Synthesis of Some Vinyl Derivatives of Cellulose and Their Grafting Copolymerization with Styrene

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Synopsis

Some new vinyl derivatives of cellulose have been synthesized under anhydrous conditions using potassium cellulosate. The unsaturated groups were introduced by esterification with acryloyl chloride and by etherification with vinylbenzyl chloride or via 5-chloromethylsalicylaldyhyde derivatives. Levels of cellulose substitution of from ~10–75% of glucose residues were achieved. Polystyrene was readily grafted onto all the derivatives via solution polymerization in toluene, using azobisisobutyronitrile as a thermal initiator. Weight fractions of styrene of up to ~0.4 were readily obtained.

INTRODUCTION

During our search for improved polymeric supports for use in solid phase synthesis of peptides[1] and oligonucleotides,[2] we found a need for the synthesis of some polymerizabale derivatives of cellulose. It was hoped to employ these as macromolecular templates for the production of porous supports based on crosslinked polystyrene, which would retain a favorable polar character applicable to the solid phase method.[3,4] It was also necessary for us to demonstrate that these derivatives would indeed copolymerize with styrene, and an examination of the solution grafting of this monomer onto our derivatives seemed an appropriate way of achieving this.

We are conscious that the efficient grafting of linear polymers onto celllulose is a potentially important technological process in itself, and, though we have no direct interest in this, we feel it might be useful to other groups to describe our findings. Methods of grafting vinyl polymers onto cellulose have been excellently reviewed.[5–7] Perhaps somewhat surprisingly the approach involving the introduction of polymerizable groups onto cellulose has not been widely exploited. Methacrylic esters of cellulose have been reported and used in grafting procedures.[8] A number of allylic groups have also been introduced and copolymerized with vinyl monomers,[9] while cellulose acetate has been treated with methacryloylethylenimine and subsequently grafted with polystyrene.[10] All of these examples refer to relatively polar vinyl substituents, and have overlooked the possibility of increasing the hydrophobic character of the cellulose species while simultaneously introducing a polymerization group. The substituents upon which we have concentrated are largely aromatic and achieve this dual result.

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EXPERIMENTAL

Materials

Cellulose powder (Whatman Standard Grade) was washed with dilute NaOH, water, dilute acetic acid, water, deionized water, methanol, and acetone, and then vacuum dried. Commercial styrene was washed with aqueous NaOH to remove the stabilizer, then with water, and dried over anhydrous $CaCl_2$. 5-Chorom-ethylsalicylaldehyde was prepared from salicylaldehyde according to a literature method.[11] All reaction solvents were dried and distilled before use. IR spectra were recorded on a Perkin-Elmer 397 as solid using KBr.

Preparation of Cellulose Acrylate (I)

Cellulose (6.5 g) in acetonitrile (100 mL) was allowed to react with potas-sium-t-butoxide (12 g) at room temperature for ~3 h. The solvent was then removed on a rotatory evaporator and the dry residue was rotated under reduced pressure at 50°C for another 1 h. The potassium cellulosate formed was sus-pended in acetonitrile (100 mL) and allowed to swell for ~1 h at room tempera-ture. An excess of acryloyl chloride (20 g) in acetonitrile (50 mL) was added dropwise to the stirred mixture at room temperature. Stirring was continued overnight at room temperature and then for another 2 h at 50°C. The cellulose product was filtered, washed with ethanol, water, ethanol, and acetone, and then dried in vacuum at 50°C. A yield of 7.5 g of product (I) was obtained. IR (KBr) showed absorption at 1720 cm^{-1} (C=O of ester).

Preparation of p-Vinylphenylmethylcellulose (II)

This was prepared from potassium cellulosate and p-vinylbenzylchloride es-sentially as described for cellulose acrylate (I) using a mixture of acetonitrile–toluene as solvent. IR (KBr) showed absorption at 1600 cm^{-1} (aromatic).

Preparation of 5-Salicylaldehyde-methylcellulose (III)

This was prepared in the same way as cellulose acrylate (I) from potassium cellulosate and 5-chloromethylsalicylaldehyde using either acetonitrile or pro-pionitrile as solvent. IR (KBr) showed absorptions at 1680 cm^{-1} (CHO) and 1610 cm^{-1} and 1495 cm^{-1} (aromatic).

Preparation of 5-Salicylideneanilide-methylcellulose (IV)

To a stirred suspension of (III) (1 g) in ethanol (20 mL) a solution of aniline (1 g) in ethanol (10 mL) was added and the reaction mixture was stirred over-night. The product was filtered and washed several times with ethanol and dried in vacuum at 60°C to give 1.2 g of (IV). IR (KBr) showed absorptions at 1620 cm^{-1} (aromatic), 1585 cm^{-1} (C=N), and 1490 cm^{-1} (aromatic).

Preparation of 5-(O-Acrylsalicylaldehyde)-methylcellulose (V).

This was prepared as the cellulose acrylate (I) from potassium salt of (III) (2 g) and excess acryloyl chloride using acetonitrile as solvent. After filtration, the product was neutralized with dilute acetic acid, washed with water, and dried in vacuum to give 2.2 g of (V). IR (KBr) showed absorptions at 1720 cm^{-1} (C=O of ester), 1685 cm^{-1} (CHO), 1615 cm^{-1} (aromatic), and 1500 cm^{-1} (aromatic).

Preparation of 5-(O-Acetylsalicylideneanilide)-methylcellulose (VI)

This was prepared in a similar way to (IV), using (V) and aniline. IR (KBr) showed absorptions at 1725 cm^{-1} (C=O of ester), 1625 cm^{-1} (C=N), 1605 cm^{-1} (aromatic), and 1500 cm^{-1} (aromatic).

Preparation of Acrylamide Derivative of 5-Salicylaldehyde-methylcellulose (VII)

To a stirred mixture of (III) (3 g) and acrylamide (5 g) in methanol (50 mL) concentrated sulphuric acid (1 mL) was added dropwise. The reaction mixture was heated with stirring on a water-bath at 60°C for 6 h. After filtration, the product was washed with methanol and acetone, and dried in vacuum at 50°C

TABLE I
Elemental Analyses of Cellulose Derivatives

Derivative	Segment[a] formula/ molecular weight	Microanalyses[b]			
		C(%)	H(%)	O(%)[c]	N(%)
Cellulose	$C_6H_{10}O_5$	44.4	6.2	49.4	—
	162	42.5	6.0	51.4	—
	$C_9H_{12}O_6$	50.0	5.6	44.4	—
I	216	44.0	5.6	50.4	—
		63.4	6.7	29.9	—
	$C_{15}H_{18}O_5$	64.7	6.5	28.8	—
II	278	44.2	6.3	49.5	—
		54.5	6.4	39.1	—
	$C_{14}H_{16}O_7$	56.8	5.4	37.8	—
III	296	51.7	5.7	42.6	—
	$C_{20}H_{21}O_6N$	64.7	5.7	25.8	3.8
IV	371	55.4	5.9	36.6	2.1
	$C_{17}H_{18}O_3$	58.3	5.1	36.6	—
V	350	49.2	5.4	45.4	—
		54.1	5.4	40.5	—
	$C_{23}H_{23}O_7N$	64.9	5.4	26.4	3.3
VI	425	55.4	5.6	35.7	3.3
		58.1	6.3	33.6	2.0
	$C_{17}H_{21}O_8N$	55.6	5.7	34.9	3.8
VII	367	45.5	5.9	47.7	0.93
		50.3	6.3	42.5	0.88

[a] Hypothetical formula assuming complete chemical modification of all primary hydroxyl groups acording to Scheme 1.

[b] In the following order: calculated from[a], experimental measurement, and experimental measurement of grafted product when appropriate.

[c] By difference.

overnight. A yield of 3.1 g of the product (VII) was obtained. IR (KBr) showed absorptions at 1670 cm^{-1} (—CONH—), 1620 cm^{-1} (aromatic), and 1500 cm^{-1} (aromatic).

### Grafting of Styrene onto Polymerizable Cellulose Derivatives

A mixture of derivatized cellulose (I), (II), (VI), or (VII) (1 g), styrene (5 g), toluene (5 g), and AIBN (0.05 g) was refluxed for 5 hr. The semisolid product was precipitated in methanol and washed exhaustively with hot acetone in a Soxhlet extractor overnight. It was dried in vacuum at 60°C.

Elemental Microanalyses

These were carried out in the usual way using a Perkin Elmer 240 Elemental Analyzer.

RESULTS AND DISCUSSION

Cellulose was derivatized according to Scheme 1 and the elemental micro-
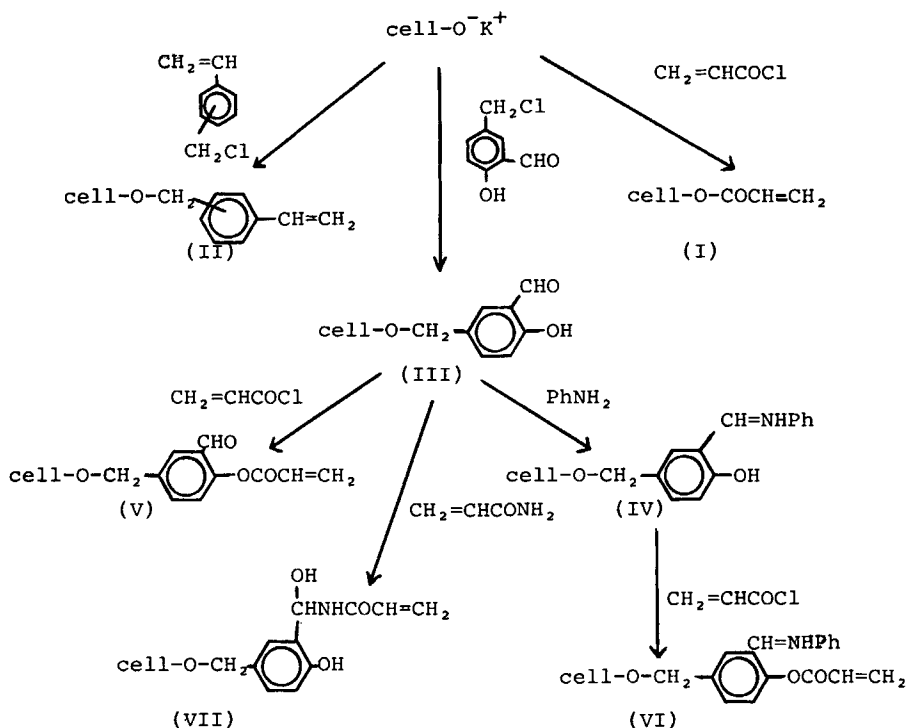
Scheme 1. Synthesis of vinyl derivatives of cellulose.

analysis of each product is shown in Table I, along with the corresponding theoretical values calculated assuming 100% functionalization. Since the analysis of the starting cellulose itself deviated somewhat from theory, an order of magnitude for the percentage substitution of the glucose units in the cellulose, y, was calculated from the expression

$$y = \frac{A - B}{C - D} \times 100$$

where
  A = % carbon found for derivatized cellulose
  B = % carbon found for starting cellulose
  C = % carbon calculated for 100% derivatization
  D = % carbon calculated for starting cellulose
The results are displayed in Table II.

In the case of the nitrogen containing derivatives (IV), (VI), and (VII), an estimate of y was also made from a comparison of the theoretical and experimental nitrogen contents. It must be emphasised that these calculations are strictly order of magnitude only, and not the least assume that the derivatizations occur strictly as shown in Scheme 1. In practice, for example, the sequence cellulose → (III) → (V) produces at (III) a mixture of residual glucose units and modified units. Subsequent esterification to (V) is shown as occurring only on the more reactive phenolic hydroxyl group, whereas in practice some reaction of residual primary hydroxyl groups on glucose segments may occur. Despite these approximations, however, the data provides a useful guide to relative degrees of functionalization. In the case of those derivatives containing nitrogen the agreement in the levels of substitution calculated from both carbon and nitrogen analyses is very good except for (VI). In the latter case, three consecutive chemical modification steps are involved, and it might be that the approximations used in the calculations are pushed too far in this instance.

The levels of grafting achieved with (I), (II), (V), (VI), and (VII) expressed as a weight fraction of styrene, x, in each grafted product was calculated using the relationship

$$E = (1 - x)A + 92.3x$$

where
    A = as before
    E = % carbon found for grafted derivative
    92.3 = % carbon calculated for a styrene segment
    These results also appear in Table II along with estimates of the ratio of grafted

TABLE II
Degree of Substitution and Grafting of Cellulose Derivatives

Derivative	Substitution[a] of cellulose (%)	Weight fraction[a] of styrene grafted	Ratio styrene[a] segments/cellulose vinyl groups
I	27	0.40	4.2
II	8.4	0.21	5.2
III	74	—	—
IV	65 (55)[b]	—	—
V	48	0.11	0.62
VI	62 (100)[b]	0.074	0.40
VII	27 (25)[b]	0.10	0.88

  [a] See text for definition and method of calculation.
  [b] Deduced from comparison of theoretical and experimental N content.

styrene segments to cellulose vinyl groups, z, calculated from

$$z = \frac{x/104}{(1-x)/F} \times \frac{100}{y}$$

where

    x, y = as before

    F = average molecular weight of a cellulose segment adjusted for the degree of derivatiation

i.e., $F = \dfrac{yG}{100} + \dfrac{(1-y)162}{100}$

where

    G = theoretical molecular weight of a derivatized cellulose segment

    162 = theoretical molecular weight of a glucose segment

    104 = theoretical molecular weight of a styrene segment

Confirmation of grafting was obtained from infrared spectra of the products. Each displayed bands characteristic of the functional groups introduced and also of polystyrene, in particular absorptions at 13.25 μ and 14.35 μ.[10] While these proved impossible to quantify, there was in general a rough correlation with x in Table II (the weight fraction of grafted styrene) providing some confirmative evidence for this data.

Clearly, then, cellulose derivatized in the manner described can be readily grafted with polystyrene. The derivatives (II), (V), (VI), and (VII) and all the grafted products readily swell in toluene clearly indicating their hydrophobic nature, whereas (I) shows no distinct change from the behavior of cellulose itself. It is therefore perhaps somewhat surprising to find that under similar conditions the weight fraction of styrene grafted is highest with (I). A possible explanation of this apparent contradiction may lie in the values of the reactivity ratios of styrene with acrylates. Little data is available on phenyl acrylates, though a comparison with alkyl methacrylates and phenyl methacrylates would predict phenyl acrylates to be somewhat more reactive than alkyl acrylates.[12] If this is indeed the case, then once a propagating oligostyryl radical reacts with one cellulose bound acrylate group, the tendency for growth to occur via other acrylate species will be larger for the phenyl acrylate species than for the single alkyl acrylate, (I). This would, of course, be reflected in a lower incorporation of styrene residues for the phenyl acrylate derivatives as observed experimentally (Table II).

Thus the process of grafting via vinyl derivatives rather than by radical transfer or termination[13] or the generation of initiating radicals on cellulose, by chemical[14,15] or radiochemical means,[16] might be expected to produce a quite different grafting pattern. Whereas initiation and transfer or termination processes might give rise to grafting of a relatively few but long polymer chains [Scheme 2 (b) and (c)], grafting via vinyl groups presents the additional possibility of polymerization along a cellulose chain, and indeed the crosslinking of one chain with another [Scheme 2(a)]. Our analyses do not, of course, distinguish between these two extreme models nor indeed any intermediate mixture of the two, but the calculated ratios of the average number of grafted styrene segments to cellulose vinyl groups is low, and not inconsistent with the latter model.
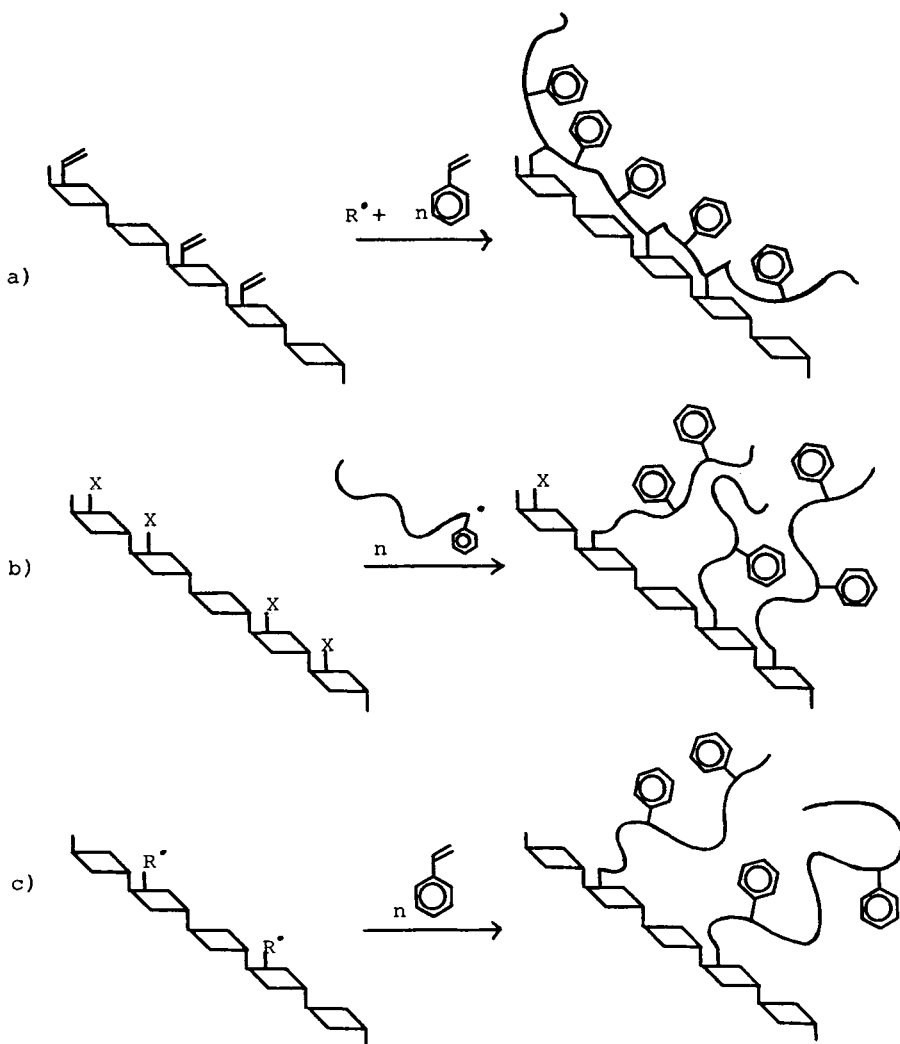
Scheme 2. Graft polymerization reactions of styrene onto cellulose derivatives. (R·) active free radical, (X) terminating group, (□) = 1,4-glucose residue).

We have not made any attempts to optimize either our derivatization reactions or the subsequent grafting processes since such a study lies outside the scope of our interest. However, we believe that our approach could be readily improved upon and is certainly worthy of further consideration and experimentation by those more directly involved in the field.

References

1. J. M. Stewart, in *Polymer-Supported Reactions in Organic Synthesis*, P. Hodge and D. C. Sherrington, Eds., Wiley, London, 1980, Chap. 7, p. 343.

2. M. J. Gait, in *Polymer-Supported Reactions in Organic Synthesis*, P. Hodge and D. C. Sherrington, Eds., Wiley, London, 1980, Chap. 9, p.435.

3. R. C. Sheppard, in *Peptides 1971*, H. Nesvadba, Ed., North-Holland, Amsterdam, 1973, p. 111.

4. E. Atherton, D. L. J. Clive, and R. C. Sheppard, *J. Am. Chem. Soc.*, **97**, 6584 (1975).

5. H. A. Krassig and V. T. Stannett, *Adv. Pol. Sci.*, **4**, 111 (1965).

6. V. T. Stannett and H. B. Hopfenberg, "Graft Copolymerization," in *Cellulose and Cellulose Derivatives*, N. Bikales and L. Segal, Eds., Wiley, New York, 1970, Vol. 5, Part 5, pp. 907–936.

7. J. T. Guthrie, *Polymer*, **16**, 134 (1975).

8. A. A. Berlin and T. A. Makarova, *Zh Obshchei Khim.*, **21**, 1267 (1951) (*Chem. Abs.* **46**, 1996 (1952).

9. M. M. Legache, M. Chateau, and J. Pomey, *C. R. Acad. Sci.*, **251**, 2353 (1960).

10. G. Faraone, G. Parasacco, and C. Cogrossi, *J. Appl. Polym. Sci.*, **5**, 16 (1961).

11. G. Wulff and A. Akelah, *Makromol. Chem.*, **179**, 2647 (1978).

12. J. Brandrup and E. H. Immergut, Eds., *Polymer Handbook*, 2nd ed., Wiley, New York, 1975.

13. E.g., B. N. Misra, J. K. Jassal, and C. S. Pande, *J. Polym. Sci., Polym. Chem. Ed.*, **16**, 295 (1978).

14. C. I. Simionescu and S. Dumitriu, *J. Polym. Sci. Part C*, **37**, 187 (1972).

15. D. N. S. Hon, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 1857 (1980).

16. V. Stannett, *Chem. Eng. News*, **25**, No. 40, 57 (1962).