polymer (**T1**)	Control polymer (**C1**)
Actual capacity [a] (mmol/g)	0.0148	0.0683
Theoretical capacity [b] (mmol/g)	0.974	0.890
%Capacity [c]	1.52	7.67
Selectivity [d]	1:6.41	1:2.34

[a] Actual capacity is the mmole of total sucrose acetate produced per gram of polymer employed.
[b] Theoretical capacity is the mmole of vinyl monomer used in polymerisation preparation divided by the polymer yielded from the preparation.
[c] %Capacity = (actual capacity/theoretical capacity) × 100.
[d] Selectivity is the mole ratio of sucrose pentaacetate to heptaacetate, e.g., 1:6.41 refers to 6.41 moles of sucrose heptaacetate produced for every mole of pentaacetate.

sembly. Thus our template technique is as follows: incorporation of monomer **3** onto a crosslinked polystyrene matrix by suspension co-polymerisation (→ **4**) [7], acidic cleavage of the 2,3,3′,4,4′-penta-*O*-acetyl sucrose (**6**) giving regions of triad trityl chloride groups on the macromolecule, polymer **5**, reaction of polymer **5** with sucrose, subsequent acetylation of the unprotected hydroxyl groups (→ **4′**), and finally cleavage of the sugar **6** and other sucrose acetates thereof from polymer **4′** (Scheme 1). Traversing the steps (v) and (iv) (Scheme 1) is a means of investigating whether **5** exhibits a "memory" for the original template molecule **6**, the results of which are disclosed in Tables 1 and 2. A control polymer **11**, prepared by directly co-polymerising monomer **1** with a styrene–divinylbenzene mixture and chlorinating the resultant polymer **10**, was also subjected to conditions (v) and (iv) (vide supra). This was done to establish whether there is any advantage in the selectivity of template polymer **5** in protecting the 6-, 6′- and 1′-positions of sucrose over that of polymer **11** having random trityl chloride distribution. The remainder of the sucralose synthesis as described elsewhere [1] involves migration of the acetyl group at the 4-position of **6** excised from polymer **4′**, to

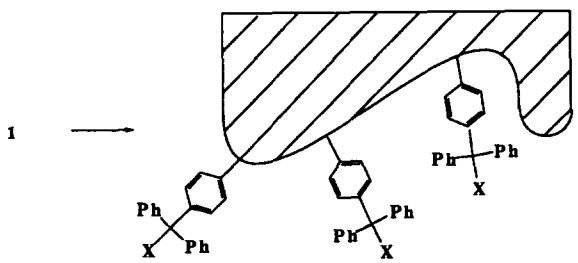
Table 2
Comparitive data of template and control polymers having 1% mole trityl chloride loading and 40% mole crosslinkage

Polymer	%Capacity	Sucrose acetate [a]				
		6		**7**	SAc_6 [b]	SAc_7 [b]
Control [c] (**C2**)	1.26×10^{-3}	9.19×10^{-6}	(1)	5.83×10^{-5}	2.71×10^{-5}	1.31×10^{-3} (16.9)
Template [c] (**T2**)	4.83×10^{-4}	2.78×10^{-5}	(2.57)	5.49×10^{-6}	–	1.49×10^{-5} (1)

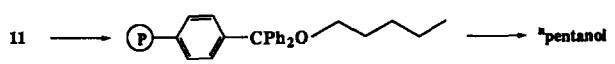
[a] Figures are mg per gram of polymer. Parenthetical figures use mole ratios with the limiting sucrose acetate product set at 1.0.
[b] SAc_6 and SAc_7 are abbreviations for sucrose pentaacetate and sucrose heptaacetate, respectively.
[c] Reproducibility of yields in both control and template experiments was confirmed to be within a ±5% error margin by repeating the solid-phase synthesis on the same batch of polymer a further two times.

the 6-position so as to provide **7**. (Actually an acid-catalysed C-4 → C-6 acetyl migration occurring during cleavage of the acetylated sucrose bound to the polymer abated the necessity of this step in some cases.) Compound **7** then can be chlorinated at the 4-, 1′-, and 6′-positions (→ **8**) using a Vilsmeier reagent and finally deacetylated (→ **9**).

The monomer, 4-vinylphenyldiphenylmethanol (**1**), was prepared according to the method of Braun and co-workers without modification [8]. Reacting **1** with equimolar amounts of thionyl chloride and 2,4,6-collidine in Me_2NCHO at 0 °C generated pure **2** in 65% yield, whereas employing conventional chlorination methods (CH_3COCl [9], $SOCl_2$ [10], HCl(g)–CH_2Cl_2 [11]) gave **2** with at least 30% concomitant anti-Markownikoff addition of HCl across the vinyl moiety as evidenced by the triplet signals at 3.44 and 2.80 ppm in the proton NMR analysis. Subsequent coupling of an excess of **2** to **6** mediated in pyridine at 80 °C afforded monomer **3** in 74% based on consumed **6**.



	X
10	OH
11	Cl



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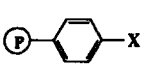
P = Macroporous Polystyrene Resin



	X
13	Li
14	$C(4MeO\text{-}C_6H_4)_2Cl$

A number of parameters were in need of consideration if the trityl groups were to be reliably juxtaposed in a triad arrangement to achieve adequate selectivity in producing sucrose pentaacetate (**6**). It was established from previous studies done on polymer (**11**) [12] that 10% mole trityl chloride loading and 20% mole crosslinkage were the most effective design parameters for polymer **11** in maximising sucrose acetate product yields; viz., among the polymers **11** of varying crosslinkage and trityl loading, control polymer **C1** gave the highest percentage capacity of 7.67% (Table 1). In incorporating the same trityl loading and crosslinkage into the design of template polymer **5**, the results in Table 1 indicate that the efficiency of control **C1** and template **T1** polymers in terms of percentage capacities are of comparable magnitudes. However, a surprising result was that the polymer **C1** was 2.74 times more selective in producing sucrose pentaacetate (three-point trityl binding) against the level of sucrose heptaacetate (one-point trityl binding) produced, compared with that of template polymer **T1**. The apparent redundancy of the template idea in this particular experiment may stem from functional group crowding in the control polymer cavity, whereby it gives rise to three-point binding to sucrose in the control polymer case by virtue of Helferich's rule [13] alone. Whereas in Wulff's study [6] it is suggested that dramatic increases in site isolation are recognised at a crosslinking of greater than 20% mole, and indeed this was the case in an experiment employing 40% mole crosslinkage template polymer as shown in the results of Table 2. A comparison between template **T2** and control **C2** polymers on the basis of mole ratios of sucrose pentaacetate to heptaacetate reveals that **T2** is 43.4 times more selective in producing sucrose pentaacetate than is the control polymer, **C2**. Certainly this result substantiates our proposal that **5** retains a "memory" for the template molecule **6** imprinted by co-polymerisation of **3**. The yields of **6** and **7** are minuscule but the percentage of trityl functions employed in yielding product (actual capacity) as a fraction of the trityl content introduced at the suspension polymerisation stage (theoretical capacity) is also small.

Several experiments were undertaken in an attempt to account for the extremely low yields of sucrose acetate product generated from both polymer **4'** and the control polymer equivalent (derived from **11**). A GLC assay of the amount of **6** and **7** released from polymer **4** would be indicative of the extent of those triad trityl groups residing at reactive cavity sites in polymer **5**. Thus in one particular experiment, a total of 1.66 mmol of sucrose pentaacetate (both **6** and **7**) was assayed as being released from 1 g of polymer **4**. This corresponds to a mere 4.9% of the co-polymerised monomer **3** being accessible to the acidic cleavage condition: the other 95.1% of **3** presumably has been incorporated into the highly crosslinked nuclei of the polymer. In a GLC assay of the amount of sucrose pentaacetate released from a HCl(g)–CH_2Cl_2-treated sample mixture containing filtrate and washings taken from polymer **4**, it was estimated that merely 0.09% of **3** had not co-polymerised with the styrene–divinylbenzene co-monomer feed. Therefore it sufficed simply to base the theoretical capacity of polymer **5** on the amount of monomer **3** added at the suspension polymerisation stage. (Similarly it was assumed that the theoretical capacity of control polymer **11** can be based on the monomer **1** quantity employed in suspension polymerisation.) In an experiment designed to give information about the accessibility of a simple alcohol substrate, *n*-pentanol, towards the trityl-filled cavities of polymers used herein, polymer **11** was reacted with *n*-pentanol in

pyridine solvent, and the resultant polymer-bound trityl pentyl ether **12** was subjected to the usual acidic cleavage conditions. A GLC assay of the amount of alcohol released from polymer **12** corresponded to an actual capacity of 0.222 mmol/g. The latter figure corresponds to a percentage capacity value of 28.6% (theoretical capacity = 0.776 mmol/g). This represents a 210-fold increase in the level of participation of pendant trityl chloride groups protecting an alcohol substrate compared with that for sucrose protection. (The same polymer **11**, gave a 0.136% capacity for the sucrose case.) The huge discrepancy in percentage capacity for the two different substrates, sucrose and *n*-pentanol, would imply that the diffusion behaviour of sucrose to or from the reactive sites (or both) has been severely restricted. This seems hardly surprising in the light of a hydrophobic microenvironment in such polystyrene-based polymers being inherently incompatible towards the polyhydroxyl hydrophilic sucrose substrate.

The post-polymerisation approach of chemical modification of pre-formed polymers is the alternative to direct co-polymerisation for the preparation of trityl chloride functionalised polymers. The polymeric 4,4′-dimethoxytrityl chloride **14**, prepared via a lithiated polystyrene species **13**, has been demonstrated by Fyles and Leznoff to exhibit a percentage capacity as high as 89% towards binding to 1,7-heptanediol [14]. However, in our hands, the same polymer, prepared without modification, managed only a 0.02% capacity towards the sucrose substrate. Therefore the problem of low yields of sucrose acetate is one that seems confined to the diffusion behaviour of sucrose in the resins prepared either by post-polymerisation or by co-polymerisation methods, rather than the way the trityl groups become incorporated into the polymeric backbone. Future studies will be aimed at elucidating the diffusion and reactivity of sucrose in the resin cavities by physical measurements, namely, inverse gel-permeation chromatography [15], and solid-phase ^{13}C NMR and FTIR [16] spectroscopy.

1. Experimental

General.—Gas–liquid chromatographic (GLC) analyses were made with a Pye Unicam Model PU4500 gas chromatograph. Infrared absorptions were recorded using a Perkin-Elmer 683 model. ^1H NMR spectra were recorded in deuteriochloroform routinely at 100 MHz and analytically at 270 MHz using a JEOL PS 100 and a JEOL GX 270 spectrometer, respectively. Chemical shifts are reported in δ-values relative to tetramethylsilane, and J-values are given in Hz. Optical rotations were measured in chloroform solutions using a Bellingham and Stanley Pepol 60 polarimeter. $[\alpha]_D$-Values are given in units of 10^{-1} deg cm^2 g^{-1}. TLC was performed on aluminum sheets precoated with Kieselgel-60 F_{254} (Art. 5554; E. Merck). Detection was first by UV (254 nm), then by charring with a solution of 4% concd H_2SO_4 in MeOH. Column chromatography was carried out on Kieselgel-60 (Art. 7734; 70–230 mesh; E. Merck). Compound **6** [17] and 4-vinylphenyldiphenylmethanol **1** [8] were obtained from Tate and Lyle Speciality Sweeteners and were used as received. The commercial styrene (Aldrich, 99%, inhibited with 10–15 ppm 4-*tert*-butylcatechol) and divinylbenzene (Aldrich, tech., 55%, mixture of isomers) were washed three times with 1% aq NaOH, twice with water and brine to remove the stabiliser present, followed by distillation under reduced

pressure. For an oil-in-water suspension polymerisation being carried out at 80 °C, the preferred suspension surfactant was polyvinyl alcohol, 100% hydrolysed (Aldrich, average mol wt 86,000). All reactions were conducted under pre-dried N_2 gas unless stated otherwise. Organic extracts were dried over $MgSO_4$ and evaporated at aspirator pressure using a rotary evaporator. Solvents were dried and purified using standard methods [18].

4-Vinylphenyldiphenylmethyl chloride (**2**).—A stirred mixture of alcohol **1** (2.86 g, 10 mmol), 2,4,6-collidine (1.45 mL, 11 mmol), hydroquinone (20 mg) in 5 mL of anhydrous Me_2NCHO under nitrogen was cooled to −20 °C (iced brine). Thereafter, with the aid of a pressure-equalising dropping funnel, $SOCl_2$ (0.73 mL, 10 mmol) in 5 mL of Me_2NCHO was added dropwise over a period of 30 min. Then the reaction mixture was kept at 0 °C for 1.5 h and reacted for a further 1 h at room temperature. The reaction mixture was diluted with 30 mL of diethyl ether, washed successively with saturated copper sulfate solution until washings returned to a blue appearance and dried. The mixture was evaporated free of solvent, and a 20 mL portion of dry petroleum ether (bp 80–100 °C) was added to precipitate out any polymerised trityl chloride. The yellow solution was decanted into a flask, and the latter process was repeated several times using a 1:1 mixture of Et_2O–petroleum ether until the supernatant was free of polymer byproduct. The solvents were then evaporated and dried in vacuo to give **2** as a yellow oil (1.98 g, 65.0%) IR ν_{max} (Nujol) 2980, 1490, 1485, 760, 735, 695 cm^{-1}. NMR data: δ_H (100 MHz) 5.28 (dd, 1 H, J_{gem} 1.0, J_{vic} 12.0 Hz, $=CH_2$), 5.76 (dd, 1 H, J_{gem} 1.0, J_{vic} 18.0 Hz, $=CH_2$), 6.72 (dd, 1 H, J_{cis} 16.0, J_{trans} 20 Hz, =CH-), 7.1–7.7 (m, 14 H, ArH). Anal. Calcd for $C_{21}H_{17}Cl$: C, 82.7; H, 5.6; Cl, 11.6. Found: C, 82.4; H, 6.0; Cl, 11.6.

2,3,4-Tri-O-acetyl-6-O-(4-vinylphenyldiphenylmethyl)-α-D-glucopyranosyl 3,4-di-O-acetyl-1,6-di-O-(4-vinylphenyldiphenylmethyl)-β-D-fructofuranoside (**3**).—The above preparation of the chloride **2** was doubled up in scale. Upon completion of the reaction and without copper sulfate extraction, diethyl ether was added repeatedly and decanted free of polymer byproduct until the ethereal solution was colourless. A further 10 mg of hydroquinone was added to the solution and then the mixture was evaporated in vacuo. Further addition of 1:1 Et_2O–petroleum ether (bp 80–100 °C, 40 mL) precipitated out any residual polymerised trityl chloride. Decanting and evaporation of the polymer-free supernatant gave a dark syrup to which **6** (0.55 g, 1.00 mmol) and pyridine (5 mL) were added. The reaction mixture was heated at 80 °C for 3 h with stirring and then left to stir overnight at room temperature. The reaction was then quenched by the addition of MeOH (30 mL) and the solvent was evaporated in vacuo. Diethyl ether (40 mL) was added to the residue, filtered free of collidinium hydrogen chloride salt, and then diluted with CH_2Cl_2 (150 mL). The solution was washed with saturated copper sulfate solution until aqueous washings had attained its original blue colour, dried (Na_2SO_4), and evaporated to a residue. To the latter was added diethyl ether (30 mL), the precipitated polymer byproduct was filtered off, the filtrate evaporated to a residue and purified by column chromatography [97:3 benzene–Et_2O then 2:1 Et_2O–petroleum ether (bp 40–60 °C)], to afford monomer **3** (1.00 g, 73.8%), which was recrystallised from Et_2O–petroleum ether (bp 40–60 °C): mp 90–93 °C; $[\alpha]_D^{21}$ +71.9° (*c* 0.54); IR ν_{max} (Nujol) 2995, 1760, 1100, 890, 650 cm^{-1}. NMR data: δ_H (270 MHz) 1.71, 1.98, 2.01, 2.03, 2.11 (5s,

15 H, $COCH_3$), 3.20 (m, 1 H, H-1′), 3.30 (m, 1 H, H-6′), 4.00 (m, 1 H, H-5), 4.15 (m, 1 H, H-5′), 4.80 (m, 1 H, H-2), 5.20 (m, 3 H, CH_2=, H-3 or H-4), 5.40 (m, 2 H, H-4′ and H-1), 5.70 (m, 1 H, CH_2=), 5.85 (m, 1 H, H-3′), 6.65 (m, 1 H, =CH-), 7.1–7.8 (m, 42 H, ArH). Anal. Calcd for $C_{85}H_{80}O_{16}$: C, 75.2; H, 5.9. Found: C, 75.4; H, 5.8.

*Polymerisation procedure; polymer-bound 2,3,4-tri-*O*-acetyl-6-*O*-(triphenylmethyl)-α-*D*-glucopyranosyl 3,4-di-*O*-acetyl-1,6-di-*O*-(triphenylmethyl)-β-*D*-fructofuranoside* (**4**) *and polymer-bound triphenylmethanol* (**10**).—The method of preparation by suspension polymerisation of styrene and divinylbenzene in the presence of monomers **1** or **3** was carried out following the conditions of Hodge and Sherrington [19].

The stabiliser, polyvinyl alcohol (1.0 g), was weighed into a 250-mL Quickfit conical flask equipped with a condenser, and a 45-mm magnetic impeller. Water (100 mL) was added, the whole apparatus was flushed with N_2 gas, and the oil bath temperature was adjusted to 80 °C. At maximum stirring rate the co-monomer feed [2] was added, followed by benzoyl peroxide initiator (200 mg), to yield polymer resin after being left to stir for 12 h under nitrogen. The product beads were collected by suction filtration, washed with water (4 × 50 mL), acetone (4 × 50 mL), dichloromethane (4 × 25 mL), and again with acetone to remove the remaining initiator and stabiliser. The beads were then dried in an evacuated drying pistol at 60 °C and 10 Torr overnight to yield typically 8–10 g (80–100%) of material.

Template polymer protecting agent (**5**).—The polymer **4** (5.0 g) was suspended in dry dichloromethane (100 mL) at 0 °C, and HCl was slowly bubbled into the mixture for 1 h. The reaction was followed by TLC using 45:5:1 EtOAc–EtOH–H_2O or 4:1 diethyl ether–acetone. More conveniently, cleavage of the sugar was also done by adding 50 mL of 10% trifluoroacetic acid in $CHCl_3$ or 0.3 N anhydrous HCl in dioxane (50 mL) to the above quantity of polymer and stirring for 2 h at room temperature. In all the above cases, control experiments were done to ascertain cleavage conditions which did not lead to glycosidic hydrolysis of compound **6** after being cleaved from the polymer. This was particularly evident when initial experiments were done with HBr and acetic acid. Prior to use, polymer **5** was washed with acetone (4 × 25 mL), dichloromethane (4 × 50 mL), and acetone (4 × 25 mL) to remove any remaining acetate **6**, and the washings were tested using TLC and shown to be free of sugar. If the polymer was stored over long periods of time, then rechlorination of the trityl functions was done by reaction with acetyl chloride in benzene at 80 °C overnight.

Polymer-bound triphenylmethyl chloride (**11**).—Polymer **10** (5.0 g) in 100 mL of 20% acetyl chloride in dry benzene was refluxed overnight at 80 °C under nitrogen. The resultant polymer **11** was rapidly filtered, washed with dry benzene (4 × 50 mL) and dry CH_2Cl_2 (4 × 50 mL) and dried under vacuum.

Template polymer-bound sucrose and control polymer-bound sucrose.—Finely powdered sucrose (0.5 g) was dissolved in dry pyridine (20 mL) at reflux temperature, and

[2] The co-monomer feed consisted of an amount of divinylbenzene required to give the desired mole percentage of crosslinkage, along with an amount of the trityl-containing monomer (compounds **3** or **1**), which would yield the desired level of trityl functionalisation. The remaining monomeric component added was styrene, to make a total of 10 g of co-monomer feed, and 10 mL of toluene was added to the mixture as diluent.

after cooling to 80 °C, polymer **5** or **11** (5.0 g) was added, and the mixture was stirred for 24 h at 80 °C. At the end of this period, the polymer was filtered and washed with pyridine (4 × 10 mL), MeOH (4 × 25 mL), and acetone (4 × 25 mL) to yield polymer-bound sucrose. The final washing of acetone was reduced in volume by evaporation and shown to contain no free sucrose on testing by TLC.

Template polymer-bound sucrose acetate (**4'**) *and control polymer-bound sucrose acetate.*—The above template polymer-bound sucrose or control polymer-bound sucrose (5.0 g) was added to pyridine (7.5 mL) in a round-bottom flask equipped with a condenser and drying tube. The mixture was heated to 80 °C, and acetic anhydride (5.0

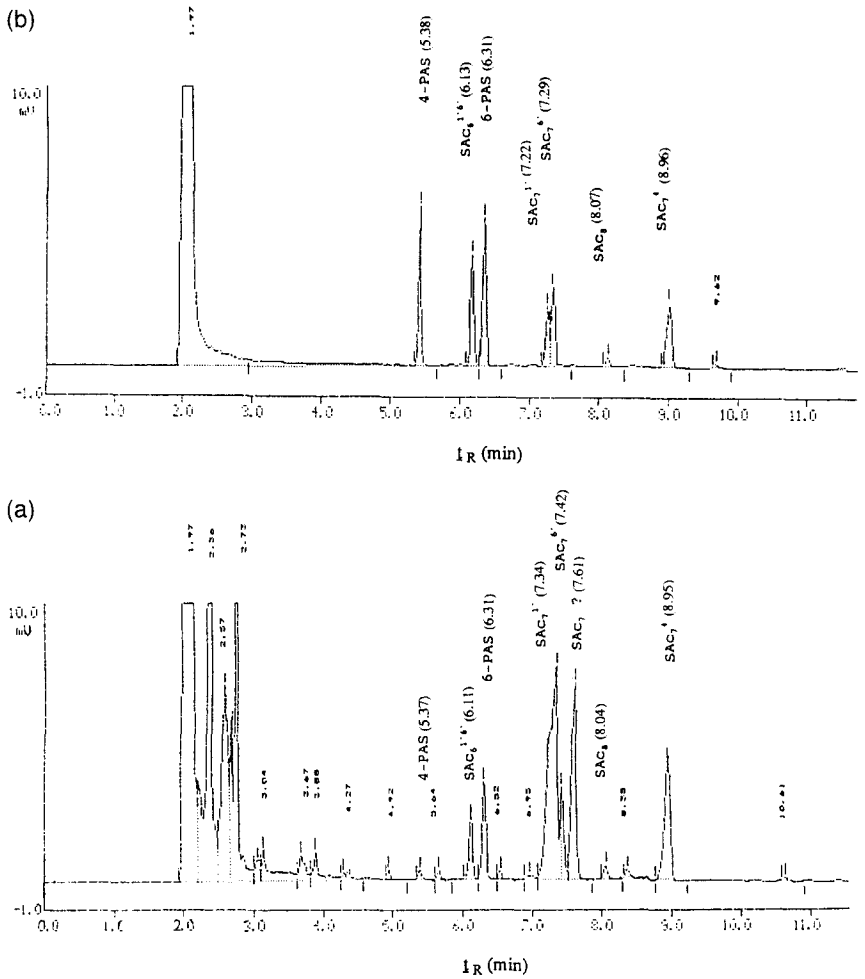


Fig. 1. (a) A chromatograph of sucrose acetates from the product mixture. SAc_n^x = Sucrose acetate. Subscripts range from $n = 6$ (hexaacetate) to $n = 8$ (octaacetate), and x is the positional isomer, e.g., SAc_7^4 = sucrose heptaacetate with a free hydroxy group at the 4-position. (b) A chromatograph of sucrose acetate standards.

mL) added from the top of the condenser; the reaction mixture was stirred for 24 h at 80 °C. The polymer was then filtered and washed with pyridine (4 × 10 mL), MeOH (4 × 25 mL), acetone (4 × 25 mL), and dichloromethane (4 × 50 mL). The final washing of dichloromethane was reduced in volume by evaporation and shown not to contain free sugar by TLC.

Both polymer **4'** and the control polymer equivalent were subjected to the same acidic cleavage conditions as described in the case of polymer **4**.

Sample preparation for gas–liquid chromatography.—After acidic cleavage the polymer was washed with dichloromethane (4 × 50 mL). The washings were combined with the product filtrate, washed successively with water, saturated $NaHCO_3$ solution, and then brine, dried (Na_2SO_4), and evaporated to give an oil. The latter was taken up in 0.25-mL volumes of dry pyridine and trimethylsilylimidazole (TMSIM) and heated at 80 °C for 0.5 h.

Gas–liquid chromatographic (GLC) analysis.—The TMS sugars were separated on a 25 m × 0.22 mm (i.d.) fused-silica capillary column of medium polarity (S.G.E., BP-5 type). The column oven, injector, and flame-ionisation detector were held isothermally at 300 °C. The helium carrier gas was set at an average linear velocity of 0.21 m/s. The splitting ratio was 1:150, and detector flow rates were hydrogen 40 mL/min and air 400 mL/min.

Interpretation of chromatograms.—Each sugar present in the unknown sample was characterised by noting its retention time, i.e., by taking a chromatogram of the unknown containing a particular standard under investigation and noting whether their retention times were the same (see Fig. 1). The quantity of sucrose acetate present in the unknown was ascertained by external calibration. The concentration of standards was 20 mg/mL, and each was derivatised in the manner described above. For an equivalent amount of dry unknown sample, the same solvent volume and derivatisation conditions were employed. Therefore, the concentration of a sucrose acetate component in the unknown sample was calculated by comparing its peak size of the same component belonging to the standard sample.

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