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Yoshinobu Naoshima[a]; Charles E. Carraher Jr.[bc]; Timothy J. Gehrke[b]; Masahide Kurokawa[a]; David Blair[b]
[a] Department of Chemistry, Okayama University of Science, Okayama, Japan [b] Wright State University, Dayton, Ohio [c] Florida Atlantic University, Boca Raton, Florida

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Chemical Modification of Dextran through Reaction with Biscyclopentadienyltitanium Dichloride and Dibutyltin Dichloride as a Function of the Reaction System

YOSHINOBU NAOSHIMA

Department of Chemistry
Okayama University of Science
Ridai-cho, Okayama 700, Japan

CHARLES E. CARRAHER JR.* and TIMOTHY J. GEHRKE

Wright State University
Dayton, Ohio 45435

MASAHIDE KUROKAWA

Department of Chemistry
Okayama University of Science
Ridai-cho, Okayama 700, Japan

DAVID BLAIR

Wright State University
Dayton, Ohio 45435

---

*Present address: Florida Atlantic University, Boca Raton, Florida 33431.

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ABSTRACT

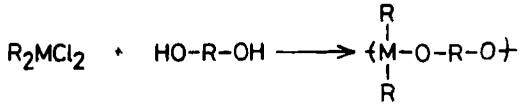
Dextran was modified through condensation with biscyclopentadienyltitanium dichloride and dibutyltin dichloride by employing a number of solution and interfacial condensation systems. The modified dextran is rapidly synthesized (within 30 s) in good yield with moderate to high degrees of substitution. The products are complex with chains composed of a variety of substituted and unsubstituted glycopyranose units.

INTRODUCTION

The recognition that the supply of coal and petroleum is limited, varying in cost and, at times, environmentally unacceptable has refocused our attention on the use of renewable resource materials as feedstocks for the chemical industry, including coatings, plastics, and elastomers application. Further, going beyond their renewable nature and abundance, natural feedstocks may themselves provide valuable properties, some offering three-dimensional networks which are biodegradable and which may act as internal plasticizers and networks to form blends and composites [1].

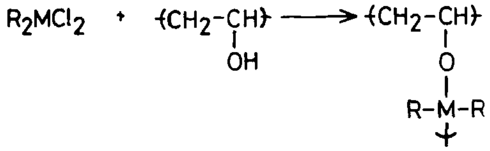
Carbohydrates are the most abundant (weightwise) class of organic compounds, constituting almost three-fourths of the dry weight of the plant world. They are diverse with respect to both occurrence and structure and represent a great storehouse of energy and feedstock. About 4 × 10^{11} tons of sugar are produced annually through natural photosynthesis.

Carraher and co-workers have synthesized a number of titanium and tin polyethers (Structure 2; [2-6]) and modified poly(vinyl alcohol)



$$R_2MCl_2 + HO{-}R{-}OH \longrightarrow \left(\overset{R}{\underset{R}{M}}{-}O{-}R{-}O \right)$$

1 2



$$R_2MCl_2 + \left(CH_2{-}\underset{OH}{CH} \right) \longrightarrow \left(CH_2{-}\underset{\substack{| \\ O \\ | \\ R-M-R \\ +}}{CH} \right)$$

3

(3; [7, 8]) through condensation with a variety of metal-containing reactants, including organostannanes and bicyclopentidienyltitanium dichloride (BCTD).

Recently Carraher and co-workers extended this to the modification of cellulose derived from cotton [9, 10]. Even more recently, this was extended to the modification of dextran [11, 12].

Here we report the modification of dextran as a function of a number of low-temperature condensation systems.

EXPERIMENTAL

Dibutyltin dichloride (Fisher Scientific Co., Fairlawn, New Jersey), biscyclopentadienyltitanium dichloride (BCTD) (Aldrich, Milwaukee, Wisconsin), and dextran (USB, Cleveland, Ohio; molecular weight 2-3 $\times 10^5$) were employed as received. Reactions were conducted by use of a 1-pint Kimex emulsifying jar placed on a Waring Blendor (Model 1120) with a "no load" stirring rate of 18 500 rpm. For the classical interfacial condensations, dextran was dissolved in doubly distilled water (DDW) and base added. The organometallic reactant was dissolved in an organic liquid, typically chloroform or carbon tetrachloride. The organic phase was added to the emulsifying jar, the cap screwed on, and stirring begun. The aqueous phase was added through a hole in the jar lid through a powder funnel. Addition requires 35 s or less. For aqueous solution systems, the above was repeated, except that the Cp_2TiCl_2 is also dissolved in DDW. To minimize the competing hydrolysis-related reactions with Cp_2TiCl_2, which form such products as $Cp_2Ti(OH)_2$, the aqueous solution containing dissolved Cp_2TiCl_2 was used within 1 h after addition of the titanium-containing reactant to the water. For inverse interfacial systems, the BCTD was dissolved in DDW, and the dextran dissolved in a suitable organic liquid. For the aqueous two-solvent solution systems employing BCTD, the BCTD was dissolved in DMSO and the dextran and base dissolved in DDW. For the nonaqueous interfacial systems, dextran and base were dissolved in DMSO, and DBSD was dissolved in a suitable nonpolar organic liquid, such as decane, cyclohexane, or hexane. For the layered interfacial systems, the liquid stannane acts as the total organic phase. All products were obtained as precipitates by suction filtration. Repeated washings with a typical organic liquid, such as carbon tetrachloride, and water assisted in the purification of the product.

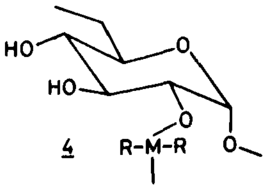
Solubility studies were carried out by placing about 20 mg sample in with 3 mL liquid. Elemental analysis for tin was conducted as described in Ref. 11. Elemental analysis for titanium was conducted by heating known weights of samples till a white product (titanium dioxide) was formed or through use of $HClO_4$ [12]. Physical characterization sequences are described in Ref. 12.

RESULTS AND DISCUSSION

Dextran was the polysaccharide chosen for preliminary study. It is water soluble, so that aqueous reaction systems can be evaluated. Further, it is readily available on a large scale in a wide variety of molecular weights, permitting further studies involving the extent of modification as a function of dextran molecular weight. Dextran is primarily found in yeast and bacteria and is a 1-6 storage polysaccharide of D-glucose.

Dibutylin dichloride was chosen for a variety of reasons, including 1) our previous experience with this compound that could be directly applied to the present study; 2) a lower cost than other organostannane dihalides; 3) availability in box car quantities; 4) the fact that products derived from it generally show good inhibition to mildew and rot and only moderate toxicity to mammals. The reasons for the use of biscyclopentadienyltitanium dichloride included points 1) and 3), and that it is the least expensive of the Group IVB metallocene dihalides, is relatively nontoxic to mammals, and exhibits some catalytic and ultraviolet stability properties that might be extended to products containing the organometal-containing moiety. The use of metals allows the ready identification of the extent of modification through analysis of the metal content of the product. Further, use of difunctional reactants typically ensures formation of insoluble products if reaction occurs since some degree of crosslinking should occur. This allows easy collection of the product.

Structural analysis is based on IR, MS, elemental analysis, and control reactions. Briefly, the products contain a variety of units such as



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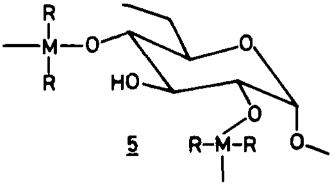

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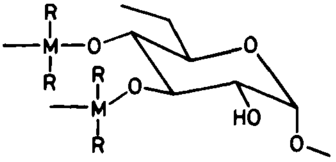

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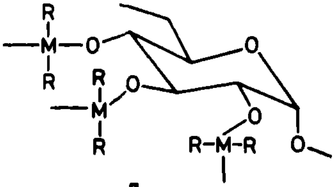

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those depicted in 4-7 and also include unreacted sugar units. A detailed discussion of the structural aspects associated with the products is contained in Ref. 12.

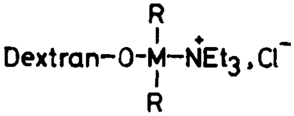
The major purpose of this research was the preliminary evaluation of a number of potential condensation systems to determine which systems might be useful in the modification of additional mono-, di-, and polysaccharides such as starch, sucrose, and glucose.

There are three general condensation techniques; thermal, solution, and interfacial. The thermal method was not used since true solution of polysaccharides cannot be effected in the "neat" state through heating (glucose units experience ring opening about 200°C) and systems utilizing less energy are favored for industrial acceptance if other factors are the same.

A number of solution condensation systems have been devised. A homogeneous reaction medium is the sole requirement, thus single and multiliquid systems have been devised. For the present study, only several systems were evaluated (for results see Tables 1-3). Product is rapidly obtained in high yield for the simple H_2O-DMSO-NaOH systems with both metal-containing reactants. The aqueous solution system cannot be used with organostannates since they are not soluble in water. BCTD undergoes hydrolysis in water, forming a variety of ionic species, but if the reaction is run within about 30 min after addition of the BCTD to water, the major ionic forms react to insert the Cp_2Ti moiety, giving products comparable to those synthesized in nonaqueous and aqueous interfacial systems, the major difference appearing to be a difference in the nature of the end group of the titanium-containing polymers (see, for instance, Refs. 2, 4, 13-15).

Thus actual weights and percentages based on an assumed structure are reported. While a variety of structures can be used in calculating product yield, we have chosen structures that reflect somewhat the average degrees of substitution based on the determination of the metal content. For products derived from BCTD and dibutyltin dichloride, DBSD, yield is based on a repeat unit containing 1.5 Cp_2Ti or Bu_2Sn units for each sugar unit.

Systems employing triethylamine as the added base typically have end groups of form 8. This is substantiated by infrared and mass spectroscopy as well as synthesis and properties of model compounds (for BCTD-derived products; Ref. 12).



$$\text{Dextran-O-}\overset{R}{\underset{R}{M}}\text{-}\overset{+}{N}Et_3,Cl^-$$

8

TABLE 1. Results for Aqueous Solution Condensation Systems Employing BCTD[a]

Base, mmol	Base	Time, s	Yield, %	Yield, g	Ti, %	Ti,[b] %
3	Et_3N	15	0	0	-	
3	Et_3N	30	33	0.09	29[c]	21
3	NaOH	15	0	0	-	
3	NaOH	30	0	0	-	
1	$Ba(OH)_2$	30	14	0.04	22[c]	18
1	TED[d]	30	0	0	-	
2	TED[d]	30	18	0.05	26[c]	18
3	TED[d]	30	28	0.08	29[c]	18
2	Bu_3N	30	0	0	-	
3	Bu_3N	30	31	0.09	28[c]	21

[a] Reaction conditions: Dextran (1.00 mmol) and added base in 50 mL H_2O added to stirred (18 500 rpm) solutions of Cp_2TiCl_2 (1.00 mmol) in 50 mL H_2O at 25°C.

[b] By use of $HClO_4$.

[c] Incomplete combustion.

[d] TED = triethylenediamine.

TABLE 2. Results for Two-Solvent Systems Employing BCTD[a]

Cp_2TiCl_2, mmol	Dextran, mmol	Base, mmol	Time, s	Yield %	Yield g	Ti, %
1	1	Et_3N(3)	30	0	0	-
1	1	Et_3N(3)	60	0	0	-
1	1	Et_3N(3)	120	0	0	-
2	3	NaOH(6)	90	124	0.705	13

[a] Reaction conditions: Dextran and added base dissolved in 50 mL H_2O added to stirred (18 500 rpm) solutions of Cp_2TiCl_2 in 50 mL DMSO at 25°C.

TABLE 3. Results for Solution Condensation Systems Employing DBSD[a]

Brief description of system	Yield		Sn, %
	%	g	
DMSO/DMSO (Et_3N, Me_4NCl)	0	0	-
DMSO (Bu_2SnCl_2)/H_2O (Dextran, NaOH)	71	1.5	17
DMSO/DMSO (Me_4NCl)	0	0	-
DMF (LiCl)/DMF (LiCl)	0	0	-
DMF (LiCl)/DMF (LiCl, Et_3N)	0	0	-
DMSO/DMSO (NaOH, Me_4NCl)	0	0	-

[a] Reaction conditions: Dextran (4 mmol) and added base and/or salt (12 mmol of each) in 40 mL liquid are added to stirred (18 000 rpm) solutions containing dibutylin dichloride (6 mmol) at 25°C for a stirring time of 30 s.

A number of interfacial condensation systems have been developed by Morgan, Carraher, and others. The classic interfacial system consists of an aqueous phase, here containing the water-soluble dextran and added base, and a water-immiscible organic phase, here containing the BCTD (see Tables 4 and 5 for representative results). Product yield was found to be dependent on the nature and amount of base employed.

An inverse interfacial system was employed to form polyethers (form 2). Here the dextran and added (typically organic) base are contained in the organic liquid phase and BCTD in water. Small yields of the modified dextran are produced by such inverse interfacial systems (see, for instance, Table 6).

Nonaqueous interfacial systems were developed with the dextran dissolved in a suitable organic solvent, typically a dipolar aprotic liquid, such as DMSO, and the metal halide dissolved in a long-chain hydrocarbon liquid, cyclohexane, or carbon tetrachloride (many of these combinations form immiscible liquid pairs). Several successful combinations have been found for DBSD systems (Table 7), but none for BCTD.

TABLE 4. Effects of Added Base for Aqueous Interfacial Systems Employing BCTD[a]

Cp_2TiCl_2, mmol	Dextran, mmol	Base, mmol	Stirring time, s	Yield		Ti	
				%	g	%[b]	%[c]
		Triethylamine					
3	2	0	30	0	0	-	-
3	2	3	30	0	0	-	-
3	2	6	30	12	0.09	30[d]	19
3	2	9	30	31	0.23	27[d]	18
3	2	12	30	51	0.38	17	15
3	2	15	30	69	0.51	19	16
2	1	3	30	0	0	-	-
2	1	6	30	30	0.15	29[d]	21
2	1	9	30	52	0.25	23[d]	16
1.3	1	3	30	3	0.01	-	-
1.3	1	6	30	41	-.13	19	18
1.3	1	9	30	50	0.16	18	17
1	1	3	15	0	0	-	-
1	1	3	30	37	0.09	29[d]	21
		Triethylenediamine					
1	1	2	30	18	0.05	26[d]	18
1	1	3	30	28	0.08	29[d]	18
		Tributylamine					
1	1	3	30	31	0.09	28[d]	21
		Barium Hydroxide					
1	1	0.5	30	0	0	-	
1	1	1	30	16	0.04	22	
1	1	1.5	30	0	0	-	

(continued)

TABLE 4 (continued)

Cp_2TiCl_2, mmol	Dextran, mmol	Base, mmol	Stirring time, s	Yield		Ti	
				%	g	%[b]	%[c]
		Sodium Hydroxide					
2	3	4	30	0	0	-	
2	3	6	30-120	0	0	-	
2	3	9	30	0	0	-	
3	3	6	30	0	0	-	
3	3	6	80	65	0.48	13	

[a] Reaction conditions: Dextran and added base dissolved in 50 mL water and added to stirred (18 500 rpm) solutions of BCTD in 50 mL $CHCl_3$ at 25°C.

[b] By thermolysis.

[c] By use of $HClO_4$.

[d] Incomplete oxidation to titanium dioxide.

TABLE 5. Results for the Aqueous Interfacial Systems Employing DBSD

Organotin dihalide, mmol	Dextran, mmol	Base nature	Base amount, mmol	Yield		Sn, %
				g	%	
6	4	NaOH	12	1.7	81	23
6	4	Et_3N	72	2.8	130[a]	39
6	4	Piperidine	24	1.9	90	17
6	4	Quinuclidine	12	1.6	76	12
6	4	4-Dimethyl aminopyridine	24	0.64	31	24

[a] Reduced to 100% assuming 2.5 units of Bu_2Sn per sugar unit which would contain 38% Sn.

TABLE 6. Results for the Inverse Interfacial Systems Employing BCTD[a]

	Yield		Ti	
Base	%	g	%	%[b]
Et_3N	7	0.021	31[c]	
TED	5	0.015	33[c]	17
Bu_3N	0	0	-	

[a] Reaction conditions: Dextran (1.00 mmol) and added base (3.00 mmol) in 50 mL of C_6H_5CN added to stirred (18 500 rpm) solution of Cp_2TiCl_2 (1.00 mmol) in 50 mL H_2O for 30 s stirring at 25°C.

[b] Use of $HClO_4$.

[c] Incomplete combustion.

TABLE 7. Results for Nonaqueous Interfacial Systems Employing DBSD[a]

		Yield		
Added base	Solvents	%	g	Sn, %
NaOH[b]	Decane/DMSO	48	1.0	16
Triethylene diamine	Decane/DMSO	43	0.9	21
Triethylamine	Decane/DMSO	0	0	-

[a] Reaction conditions: Dextran (4 mmol) and added base (12 mmol) in 40 mL of decane are added to stirred (18 000 rpm) DMSO (40 mL) solutions containing dibutyltin dichloride (6 mmol) at 25°C for a stirring time of 30 s.

[b] Added as a solid.

TABLE 8. Yield and Tin Content for Products Synthesized Employing Layered Liquid Organostannane Interfacial Systems

Reactants	Yield (%)	Yield (g)	Sn, %
Bu_3SnCl^a	2	0.1	-
Pr_3SnCl^a	0	0	-
$Bu_2SnBr_2{}^b$	62	1.3	10
$Bu_2SnBr_2{}^c$	43	0.9	10
Bu_2SnBr_2	71	1.5	9

[a] Reaction conditions: Dextran (4 mmol) and sodium hydroxide (12 mmol) in 40 mL water are added to liquid stannanes (6 mmol) at 25°C for a stirring time of 30 s and a stirring rate of 18 000 rpm.

[b] Reaction conditions as in footnote a except the stannane is added to the stirred aqueous phase.

[c] Reaction conditions as in footnote b except for the use of triethylamine as the added base.

An additional aqueous interfacial system was developed by us in which the Lewis base, here dextran, and any added base are dissolved in water, with the second phase consisting of only the Lewis acid present as a liquid. Both BCTD and DBSD are solids, so this system was tested with a number of liquid organostannate halides. Product was obtained from the majority of systems tested (Table 8).

Table 9 contains a summary of results as a function of reaction system. Dextran was successfully modified through condensation with BCTD and DBSD by employing a number of reaction systems. Results should be applicable to other polyhydroxylic compounds of comparable solubility.

TABLE 9. Summary of Systems Evaluated

System	Description	General comments	
		Cp_2TiCl_2	Bu_2SnCl_2
Interfacial—classical[a]	H_2O/organic	Good (Table 4)	Good (Table 5)
Aqueous interfacial–liquid Lewis acid[b]	H_2O/liquid Lewis acid	Not applicable	Good for liquid stannanes (Table 8)
Inverse aqueous interfacial[c]	Organic (Lewis base)/ H_2O (Lewis acid)	Variable (Table 6)	Not applicable
Nonaqueous interfacial[d]	Like Decane/DMSO	Unsuccessful	Variable (Table 7)
Solution-one solvent and two solvent systems (including addition of Group IA salts)[e]	Like DMSO/DMSO; H_2O; DMSO-LiCl	Variable (Tables 1 and 2)	Largely unsuccessful (Table 3)

[a] Dextran dissolved in water and the metal-containing reactant dissolved in a suitable organic liquid.

[b] Dextran dissolved in water with the organic phase consisting solely of a liquid metal-containing reactant.

[c] Dextran dissolved in a suitable organic liquid and the metal-containing reactant dissolved in water.

[d] Immiscible liquid pairs are employed as the solvents, and each reactant is dissolved in one of the two liquids. Liquid combinations are cited in C. Carraher, Interfacial Synthesis, Vol. II, Polymer Applications and Technology (F. Millich and C. Carraher, eds.), Dekker, New York, 1977, Chap. 21.

[e] Solution systems including: 1) wholly aqueous systems where each reactant is dissolved in water, 2) aqueous-nonaqueous miscible pairs, 3) nonaqueous liquids and nonaqueous liquid-inorganic salt combinations, and 4) nonaqueous miscible liquid combinations.

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