Preparation and Characterization of Cellulose Monoacetates: The Relationship between Structure and Water Solubility†

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ABSTRACT: A new and highly efficient synthetic method for the preparation of cellulose monoacetates (CMA) has been developed. The method is based on high-temperature metal-catalyzed or carboxylic acid promoted methanolysis of cellulose triacetate or cellulose diacetate. The method provides water-absorbent or water-soluble CMA depending upon the type of catalyst or promoter selected. Evidence is presented which demonstrates that, for cellulose monoacetates with a degree of substitution in the range 0.5–0.9, water solubility is determined by the molecular weight of the polymer and by the monomer composition of the cellulose acetate.

Water-soluble and water-absorbent polymers are extremely important commercial products. A complete list of commercial applications is virtually impossible as these polymers have found widespread use in adhesives, cosmetics, foods, pharmaceuticals, and coatings. In 1988 alone, the worldwide consumption of water-soluble polymers was estimated to be 1030 thousand metric tons.[1] Cellulose ethers, e.g., (hydroxypropyl)cellulose and (carboxymethyl)cellulose, accounted for approximately 234 thousand metric tons of these water-soluble polymers.

Despite being known since 1929,[2] cellulose esters with an affinity for water, as typified by water-soluble cellulose monoacetate (CMA, vide infra), are conspicuously absent from the list of commercially available water-soluble and water-absorbent polymers. There are many reasons for the lack of commercial exploitation of this biodegradable and renewable resource as a source of water-soluble polymer. The principal reason is that the only known method of preparation that provides water-soluble CMA involves hydrolysis of cellulose triacetate (CTA) in an aqueous mineral acid medium.[3,4] A number of drawbacks are associated with this type of procedure, which render it commercially unattractive, e.g., long reaction times, continuous or sequential addition of water in order to maintain reaction rates, dilute reaction mixtures, and difficult product isolation and recovery of byproducts. Since the initial report, a number of papers have appeared that describe the hydrolysis of cellulose acetate[5] or the direct esterification[6] of cellulose as means of preparing CMA. All of these methods either have problems similar to those described above or do not provide a water-soluble cellulose ester.

In addition to the limitations in synthetic techniques, analytical methods suitable for detailed characterization of CMA have not been available. Recognizing this problem, Kamide et al.[4,7-10] and others[11,12] have devoted significant research effort to this rather formidable problem. Based on their work, it is proposed that the two basic requirements for water-soluble CMA are (i) that the degree of substitution (DS, the number of substituents per anhydroglucose ring where the maximum DS is 3) be in the range 0.5–1.1 and (ii) that the relative degree of substitution (RDS) among the three possible substitution sites be roughly equal.[3,4] Early work by Kamide et al.[7] suggests that water solubility is not dependent on weight-average molecular weight although Shibata et al.[3] have since suggested that there may be a relationship between polymer molecular weight and water solubility. Recently, it has been noted that fulfillment of these two requirements does not necessarily provide water-soluble CMA; the monomer composition of the cellulose acetate polymer (Figure 1), in particular the amount of 3-substituted acetyl monomer, apparently plays an equally important role.[4]

From these observations, we concluded that two fundamental needs must be addressed if CMA is to become a commercially viable product. Foremost, synthetic techniques that circumvent the serious problems associated with aqueous hydrolysis had to be developed. To provide guidance to the synthetic effort, analytical techniques that can be used to probe the structural characteristics responsible for imparting water solubility or water absorbance to CMA had to be found. In the following report, we disclose the metal-catalyzed and carboxylic acid promoted preparation of CMA and describe how nuclear magnetic resonance spectroscopy techniques (NMR) can be used to probe the relationship between structure and water solubility in this important polymeric material.

Experimental Section

Proton NMR data were obtained on a JEOL Model GX-270 NMR spectrometer operating at 270 MHz. The sample tube size was 5 mm and the sample concentration was 30 mg (±1 mg)/mL of DMSO-d_6. One to two drops of trifluoroacetic acid (TFA) was added to the sample to shift residual water from the spectral region of interest. All proton NMR spectra were recorded at 80 °C. Carbon-13 NMR data were obtained on a JEOL Model GX-270 NMR spectrometer operating at 67.9 MHz. The sample concentration was 100 mg (±1 mg)/mL of DMSO-d_6. Three to five milligrams of $Cr(AcAc)_3$ was added to each sample as a relaxation agent. The sample tube size was 10 mm. Each carbon-13 NMR spectrum was acquired at 80 °C, the pulse delay was 1.0 s, and 12 000–16 000 scans were used to acquire each spectrum. Each spectrum was collected with 32 768 points and was zero-filled to 65 536 points to give a resolution of 0.52 Hz. Prior to integration of each spectrum, a 10th order polynomial baseline correction was applied. Carbon-13 chemical shifts are reported in parts per million from tetramethylsilane with the center peak of DMSO-d_6 (39.5 ppm) as an internal reference. All NMR spectra were processed by using a 8 Mbyte Mac II Macintosh Computer, with VersaTerm Pro as an emulation package and MacDraw II as a graphics package, interacting with Hare's FTNMR software[13] running on a VAX 8800 computer.

GPC data were acquired on a Waters Model 150C high-temperature gel permeation chromatograph operating at 60 °C. The mobile phase was DMF containing 0.5% LiBr. Sample size was 20–25 mg/10 mL and the injection volume was 100 μL. Molecular weights are reported in polystyrene equivalents. Caution must be exercised in obtaining and interpreting GPC data, as we have observed that these materials will associate in solution.

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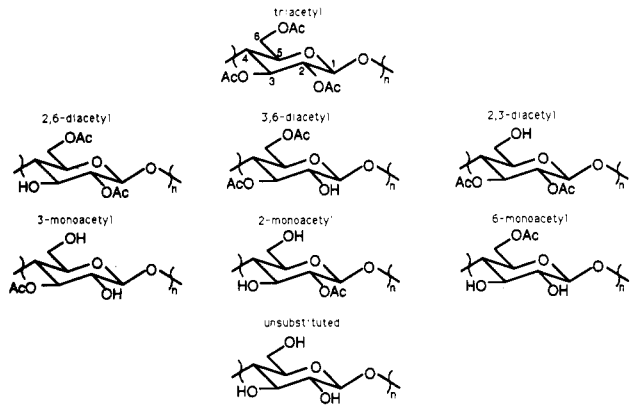

Figure 1. Hydrolysis of CTA or direct esterification of cellulose provides a cellulose acetate that can be considered to be a copolymer consisting of eight monomers as illustrated in this figure. In the absence of hydrogen bonding, these isomers can give rise to 12 distinct carbonyl carbon or methyl acetyl proton resonances.

Table I
Conditions for the Preparation of CMA 1-8 in MeOH

CMA	catalyst	temp, °C	pressure, psi N_2	heatup time, min	reactn time, h	yield, %
1	Bu_2SnO	155	1000	120	3	86
2	$Zn(OAc)_2$	155	1000	45	2	76
3	$Mg(OAc)_2$	140	200	150	4	73
4	$ZnCl_2$	155	500	75	3	90
5	$Zn(OAc)_2$	140	200	80	5	75
6	$Mo(CO)_6$	140	200	75	7	66
7	MoO_3	155	1000	70	3	87
8	AcOH	150	35	66	12	89

Intrinsic viscosity was measured on a Schott Gerate AVS24 instrument operating at 25 °C. Sample concentration was 0.25 g/100 mL of DMSO.

Water solubility was determined by visual inspection of the solution that resulted from rolling 1 g of CMA with 10 mL of water overnight at room temperature. For water-absorbent material, 1 g of CMA in 10 mL of water was rolled overnight at room temperature. The sample was centrifuged and excess liquid was decanted from the water-swollen CMA before weighing. Percent water absorption was defined as [(weight of water-swollen CMA)/(g of dry CMA)] × 100.

Cellulose Monoacetate Preparation. Metal Catalyzed. The following procedure typifies the metal-catalyzed preparation of CMA. Sixty grams of cellulose diacetate (DS = 2.45), 237 g of MeOH, and 200 mg of dibutyltin oxide were heated at 155 °C (2-h heatup time) at 1000 psi initial nitrogen pressure for 3 h in an autoclave. After cooling, the solvents were removed by filtration and the solids were dried under vacuum at 60 °C to provide 40.8 g (86%) of 1. The experimental details for 1 as well as for 2–7 are tabulated in Table I.

Carboxylic Acid Promoted. Sixty grams of cellulose triacetate (DS = 2.98), 211 g of MeOH, and 351 g of acetic acid were heated at 150 °C (66-min heatup time) at 35 psi initial nitrogen pressure for 12 h in an autoclave. After cooling, the solvents were removed by filtration and the solids were dried under vacuum at 60 °C to provide 44.3 g (89%) of 8. CMA 11–15 were prepared in a similar fashion.

Aqueous Hydrolysis. CMA 9 and 10 were prepared according to the method of Malm[2] and Fordyce.[14]

Results and Discussion

Synthetic Studies. As we have noted, the only method known to provide water-soluble CMA is mineral-acid-catalyzed aqueous hydrolysis of highly substituted CA (DS = 2.4–3.0). Metal-catalyzed hydrolysis of cellulose acetate has been described by Murray and Staud[5b] but the product of their reaction had no affinity for water. Similarly, the direct esterification of cellulose in a homogeneous reaction mixture has been described[6] but none of the products of these reactions were water soluble.

In the course of our research program in cellulose chemistry, we became aware of the potential commercial utility of water-soluble cellulose esters and of the difficulties associated with preparing these materials. These observations led to work in our laboratories designed to address this synthetic challenge. We have found that cellulose monoacetates that are either water absorbent or water soluble can be easily prepared by treating cellulose acetates (DS = 2.5–3.0) with a metal catalyst or a carboxylic acid in a solvent such as methanol at elevated pressures and temperatures. This process has numerous advantages over prior methods. Reaction times are much shorter, the product is isolated simply by cooling and filtering, and the reaction byproducts (e.g., methyl acetate) can be recycled much more efficiently. Table I gives a summary of these efforts for some selected samples.

As Table I illustrates, reaction temperatures of 140–160 °C are generally required for both the metal-catalyzed and carboxylic acid promoted reactions. A wide range of pressures (35–1000 psi) was used in these reactions and was found to have no effect on reaction rates. Reaction times for the metals were generally the same (2–7 h) but about half of that required for carboxylic acid promoted hydrolysis. As Table I demonstrates, a wide range of metals are effective in catalyzing the hydrolysis of cellulose acetate. The nature of the metal counterion (cf. 5 and 6, Table I) apparently does not play a significant role in determining hydrolysis rates or observed properties of the CMA. Similarly, the initial oxidation state of the metal[15] (cf. 7 and 8, Table I) seems to have no effect on hydrolysis rates or observed properties. Although a number of metals are effective in catalyzing the hydrolysis of cellulose acetate, only molybdenum was found to provide water-soluble CMA; all other metals gave water-absorbent CMA (vide infra). The role of the metal in these reactions is not obvious, particularly in the case of molybdenum. However, the metals are critical to the success of these reactions. When the methanolysis is run with no metal or acid present, 9 h at 175 °C is required to prepare a CMA (DS = 0.69, IV = 1.38) that is not water soluble and only marginally water absorbent.

A number of alcohols may be used for solvolysis of CTA in the presence of metal catalysts or carboxylic acid promoters. The crucial criterion for the alcohol used is that it be a nonsolvent for CMA, promoting precipitation of the product and easy product recovery by direct filtration. The key difficulty in the carboxylic acid promoted methanolysis is the adjustment of the amounts of acetic acid and methanol used to achieve the desired reaction rate while simultaneously controlling the solubility of the product in the final reaction mixture. As expected, concentration, temperature, and the amount of methanol may be used to manipulate reaction rates. The difficulty in achieving this balance is illustrated in the examples of Table II, which demonstrates the sensitivity of yield as well as DS and molecular weight to the relative amounts of methanol and acetic acid used. The effect of solvent composition on yield is revealed by examples 12–14, in which products of similar DS and molecular weight are recovered in yields ranging from 14 to 83% governed only by concentration and composition of the solvent mixture. Yield increases as the concentration and methanol/acetic acid ratio increase. Lower CTA concentrations in acetic acid lead to lower product molecular weights (cf. examples 11 and 12). Therefore, to obtain high reaction rates while preserving molecular weight, it is desirable to

Table II
Acetic Acid Promoted Methanolysis of CTA

						GPC					
CMA	CTA, g	MeOH, mL[a]	HOAc, mL	DS	IV (DMSO)	$M_n \times 10^5$	$M_w \times 10^5$	$M_z \times 10^5$	M_w/M_z	yield, %	H_2O solubility, %
11	82.5	116 (196)	300	0.40	0.63	0.4	0.7	1.1	1.6	90	44
12	82.5	150	400	0.79	0.20	0.2	0.3	0.5	1.6	14	100
13	82.5	116 (36)	375	0.79	0.23	0.2	0.5	0.8	2.0	56	100
14	90	104 (100)	338	0.75	0.36	0.3	0.6	1.1	2.4	83	100
15	75	126	354	1.19	0.24	1.3	1.5	1.7	1.1	38	44

[a] In somes instances, a portion of the MeOH was added after 4 h of reaction time. These volumes are indicated in parentheses.

Table III
DS, RDS, IV, and GPC for CMA 1–10

			RDS (carbonyl)			RDS (ring)				GPC			
	catalyst	DS	C6	C3	C2	C6	C3	C2	IV (DMSO)	$M_n \times 10^5$	$M_w \times 10^5$	$M_z \times 10^5$	M_w/M_n
absorbs water													
1	Bu_2SnO	0.62	0.10	0.34	0.22	0.11	0.28	0.23	1.47	1.1	2.5	4.5	2.3
2	$Zn(OAc)_2$	0.69	0.15	0.29	0.25	0.14	0.30	0.25	1.63	1.4	2.6	4.3	1.9
3	$Mg(OAc)_2$	0.41	0.12	0.16	0.13	0.13	0.13	0.13	1.91	2.4	2.8	3.3	1.2
4	$ZnCl_2$	0.64	0.10	0.30	0.24	0.10	0.27	0.27	1.49	1.2	2.5	4.4	2.1
5	$Zn(OAc)_2$	0.72	0.14	0.33	0.25	0.18	0.30	0.24	1.70	1.2	2.3	3.8	1.9
water soluble													
6	$Mo(CO)_6$	0.48	0.03	0.28	0.17	0.04	0.28	0.16	0.55	0.4	0.8	1.2	2.0
7	MoO_3	0.50	0.00	0.27	0.24	0.00	0.25	0.25	1.16	0.7	1.6	3.0	2.3
8	AcOH	0.72	0.20	0.28	0.24	0.19	0.29	0.24	0.53	0.4	0.9	1.5	2.1
9	H^+/H_2O	0.77	0.17	0.34	0.25	0.16	0.33	0.28	1.21	1.1	1.8	2.5	1.6
10	H^+/H_2O	0.69	0.20	0.27	0.21	0.21	0.27	0.21	1.11	0.6	1.1	1.6	2.0

Table IV
Carbon-13 NMR Chemical Shifts for the Carbonyl Carbons of CMA 1–10

	chemical shifts[a]														
	C6	6-tri	C6	C6	3-m*	3-m	2,3-di*	2,3-di	3,6-di*	3,6-di	3-tri*	3-tri	2,3-di	2-tri	2-m, 2,6-di
b	170.03	169.94	169.87	169.79	169.55	169.52	169.44	169.39	169.26	169.19	169.14	169.10	168.85	168.73	168.63
1	170.02	169.95		169.80		169.52		169.38			169.12		168.83	168.72	
2		169.97		169.82	169.55			169.41			169.14		168.86	168.76	
3		169.97		169.80				169.41			169.13		168.85		168.65
4	170.02	169.97			169.54			169.41	169.25		169.14		168.85	168.75	
5	170.03	169.97		169.81	169.55			169.41	169.25		169.15		168.86	168.76	
6		169.96			169.55		169.43		169.26		169.15		168.86	168.75	
7					169.55		169.42						168.85	168.75	
8	170.03	169.96		169.80	169.53			169.41	169.26		169.14		168.85	168.73	
9		169.93		169.80		169.52		169.41	169.24		169.12		168.83	168.67	
10		169.97			169.55		169.44		168.29		169.14		168.85	168.72	

[a] Underlining indicates the acetyl of a diacetyl monomer; * indicates hydrogen-bonding acetyl. [b] Chemicals shifts taken from ref 16 using the CA with a DS = 1.06 as the reference cellulose acetate.

run the reaction with the highest concentration and methanol/acetic acid ratio possible, without rendering CTA insoluble in the reaction mixture.

Although alcohols are the solvents of choice in the metal-catalyzed reactions, cosolvents such as *N*-methyl-2-pyrrolidone, methyl ethyl ketone, or H_2O can be employed. These cosolvents are generally used to aid in isolation as they lead to the formation of a granular solid.

Characterization. In the preceding paper,[16] we described the preparation and characterization by NMR spectroscopy of a series of cellulose acetates labeled at the carbonyl carbons with carbon-13. We identified a total of 16 carbonyl carbon resonances, which were assigned to carbonyls attached to either a C2, a C3, or a C6 hydroxyl. In the case of the C2 and C3 carbonyls, the carbonyl resonances were assigned to specific monomers in the polymer backbone. Although we are limited by resolution and by our inability to assign all of the C6 carbonyl resonances, we have found the assignments given in that report to be invaluable in addressing structure–property relationships of CMA.

Figure 2 shows typical proton-decoupled ^{13}C NMR spectra of the carbonyl carbon region of CMA 1–10 to which mild resolution enhancement has been applied. Table III gives the DS for each sample as well as the RDS determined from the carbonyl carbons and the RDS determined from the ring carbons by the method of Shibata et al.[12] The RDS determined from the ring carbons serves as an internal check on our carbonyl carbon resonance assignments. Also included in Table III are intrinsic viscosities, molecular weights, and polydispersities for each sample. Tables IV and V give the chemical shifts and carbonyl peak areas for the five water-absorbent and five water-soluble CMA samples (1–10). The first row indicates the monomer to which a resonance has been assigned, underlining indicates the acetyl of a diacetyl monomer to which the resonance is assigned, and an asterisk indicates an acetyl whose chemical shift is perturbed by hydrogen bonding.

A number of general observations can be made from the data contained in Tables III–V. Beginning with Table III, we can see that the intrinsic viscosities and the molecular weights of the water-absorbent CMA are consistently greater than those for the water-soluble CMA. For example, the M_w range for the water-absorbent CMA is $(2.3–2.6) \times 10^5$, while the corresponding values for water-soluble CMA encompass the $(0.9–1.6) \times 10^5$ range. Likewise, the IV range for the water-absorbent CMA is

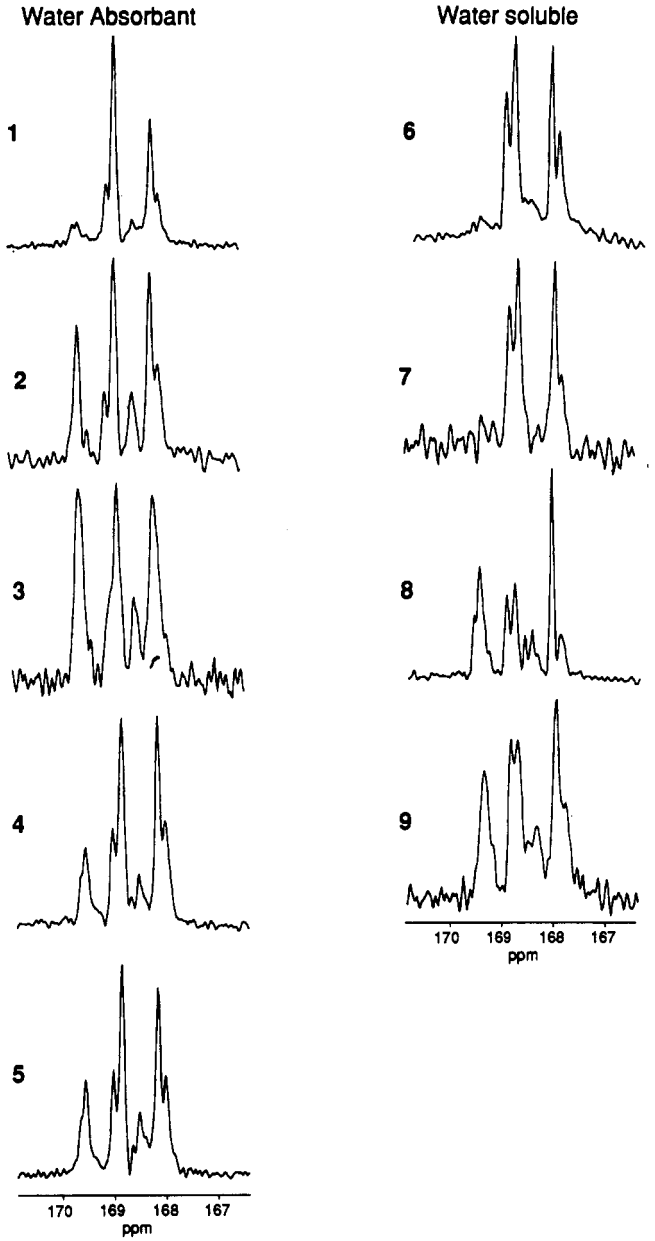

Figure 2. Resolution-enhanced proton-decoupled carbon-13 NMR spectra (67.9 MHz) of the carbonyl carbon region of CMA 1–9.

1.47–1.91 while the IV range for the water-soluble CMA is 0.53–1.21. Kamide and Saito[7] have reported that water-soluble CMA at a fixed DS does not show a molecular weight dependence up to $M_w = 1.45 \times 10^5$, a value that is near the upper limit for our water-soluble CMA. The IV and GPC data for **1–10** show that there is a general distinction in molecular weights between water-absorbent and water-soluble CMA at similar DS values. From these data we conclude that molecular weight (i.e., degree of polymerization) is a structural feature that contributes to the property of water affinity for CMA.

The RDS values for CMA **1–10** (Table III) determined from the carbonyl and ring carbons are in good agreement. Both Shibata et al.[3] and Kamide et al.[4] have suggested that a structural parameter that contributes to water solubility is the RDS at the C2, C3, and C6 hydroxyls. On the basis of their samples, they conclude that the RDS at the C6 hydroxyl must not exceed the total RDS at the C2 and C3 hydroxyls; i.e., the RDS at the three possible sites of substitution must be roughly equal. Examining the water-soluble CMA **6–10** first, we find that this structural requirement is basically fulfilled for CMA **8–10**. However, water-soluble CMA **6** and **7** have virtually no acetyls at the C6 position and, in both cases, the C3 hydroxyl RDS exceeds the C2 hydroxyl RDS. Furthermore, the water-absorbant CMA have RDS values quite similar to those of the water-soluble CMA **6–10**. Kamide[4] has also proposed that a necessary condition for water-soluble CMA is that the degree of substitution at the C3 hydroxyl be greater than ca. 0.2. From Table III we can see that every CMA meets this requirement except for CMA **3**, which is water absorbent. On the basis of these data, we find no correlation between RDS values and the property of water solubility or water absorbency.

An average of ca. 8 carbonyl resonances is observed in the ^{13}C NMR spectra of CMA **1–10** (Table IV). We found no clear differences in chemical shifts between the water-absorbent and water-soluble samples. We do note, however, that we have assigned the 3-acetyl of the 2,3-diacetyl monomer for the water-absorbent CMA to be a non-hydrogen-bonding monomer. For water-soluble CMA, the same resonance for three of the five examples was assigned to a hydrogen-bonding monomer.

On close inspection of Table V, one finds that the principle differences in monomer composition between water-absorbent CMA **1–5** and water soluble CMA **6–10** are the relative ratios of the 3-monoacetyl monomer to the 2,3-di-, and 3-tri-, and/or total 3-substituted monomer. The ratio of 3-monoacetyl monomer DS to total DS also provides a clear distinction between water-soluble and water-absorbent CMA. These values have been tabulated in Table VI. In general, we find that for water-absorbent CMA (3-m/2,3-di) < 0.5, (3-m/3-tri) < 1.1, and (3-m/total 3-acetyl) < 0.25. For water-soluble CMA, the inequalities are reversed. For water-absorbent CMA **1–5**, the ratio of DS due to the 3-mono monomer to the total DS is generally 0.11 or less, whereas for water-soluble CMA **6–10** this ratio is greater than 0.11. These data show that the structural requirement, as expressed in terms of monomer composition, for water solubility is that the number of 3-monoacetyl monomer repeat units be greater than 10–11 per 100 monomers. It is very easy to focus only on the acetyl substituents and neglect the unsubstituted hydroxyls. However, the ratio of 3-monoacetyl monomer to the remaining 3-acetyl monomers clearly illustrates the importance of the C2 hydroxyl to water solubility. In conjunction with current knowledge of cellulose crystal structure,[17] we feel that the data suggest a minimum level of 3-acetyl substituents must be present for disruption of intra- and/or intermolecular hydrogen bonding while still maintaining a delicate balance of C2 hydroxy to ensure the hydrophilicity of the polymer backbone. Apparently the C6 hydroxyl is too remote from the central axis of the polymer backbone to have a significant hydrophilic influence and, as such, can only exert a negative influence on water solubility of CMA. This hypothesis, of course, suggests that the solubility of a cellulose derivative in water can be increased by increasing the hydrophilicity of the functional group attached to the C6 carbon.[18]

Our conclusions regarding the interplay of molecular weight and acetyl distribution in relationship to water affinity are best illustrated by considering individual examples. In water-soluble CMA **6**, **7**, **9**, and **10**, the relative ratios of 3-monoacetyl monomer are easily within the boundaries established for water solubility. However, CMA **6** and **7** have virtually no acetyls attached to the C6 hydroxy, which is illustrative of the neutral effect of the C6 hydroxyl. CMA **8** has RDS values similar to those of CMA **9** and **10** but the 3-monoacetyl monomer ratios are

Table V
Carbonyl Peak Area for CMA 1–10[a]

	C6	6-tri	C6	C6	3-m*	3-m	2,3-di*	2,3-di	3,6-di*	3,6-di	3-tri*	3-tri	2,3-di	2-tri	2-m, 2,6-di
absorbs water	170.03	169.94	169.87	169.79	169.55	169.52	169.44	169.39	169.26	169.19	169.14	169.10	168.85	168.73	168.63
1	3.9	3.9		2.9	10.6			37.5			6.7		24.0	10.6	
2		19.4		2.8	5.6			25.0			12.0		21.3	13.8	
3		26.8		2.7				28.6			9.8		28.6		3.6
4	2.7	12.7			8.2			27.3	2.7		8.2		20.9	17.3	
5	3.7	12.0		2.8	11.1			24.1	1.9		9.3		20.4	14.8	
water soluble															
6		6.5			20.4		23.7		4.3		8.6		19.4	17.2	
7					19.0		35.0						29.0	17.0	
8	5.5	20.2		2.8	9.9			16.3	3.7		9.0		24.1	8.6	
9		19.4		2.8	14.8		14.8		4.6		10.2		21.3		12.0
10		29.1			12.6		10.7		6.8		9.7		20.4	10.7	

[a] Chemicals shifts taken from ref 16 using the CA with a DS = 1.06 as the reference cellulose acetate; * indicates hydrogen-bonding acetyl.

Table VI
Percent Water Solubility and Ratio of 3-Acetyls for CMA 1–10

	3-m/2,3-di	3-m/3-tri	3-m/total 3-acetyl	3-m DS/DS	water solubility, %	water absorption, %
absorbs water						
1	0.28	1.58	0.19	0.11		713
2	0.22	0.47	0.13	0.06		1137
3	0.00	0.00	0.00	0.00		1016
4	0.30	1.00	0.18	0.18		945
5	0.46	1.19	0.24	0.11		958
water soluble						
6	0.86	2.37	0.36	0.20	93	
7	0.54	∞	0.35	0.19	100	
8	0.61	1.10	0.26	0.10	100	
9	1.00	1.45	0.33	0.15	100	
10	1.20	1.30	0.32	0.13	100	

marginal. In this example, the molecular weight of the polymer is quite low (Table III), demonstrating the forgiving nature of this structural parameter. For the water-absorbent CMA, the C6 RDS values cover a very wide range, which again is indicative of the relative lack of influence of the C6 hydroxyl on water solubility. For CMA 1, the 3-m/3-tri and 3-m/DS ratios are marginal, but the other values are acceptable and the molecular weight is large. It should be noted that this example has the lowest water absorbencies of any given in Table VI. All of the 3-monoacetyl monomer ratios for CMA 5 are marginal, but this example has one of the highest IV and molecular weight values given in Table III.

Conclusions

In this report we have described new and highly efficient synthetic methods for the preparation of CMA. By simply choosing the appropriate catalyst and reaction conditions, properties such as water solubility or water absorbence can be selected. Choice of catalyst also permits versatility in selecting the RDS at the hydroxyls attached to C2, C3, or C6. Product isolation is greatly simplified since the product is isolated by a simple filtration upon cooling of the reaction mixture. Since mineral acids are not used, contamination of the CMA by neutralization salts is avoided. Difficult recovery of solvents from a dilute aqueous reaction mixture is avoided and reaction byproducts such as MeOAc have commercial utility.

Evidence has also been presented that relates the property of water affinity to polysaccharide structure. We have found that within the DS range 0.5–0.9, the structural parameters that determine CMA water solubility are polymer molecular weights and monomer composition. In general, a CMA with a low molecular weight (IV < 1.4; M_w < 2.0×10^5) containing greater than 10–11 3-monoacetyl monomers per 100 repeat units will be water soluble. The results from this probe of the cellulose ester structure–property relationship should lead to a better understanding of how to modify the structure of cellulose in order to obtain a desirable property.

References and Notes

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Registry No. AcOH, 64-19-7; Bu_2SnO, 818-08-6; $Zn(OAc)_2$, 557-34-6; $Mg(OAc)_2$, 142-72-3; $ZnCl_2$, 7646-85-7; $Mo(CO)_6$, 13939-06-5; MoO_3, 1313-27-5; H_2O, 7732-18-5; cellulose diacetate, 9035-69-2; cellulose acetate, 9004-35-7; cellulose triacetate, 9012-09-3.