647. *Methyl Glucosides as Transfer Agents in Polymerisation of Acrylonitrile and Styrene.*

By G. MACHELL and G. N. RICHARDS.

Methyl 6-deoxy-6-dipropylamino-β-D-glucopyranoside and methyl 6-deoxy-6-mercapto-α-D-glucopyranoside have been synthesised. The transfer constants of these and other glucoside derivatives have been determined in polymerisation of acrylonitrile and styrene. The results are in accordance with earlier results on the use of tertiary amines and thiols as transfer agents. The use of the transfer reaction in graft polymerisation on cellulose derivatives is discussed.

THE transfer reaction in free-radical addition polymerisation may be summarised as:

$$R\cdot + T \longrightarrow P + T\cdot$$
$$T\cdot + M \longrightarrow T\text{-}M\cdot$$

where R· is a growing polymer radical, P a " dead " polymer molecule, M the monomer, and T the transfer agent. The new radical T· is usually capable of initiating polymerisation as shown. When T represents a preformed polymer, transfer at a modified end-group has been used to prepare block copolymers,[1] and if transfer occurs at points along the preformed polymer the transfer reaction initiates graft polymerisation. In order to consider the possibility of using cellulose derivatives as transfer agents to produce graft copolymers in this way it was necessary to know the relative transfer efficiency of various groupings which could be attached to the cellulose molecule. The transfer constants of a range of glucoside derivatives have therefore been determined. Three of those studied were new compounds.

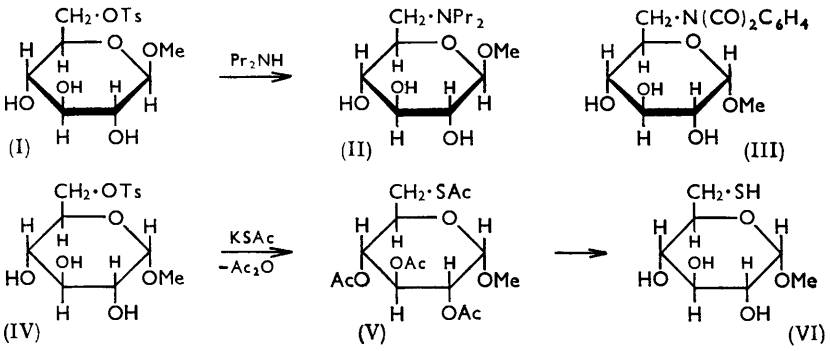
Methyl 6-deoxy-6-dipropylamino-β-D-glucopyranoside (II) was prepared by heating methyl 6-*O*-toluene-*p*-sulphonyl-β-D-glucopyranoside (I) with dipropylamine, reaction being analogous to that used by Freudenberg and Smeykal [2] to prepare a 6-deoxy-6-dimethylaminogalactose derivative. Methyl 6-deoxy-6-phthalimido-α-D-glucopyranoside (III) was similarly prepared by treatment of methyl 6-*O*-toluene-*p*-sulphonyl-α-D-glucopyranoside (IV) with potassium phthalimide.

Apart from 1-deoxy-1-mercapto-derivatives, the only deoxymercapto-derivative of an aldose or aldoside with a free thiol grouping so far isolated and properly characterised is the 6-deoxy-6-mercapto-D-glucose of Ohle *et al.*,[3] which was prepared by treatment of a 5,6-anhydro-sugar with hydrogen sulphide. Owen and his co-workers [4] have, however, prepared several thiols in the hexitol series and one of their methods has now been successfully employed in the glucoside series as follows. Methyl 6-*O*-toluene-*p*-sulphonyl-α-D-glucopyranoside (IV) was heated with potassium mercaptoacetate in acetone, yielding

[1] Bamford and White, *Trans. Faraday Soc.*, 1956, **52**, 716.
[2] Freudenberg and Smeykal, *Chem. Ber.*, 1926, **59**, 100.
[3] Ohle and Merten, *Chem. Ber.*, 1935, **68**, 2176.
[4] Creighton and Owen, *J.*, 1960, 1024 and earlier references.

methyl 6-acetylthio-6-deoxy-α-D-glucopyranoside which was then acetylated. The tetra-acetyl derivative (V) was then catalytically deacetylated to methyl 6-deoxy-6-mercapto-α-D-glucopyranoside (VI): the analysis and infrared spectrum were in agreement with this structure.

The transfer constants of compounds (II), (III), and (VI) and several other glucosides



were determined in the polymerisation of acrylonitrile in dimethylformamide solution with azodi-isobutyronitrile as catalyst and also in the uncatalysed bulk polymerisation of styrene. The results are summarised in Tables 1 and 2.

Experimental

Preparation of Methyl 6-Deoxy-6-dipropylamino-β-D-glucopyranoside (II).—Methyl β-D-glucopyranoside (20 g.) was converted by Compton's method [5] into methyl 2,3,4-tri-*O*-acetyl-6-*O*-toluene-*p*-sulphonyl-β-D-glucopyranoside (22·5 g.), m. p. 167—168°, $[\alpha]_D^{20}$ +6·5° (*c* 4 in chloroform), $[\alpha]_D^{20}$ +3° (*c* 2 in pyridine) {Helferich *et al.*[6] give m. p. 171°, $[\alpha]_D^{20}$ +33·1° (*c* 7 in pyridine)} (Found: C, 50·6; H, 5·5; OMe, 6·7. Calc. for $C_{20}H_{26}O_{11}S$: C, 50·6; H, 5·5; 1OMe, 6·5%). A portion (3·50 g.) of this product was suspended in dry methanol (100 ml.), and sodium methoxide (0·05 g.) in methanol (3 ml.) was added. Dissolution was complete after ½ hour's stirring and after a total of 18 hr. at room temperature *methyl 6-O-toluene-p-sulphonyl-β-D-glucoside* (2·25 g.) was isolated as a colourless syrup and dried at 40°/0·01 mm. over phosphoric oxide; it had $[\alpha]_D^{21}$ −11° (*c* 2 in ethanol) (Found: C, 48·5; H, 5·9. $C_{14}H_{20}O_8S$ requires C, 48·3; H, 5·8%).

The whole of the above product was heated with dipropylamine (5 ml.) at 100° for 18 hr. and then the unchanged amine was removed under reduced pressure. The residue was dissolved in water, the solution passed through a column of Amberlite resin IRA-400(OH) (15 ml.), and the effluent evaporated to a syrup which crystallised slowly. After recrystallisation from ethyl acetate the *methyl 6-deoxy-6-dipropylamino-β-D-glucopyranoside* (1·25 g.) had m. p. 117—118° and $[\alpha]_D^{26}$ −49·5° (*c* 2 in ethanol) (Found: C, 56·1; H, 9·6; N, 4·75%; equiv., 278. $C_{13}H_{27}NO_5$ requires C, 56·3; H, 9·8; N, 5·05%; equiv., 277).

Similar treatment of methyl 6-*O*-toluene-*p*-sulphonyl-α-D-glucopyranoside gave a syrup.

Preparation of Methyl 6-Deoxy-6-phthalimido-α-D-glucopyranoside (III).—Methyl 6-*O*-toluene-*p*-sulphonyl-α-D-glucopyranoside (3·0 g.), prepared as described by Cramer *et al.*,[7] and potassium phthalimide (2·0 g.) were suspended in dimethylformamide (40 ml.) and heated at *ca.* 100° for 24 hr., during which the solids slowly dissolved, and then at 110—115° for a further 4 hr After cooling, the solution was poured into water, and a small amount of phthalimide was removed. The filtrate was deionised with Amberlite resins IR-120(H) (15 ml.) and IRA-400 (carbonate) (25 ml.) and evaporated to dryness. Crystallisation of the resulting syrup from methanol–acetone and then ethyl acetate–ethanol afforded *methyl 6-deoxy-6-phthalimido-α-D-glucopyranoside* (0·83 g., 30%), m. p. 167—169°. When further recrystallised from ethanol this

[5] Compton, *J. Amer. Chem. Soc.*, 1938, **60**, 395.
[6] Helferich, Bredereck, and Schneidmüller, *Annalen*, 1927, **458**, 111.
[7] Cramer, Otterbach, and Springmann, *Chem. Ber.*, 1959, **92**, 384.

material had m. p. 171—173°, $[\alpha]_D^{22}$ +86·5° (*c* 2 in H_2O) (Found: C, 55·5; H, 5·5; N, 4·2. $C_{15}H_{17}NO_7$ requires C, 55·7; H, 5·3; N, 4·3%).

Preparation of Methyl 6-Deoxy-6-thio-α-D-glucopyranoside (VI).—A solution of methyl 6-*O*-toluene-*p*-sulphonyl-α-D-glucopyranoside [7] (IV) (10·0 g.) and potassium mercaptoacetate (4·0 g.) in acetone (400 ml.) was boiled under reflux for 7 hr., then cooled, and the crystalline potassium toluene-*p*-sulphonate filtered off (5·67 g., 94%). The filtrate was evaporated to a yellow viscous syrup (7·9 g.) which was treated with acetic anhydride (50 ml.) in dry pyridine (100 ml.) at room temperature for 20 hr. The resulting solution was poured into water and the *methyl 2,3,4-tri-O-acetyl-6-acetylthio-6-deoxy-α-D-glucopyranoside* (V) extracted with chloroform and distilled at 165—170°/0·02 mm. The distillate (6·4 g.) was a pale yellow glass, n_D^{20} 1·4792, $[\alpha]_D^{20}$ +118° (*c* 1 in chloroform) (Found: C, 48·0; H, 6·2; S, 8·5. $C_{15}H_{22}O_9S$ requires C, 47·6; H, 5·9; S, 8·5%).

The acetate (0·92 g.) was kept in dry methanol (20 ml.) containing sodium methoxide (0·05 g.) at room temperature for 20 hr. The solution was then evaporated to dryness, and the residue dissolved in water, deionised with Amberlite resins IR-120(H) and IRA-400 (carbonate), and again evaporated to a colourless syrup (0·45 g.), which was dried at 40°/0·02 mm. over phosphoric oxide. The *methyl 6-deoxy-6-thio-α-D-glucopyranoside* (VI), which was not further purified, had $[\alpha]_D^{20}$ +181° (*c* 0·5 in ethanol) (Found: C, 40·2; H, 7·0; S, 14·6. $C_7H_{14}O_5S$ requires C, 40·0; H, 6·7; S, 15·2%). The infrared spectrum was almost identical with that of methyl α-D-glucopyranoside, except for the weak S–H absorption at 2550 $cm.^{-1}$. In addition the peak at 845 $cm.^{-1}$ for the *O*-derivative was shifted to 875 $cm.^{-1}$ for the thiol and the 1250 $cm.^{-1}$ absorption was intensified.

Purification of Materials.—The purification of several of the model compounds has been described above; the remainder were purified according to the previously published methods. All of the compounds used had the appropriate elemental analyses. Acrylonitrile was purified as described by Bamford and Jenkins [8] and kept in the dark at 0°. Styrene was washed with 5N-sodium hydroxide and then with water, dried ($CaCl_2$), fractionally distilled under nitrogen at *ca.* 20 mm., and used immediately. Azodi-isobutyronitrile was twice recrystallised from toluene at <40°. Dimethylformamide was kept over phosphoric oxide at room temperature for several hours, then decanted and fractionally distilled at 1 atm. Dioxan was boiled under reflux with sodium for 4 hr., then fractionally distilled at 1 atm. from sodium just before use.

Polymerisation of Acrylonitrile.—The transfer agent (0·5—2 g.) was weighed into a glass ampoule, and acrylonitrile (10·0 ml.) and a solution of azodi-isobutyronitrile (0·020 g.) in dimethylformamide (40 ml.) added. The mixture was frozen, degassed at 0·01 mm., allowed to melt, refrozen, and again degassed at 0·01 mm. before sealing. The tubes were heated in a bath at 60° ± 0·1° for 90 min. with occasional shaking and the solution then added to methanol (150 ml.) with vigorous stirring. The precipitate was filtered off, washed with methanol, and dried at 40°/20 mm. over calcium chloride (yield 0·5—0·6 g.).

Polymerisation of Styrene.—The transfer agent (0·5—2 g.) and styrene (10·0 ml.) were degassed as above and heated in a bath at 100° ± 0·5° for 1 hr. with occasional shaking, and the polystyrene (0·1 g.) was isolated as described for polyacrylonitrile. In this case the polymer was redissolved in toluene and reprecipitated with methanol (5 vol.) before drying. In the experiments with the thiol (VI), a solution of it (0·02 g.) in dioxan (8·0 ml.) and styrene (8·0 ml.) was polymerised at 100° for 4 hr. and the polystyrene (0·2 g.) isolated as above.

Determination of Transfer Constants.—" Specific viscosities " of polyacrylonitrile and polystyrene were determined in a capillary viscometer at 25° in dimethylformamide and toluene solution respectively. The limiting viscosity number,[9] $[\eta]$, was determined from the Schulz–Sing relation,[10] $c[\eta] = \eta_{sp}/(1 + 0{\cdot}28\eta_{sp})$, where c is the concentration of polymer expressed in g./ml., and $\eta_{sp} = (t - t_0)/t_0$, with t and t_0 the viscometer flow-times.

The molecular weights were calculated from the Houwink equation ($[\eta] = K\bar{M}^{\alpha}$), the following constants being used: for polyacrylonitrile,[11] $K = 4{\cdot}72 \times 10^{-2}$, $\alpha = 0{\cdot}733$; for polystyrene,[12] $K = 1{\cdot}74 \times 10^{-2}$, $\alpha = 0{\cdot}714$.

The use of a single set of parameters for varying concentrations of transfer agents introduces

[8] Bamford and Jenkins, *Proc. Roy. Soc.*, 1953, *A*, **216**, 515.
[9] International Union of Pure and Applied Chemistry, *J. Polymer Sci.*, 1952, **8**, 257.
[10] Schulz and Sing, *J. prakt. Chem.*, 1943, **161**, 161.
[11] Bamford, Jenkins, Johnston, and White, *Trans. Faraday Soc.*, 1959, **55**, 168.
[12] Gregg and Mayo, *J. Amer. Chem. Soc.*, 1948, **70**, 2373.

errors in the determination of molecular weight from viscosity (cf. ref. 11), but since we are concerned at the present stage with relative transfer efficiencies, with a wide range of values, this procedure is considered adequate.

The transfer constants were calculated from the Mayo equation,[13]

$$\frac{1}{\bar{P}} - \frac{1}{\bar{P}_0} = C\frac{[S]}{[M]}$$

where P and P_0 are, respectively, the degree of polymerisation of polymer prepared with and without transfer agent, [S] and [M] are concentrations of transfer agent and monomer, and C

TABLE 1. *Polymerisation of acrylonitrile at* 60° *in dimethylformamide with azodi-iso-butyronitrile* (0·4 g./l.) *as catalyst.*

Transfer agent	10^2[S]/[M]	$\bar{P}$	10^2C	Transfer agent	10^2[S]/[M]	$\bar{P}$	10^2C
	0	708	0	Me 6-*O*-triphenylmethyl-α-D-glucoside	3·55	582	0·9
Me α-D-glucoside	6·70	659	0·2		3·60	586	0·8
	3·90	687	0·1	Me 2,3-di-*O*-benzyl-α-D-glucoside	2·66	596	1·0
Me β-D-glucoside	2·78	681	0·2		1·51	649	0·9
Me 6-*O*-toluene-*p*-sulphonyl-α-D-glucoside	2·19	703	<0·1	Me 6-deoxy-6-dipropylamino-β-D-glucoside (V)	1·43	337	10·9
	1·38	698	<0·1		1·19	366	11·1
Me 2,3,4,6-tetra-*O*-acetyl-α-D-glucoside	4·19	666	0·25		1·02	388	11·5
	2·03	681	0·3		0·595	474	11·8
Me 6-deoxy-6-iodo-α-D-glucoside	4·20	622	0·5	Me 6-deoxy-6-mercapto-α-D-glucoside (V)	0·13	638	12
	2·48	646	0·6		0·11	634	14
Me 6-deoxy-6-phthalimido-α-D-glucoside	1·89	666	0·5				
	1·10	685	0·5				

TABLE 2. *Bulk polymerisation of styrene at* 100°.

Transfer agent	10^2[S]/[M]	$\bar{P}$	10^2C	Transfer agent	10^2[S]/[M]	$\bar{P}$	10^2C
	0	5485	0	Me 6-deoxy-6-dipropylamino-β-D-glucoside (II)	1·93	4420	0·22
Dioxan	134·0	3350	0·009				
	134·0	3480	0·008	Me 2,3,4-tri-*O*-acetyl-6-deoxy-6-iodo-α-D-glucoside	4·02	2600	0·50
Me 2,3,4,6-tetra-*O*-acetyl-α-D-glucoside	4·53	5260	0·02		2·69	3200	0·49
	2·99	5260	0·025				
Me 6-*O*-toluene-*p*-sulphonyl-α-D-glucoside (IV)	2·22	5380	0·02	Me 2,3-di-*O*-benzyl-α-D-glucoside	2·91	2765	0·615
					2·18	3105	0·64
Me 6-*O*-triphenylmethyl-α-D-glucoside	1·80	4540	0·21	*Me 6-deoxy-6-thio-α-D-glucoside (VI)	0·164	106	557·0
	1·39	4730	0·21		0·149	118	546·0

* In 1 : 1 v/v dioxan–styrene solution (P_0 = 3415).

is the transfer constant. The adherence to the Mayo equation is shown by the linear dependence of $1/P$ with [S]/[M], in the case of methyl 6-deoxy-6-dipropylamino-β-D-glucopyranoside (II) with acrylonitrile (Table 1).

The results are shown in Tables 1 and 2.

DISCUSSION

The results in Table 1 show that the acetal, *O*-acetyl, *O*-toluene-*p*-sulphonyl, and hydroxyl groupings in methyl glucosides are very inefficient transfer agents for polyacrylonitrile radicals. The 6-deoxy-6-iodoglucoside shows a somewhat greater transfer efficiency, in accordance with the general trend observed with other halides.[14] The higher transfer constant of the di-*O*-benzyl ether probably reflects the known susceptibility of the benzyl CH_2 grouping to radical attack.[15] The 6-*O*-triphenylmethyl ether and the phthalimido-group are evidently also rather susceptible to attack by the polyacrylonitrile radical.[16]

[13] Mayo, *J. Amer. Chem. Soc.*, 1943, **65**, 2324.
[14] *E.g.*, Palit and Das, *Proc. Roy. Soc.*, 1954, *A*, **226**, 82.
[15] Cf. Walling, "Free Radicals in Solution," Wiley and Sons, Inc., New York, 1957, p. 402; Debiais, Niclause, and Letort, *J. Chim. phys.*, 1959, **56**, 41.
[16] Cf. Gregg and Mayo, *Discuss. Faraday Soc.*, 1947, **2**, 328.

Methyl 6-deoxy-6-dipropylamino-β-D-glucopyranoside (II), however, shows a very much higher transfer constant in reaction with acrylonitrile and this is almost certainly due to the resonance stabilisation of the transition-state complex between the tertiary amino-group and the polyacrylonitrile radical, which has been postulated for simple amines by Bamford and White.[1] The results of these authors on a series of amines suggest that compound (II) should be the most effective glucoside transfer agent of its (amine) type in acrylonitrile polymerisation. The thiol grouping, as in (VI), is also very effective in transfer with the polyacrylonitrile radical, but this group reacts even more readily with polystyrene radicals.

The results of Table 2 show that the acetal, *O*-acetyl, *O*-toluene-*p*-sulphonyl, and hydroxyl-groupings in the glucosides are relatively unreactive with polystyrene radicals, but the deoxyiodo- and the *O*-triphenylmethyl and *O*-benzyl ether groups show moderate reactivity, as in the reaction with polyacrylonitrile radicals. The tertiary amino-derivative (II), however, fails to show the superior reactivity which was observed with acrylonitrile (Table 1) and this is in accordance with Bamford and White's postulate [1] that the tertiary amines react most readily with radicals which are powerful electron-acceptors. The thiol (VI) has a very high transfer constant with polystyrene radicals and this is in accord with general observations on simple thiols.[17] Walling has suggested [18] that the effect is due to electron-donation to the thiol by the polymeric radical in the transition-state complex.

It is expected that these results for model compounds will be used to derive the relative reactivities of, for example, cellulose derivatives, to graft polymerisation by the transfer reaction. This type of model-compound approach has previously been used by Schonfield and Waltcher [19] with a brominated polyester and by Graham and his co-workers [20] with a thiol derivative of a polyvinyl, and the transfer constants of the polymers were similar to those of an analogous model. Our results suggest that either a deoxydipropylamino- or a deoxythio-cellulose derivative should readily form a graft copolymer with polyacrylonitrile on transfer reaction with polyacrylonitrile radicals, and that the deoxythio-derivative should be particularly efficient in similar grafting with styrene. The results also indicate that very little true transfer will occur when acrylonitrile or styrene is polymerised in presence of cellulose itself or any other common hydroxylated polymer.

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BRITISH RAYON RESEARCH ASSOCIATION, HEALD GREEN LABORATORIES,
WYTHENSHAWE, MANCHESTER, 22.
[Present addresses: AMERICAN MACHINE & FOUNDRY COMPANY,
BLOUNTS COURT RESEARCH LABORATORIES, SONNING COMMON, READING (G. N. R.).
MILLIKEN RESEARCH FOUNDATION, SPARTANBERG, S. CAROLINA,
U.S.A. (G. M.).]

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[17] Gregg, Alderman, and Mayo, *J. Amer. Chem. Soc.*, 1948, **70**, 3740; Dinaburg and Vansheidt, *J. Gen. Chem.* (*U.S.S.R.*), 1954, **24**, 840.
[18] Walling, *J. Amer. Chem. Soc.*, 1948, **70**, 2561.
[19] Schonfeld and Waltcher, *J. Polymer Sci.*, 1959, **35**, 536.
[20] Gluckman, Kampf, O'Brien, Fox, and Graham, *J. Polymer Sci.*, 1959, **37**, 411.