Synthesis and Properties of Cellulose Acetoacetates

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ABSTRACT: Cellulose acetoacetates with and without other ester groups were prepared directly from cellulose by reaction with diketene or *tert*-butyl acetoacetate (and, where appropriate, a carboxylic anhydride) in *N,N*-dimethylacetamide (DMAC)/LiCl or 1-methyl-2-pyrrolidinone (NMP)/LiCl solution. This is the only method yet described for the direct synthesis of these polymers from cellulose and, except for the triester, the only method available for synthesis of cellulose acetoacetates which do not contain another ester group. The products span the entire degree of substitution (DS) range, are amorphous, and are readily soluble in various solvents depending on DS. Cellulose acetoacetates of low DS are soluble in water. Some of these water-soluble materials can be formulated into cross-linkable coatings which have outstanding solvent resistance. Methods have been developed for the determination of DS by proton NMR spectroscopy. Proton and carbon-13 NMR resonance assignments for cellulose tris(acetoacetate) are also provided.

Introduction

Acetoacetylated polymers are interesting targets for synthesis, because of the unusual properties imparted by the acetoacetate ester group. Esterification of hydroxylated polymers by diketene or *tert*-butyl acetoacetate[1] can increase their utility for thermoset applications, since the acetoacetyl moiety has a densely packed functionality, and is susceptible to a variety of cross-linking reactions. This can occur through the methylene group (for example, by condensation with bis(aldehydes) via aldol chemistry or with bis(acrylates) via Michael addition chemistry), through the ketone group (for example, by condensation with diamines or dihydrazines), or through the β-ketoester (by chelation to transition metals), all under mild conditions. It has also been noted that, in some cases, acetoacetylation of hydroxylated polymers reduces their solution viscosity.[2] This can be a useful way to increase resin concentration and reduce organic solvent usage in coatings applications.

Cellulose esters are widely used in both coatings and plastics, and the ability to attach acetoacetyl moieties as handles for low-temperature cross-linking should be valuable in these applications. Unfortunately, there are few reports in the literature of the synthesis of acetoacetate esters of cellulose. A Standard Oil patent in 1937[3] briefly described a product obtained by contacting cotton linters with diketene using sulfuric acid catalyst; no product properties or analyses were reported. In 1950 two Eastman Kodak patents[4] described the acetoacetylation of cellulose esters such as cellulose acetate and cellulose acetate propionate with diketene. Caldwell reported a DS of acetoacetyl groups as high as 1 (DS is degree of substitution, defined as the number of substituents per anhydroglucose monomer unit) as measured by unspecified analytical techniques. Hagemeyer reported that the putative cellulose acetate acetoacetates (CA(AA)s) were readily cross-linked by formalin and alkali. Our own work confirms that soluble cellulose derivatives such as cellulose acetate (CA) or cellulose acetate propionate (CAP) can be readily acetoacetylated with diketene. Obtaining homogeneously substituted, soluble, useful cellulose acetoacetates by direct acetoacetylation of cellulose is much more difficult. The only literature report of such a transformation is that of Staudinger and Eicher in 1953.[5] By reacting amorphous regenerated cellulose (generally much more reactive than the more crystalline wood pulps and cotton linters) with diketene in acetic acid, with a sodium acetate catalyst, they were able to obtain a fully substituted cellulose acetoacetate (DS = 3.0, as measured by elemental analysis). Due to the heterogeneous nature of the reaction, it was not possible to synthesize partially substituted cellulose acetoacetates directly. The authors did not report any attempts to hydrolyze the fully substituted material to lower DS esters. We have confirmed that only the more reactive and expensive regenerated cellulose can be used under heterogeneous acylation conditions. This is because self-condensation reactions of diketene[6] destroy the reagent at a rate competitive with that of heterogeneous acylation, such that full substitution cannot be achieved.

We felt that reaction with cellulose in *solution* would be the most efficient and flexible method of acetoacetylation. Homogeneous reaction with diketene would give an increased acylation rate as needed to compete with self-condensation reactions and could have the additional benefit of direct access to the desired DS without the need for an additional hydrolysis step and product isolation. The work of Turbak[7] and McCormick[8] has shown that cellulose will dissolve in a combination of lithium chloride with amides such as *N,N*-dimethylacetamide (DMAC) or 1-methyl-2-pyrrolidinone (NMP). Further work by McCormick's group,[9] Diamantoglou,[10] and others[11] has shown that this solvent system is well-suited to reactions of cellulose with electrophiles. They have synthesized cellulose ethers, carbamates, and acetates (partially substituted without the need of a hydrolysis step) in this way.

Experimental Section

Materials. The hardwood pulp used in these experiments was Natchez HVX, available commercially from International Paper. The microcrystalline cellulose was Avicel PH-105, available commercially from FMC. Diketene was from Eastman Chemical Co. *N,N*-Dimethylacetamide and 1-methyl-2-pyrrolidinone were dried over 3-Å molecular sieves. All other reagents were purchased and used as received.

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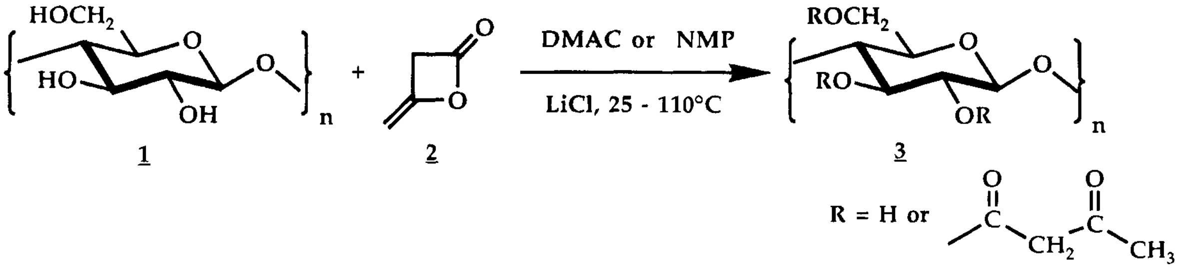

Figure 1. Synthesis of cellulose acetoacetate.

Table 1. Survey of Solvents and Reagents[a]

entry	reagent (equiv)	solvent	DS	IV	GPC (all/1000) M_n	M_w	M_z	T_g	solubility
1	tBAA (3.00)	DMAC	0.71	1.48	27.4	117	384	178	DMSO, NMP, water
2	tBAA (3.00)	DMAC	0.34	0.97	93	150	225	187	DMSO, NMP
3	tBAA (3.00)	NMP	0.72	1.26	79.6	283	925		DMSO, NMP, water
4	diketene (3.00)	DMAC	1.34	0.81	31.1	100	262	150	DMSO, NMP
5	diketene (1.00)	NMP	0.39	0.75	32.5	798	1820	182	DMSO, NMP, water

[a] tBAA = *tert*-butyl acetoacetate. All entries used hardwood pulp as the cellulose source.

Preparation of Cellulose Acetoacetate. This procedure is typical for the materials listed in Table 2. A mixture of microcrystalline cellulose (8.00 g, 49.3 mmol) and DMAC (300 mL) was heated to 150 °C over 26 min in a round-bottom flask equipped with a short-path distillation apparatus. Then lithium chloride (15.0 g) was added and the mixture heated to 170 °C over 8 min. Distillation commenced at 170 °C and continued until 77 mL of distillate had been collected. The reaction mixture was cooled to room temperature and allowed to stir overnight. In the morning the cellulose had dissolved to a crystal clear solution. The solution was heated to 110 °C, and diketene (3.73 g, 44.4 mmol, 0.90 equiv) was added dropwise. The resulting solution was stirred 30 min at 110 °C and then was cooled to room temperature. The product was precipitated using methanol and was washed by Soxhlet extraction with methanol. The properties of the dried product (10.03 g, 86% yield based on the theoretical DS(acetoacetyl) of 0.90) are listed as entry 1 of Table 2.

Preparation of Cellulose Acetoacetate Butyrate. This procedure is typical for the cellulose acetoacetate alkanoate materials listed in Tables 3 and 4. Cellulose (hardwood pulp; 8.00 g, 49.3 mmol) was dissolved in DMAC (300 mL) and LiCl (15.0 g) as described in the previous example. This clear and viscoelastic solution was heated to 110 °C. Butyric anhydride (7.02 g, 44.4 mmol, 0.90 equiv) was added dropwise at 110 °C, and then the solution was held for 27 min at that temperature. Diketene (1.24 g, 14.8 mmol, 0.30 equiv) then was added dropwise at 110 °C. The resulting solution was held 40 min at 110 °C and then cooled. The product was isolated by precipitation with methanol, followed by Soxhlet extraction with methanol. The properties of the dried product (10.22 g, 83% yield based on the theoretical DS(butyryl) of 0.90 and DS(acetoacetyl) of 0.30) are listed as entry 8 of Table 4.

Measurements. DSC spectra were obtained using a Du Pont 2100 differential scanning calorimeter. In order to provide the same thermal history, each sample was heated to 240 °C at 20 °C/min and then quenched to −78 °C. Then the spectrum was acquired while heating at 20 °C/min from −78 °C. All T_g's are reported as the midpoint of the transition observed in the second scan.

GPC data were acquired on a Waters Model 150C gel permeation chromatograph. The mobile phase was NMP, and the sample size was 20–25 mg/10 mL. All molecular weights are reported in polystyrene equivalents.

Inherent viscosities were measured at 25 °C using 0.25% solutions in dimethyl sulfoxide (DMSO).

Carbon-13 and proton NMR spectra were acquired on JEOL Model GX-400 and GX-270 NMR spectrometers in DMSO-d_6. Carbon-13 NMR spectra were obtained in 10-mm-o.d. NMR tubes at 40 °C. Proton NMR spectra were obtained in 5-mm-o.d. NMR tubes at 80 °C. All samples were dissolved in DMSO-d_6. Chemical shifts are reported relative to the chemical shift of the solvent at 39.44 ppm. DS, by proton NMR, for all substituents was determined by comparison of the integrals for acyl methyl proton resonances (0.70–1.20 ppm for the propionate and longer esters; 1.70–2.20 ppm for the acetates; and 2.10–2.45 ppm for the acetoacetates) and the backbone proton resonances of the anhydroglucose rings (2.90–5.10 ppm).

The double-quantum-filtered COSY (DQFCY) spectrum of cellulose tris(acetoacetate) (CTAA) at 80 °C was collected in two 512 × 1024 matrices with a row and column frequency width of 2324.5 Hz and 32 scans/row. Column and row digital resolution was 4.5 Hz. For this experiment, 13 mg of CTAA was dissolved in 1 mL of solvent.

HETCOR spectrum of CTAA at 40 °C was collected in a 1024 × 256 matrix with an f_2 frequency width of 11061.9 Hz (row digital resolution of 21.6 Hz), an f_1 frequency width of 2208.5 Hz (column digital resolution of 8.6 Hz), and 288 scans/row. For this experiment, 381 mg of CTAA was dissolved in 3 mL of solvent.

Results and Discussion

Our initial studies employed the addition of diketene to solutions of cellulose in DMAC/LiCl (Figure 1). In early experiments we followed closely the McCormick protocol for thermal (as opposed to room-temperature solvent exchange) dissolution of cellulose in DMAC/LiCl. The cellulose (hardwood pulp in early runs) was activated by heating to 100 °C in DMAC, and then LiCl was added. Heating was continued to 150 °C, and then the heat was immediately removed and the cellulose dissolved as the mixture was allowed to cool to room temperature over several hours. These highly viscous solutions then were heated to 100–150 °C, at which temperature viscosity was more moderate; diketene was added dropwise, and an exothermic reaction was observed. From our initial experiment we isolated a cellulose acetoacetate (CAA) with DS(acetoacetyl) = 0.71, which was fully soluble in water to the extent of up to 20 wt % of the solution (after that the solution became too viscous to observe dissolution of any more CAA at room temperature).

Table 1 shows the results of several attempts to expand upon this result with other solvents and acetoacetylating reagents. It has been shown by Witzeman *et al.*[12] that *tert*-butyl acetoacetate (tBAA) is a useful reagent for acetoacetylation of alcohols, because of its facile thermal decomposition to acetylketene and

Table 2. Synthesis of Cellulose Acetoacetates: Properties vs DS and DP

					GPC (all/1000)				
entry	cellulose[a]	diketene (equiv)	DS	IV	M_n	M_w	M_z	T_g (°C)	solubility
1	MCC	0.90	0.78	1.30	35.7	157	484	180	DMSO, NMP
2	MCC	1.80	1.58	0.79	40.9	255	854	152	DMSO, NMP
3	HWP	2.70	2.91	1.48	64.8	291	772	135	DMSO, NMP, acetone, HOAc
4	HWP	1.80	1.70	1.05	61.7	314	963	154	DMSO, NMP
5	HWP	0.90	0.84	0.39	68.5	401	1320	176	DMSO, NMP
6	MCC	2.70	2.38	0.45	23.7	76.8	212	136	DMSO, NMP, acetone, HOAc

[a] MCC = microcrystalline cellulose. HWP = hardwood pulp.

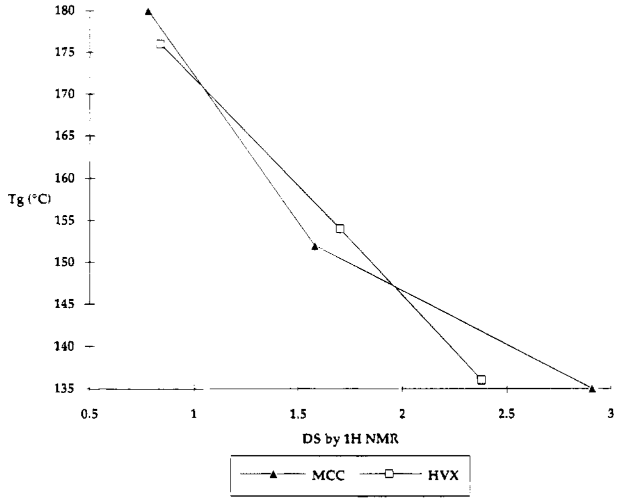

Figure 2. T_g vs DS and cellulose source for CAA.

tert-butyl alcohol. Our results show clearly that tBAA is a useful reagent for acetoacetylation of cellulose as well, despite the relatively poor nucleophilicity of the alcohol groups of cellulose. In addition, the substitution of NMP for DMAC is successful when either diketene or tBAA is used. We noted, however, that it seemed difficult to obtain high-DS cellulose acetoacetates and that the efficiency of acetoacetylation was unpredictable. Since these reactions entail the use of three hygroscopic reagents (cellulose, LiCl, and the amide solvent), we reasoned that adventitious water was the likely culprit. We designed a protocol whereby a portion of the amide solvent was distilled from the cellulose/LiCl/amide mixture during the heat-up process in order to dry the reaction mixture, and then the heat was removed and the cellulose allowed to dissolve as before. The results of the application of this technique to the synthesis of cellulose acetoacetate, using diketene in DMAC solvent, are seen in Table 2. Improvement in efficiency and repeatability was dramatic. Approximately 85–90% yields based on diketene were observed. *In addition, this new protocol gave us access to the entire DS range from 0 to 3.*

Other noteworthy observations may be made based on the data of Table 2. Similar results in terms of product DS are obtained whether the cellulose used is hardwood pulp or microcrystalline cellulose. This is a remarkable feature of this solution chemistry, since microcrystalline cellulose is unreactive even with acetic anhydride under standard heterogeneous reaction conditions. Little correlation is seen between the T_g of the product cellulose acetoacetates and the DP of the starting cellulose; instead, T_g is almost entirely a function of DS (Figure 2). Predictably, lower DS-(acetoacetyl) (resulting in more unsubstituted hydroxyl groups per anhydroglucose monomer) leads to more hydrogen bonding and a higher T_g. GPC molecular weight, conversely, is influenced by and is directly proportional to both starting cellulose DP and CAA DS. The solubility of these CAA's is generally more restricted than that for cellulose esters such as CA or CAP, of similar total DS, made by conventional means. The CAA's in Table 2, for example, are soluble in polar aprotic solvents such as DMSO or NMP, but only the most highly substituted material (DS 2.91) is soluble in acetone or acetic acid. This might be taken to imply a higher degree of stereoregularity in the CAA's; this is very likely since the conventional sulfuric acid-catalyzed process includes a step in which a cellulose triester is hydrolyzed to a partially substituted product. This reversible hydrolysis reaction results in random substitution around the anhydroglucose monomer and, presumably, along the chain. In direct solution esterification there is no opportunity for this randomization to occur. As product DS approaches 3.0, the randomness of substitution becomes less relevant. Another possibility is that the CAA's are more blocky in nature than conventional cellulose esters; we have seen no evidence to support this possibility (for example, a simplified ^{1}H NMR spectrum containing largely unsubstituted and fully substituted monomers) but cannot exclude it.

Reaction Time (h)	DS by ^{1}H NMR
0.5	2.10
1.0	2.22
3.0	2.12

Figure 3. Kinetics of cellulose esterification with diketene.

We have found that acetoacetylation is very rapid at 100–110 °C. Thus, monitoring a reaction in which diketene and wood pulp were reacted in NMP at 110 °C (Figure 3) by withdrawing samples and analyzing the product by ^{1}H NMR showed that the reaction is complete within 30 min at that temperature. No increase in product DS was seen after that time. Indeed, we found that acetoacetylation will proceed even at room temperature; reaction of diketene (4 equiv) with microcrystalline cellulose over 25 h gave a CAA with DS = 1.80 and M_w = 94 000. Not only were catalysts such as sulfuric acid and sodium acetate found to be unnecessary in this solution process, even at room temperature, but they gave little or no acceleration of the reaction and afforded products of lower DS.

We felt that for many applications it would be desirable to synthesize a cellulose "mixed" ester, containing more than one type of ester group, in which one was acetoacetyl. The second acyl group would afford us another means to adjust properties, such as compatibility with other polymers and T_g, for example. The presence of the second ester group also would be expected to reduce stereoregularity and crystallinity and therefore increase solubility. In general, aliphatic anhydrides are not as reactive as is diketene (because of the ring strain inherent in the four-membered ring

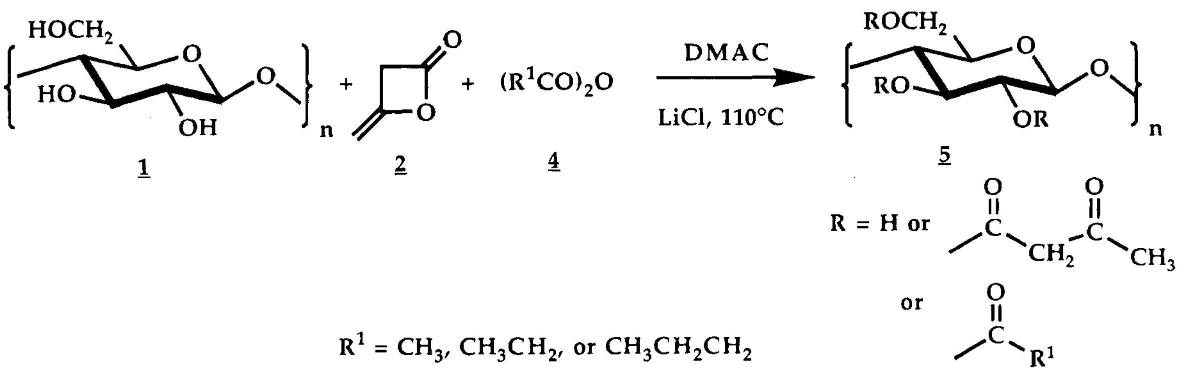

Figure 4. Synthesis of cellulose acetoacetate alkanoates.

Table 3. Cellulose Acetate Acetoacetate (CA(AA))

entry	cellulose[a]	Ac_2O (equiv)	diketene (equiv)	DS[b] Ac	AA	total	IV	GPC (all/1000) M_n	M_w	M_z	T_g	solubility
1	MCC	1.50	1.50	1.42	1.72	3.14	1.10	37.6	200	616	162	DMSO, NMP, THF, acetone, HOAc
2	MCC	0.30	1.50	0.32	1.39	1.71	1.16	49.5	272	895	156	DMSO, NMP
3	HWP	1.50	0.30	1.32	0.37	1.69	1.67	70.7	284	698	203	DMSO, NMP
4	HWP	0.30	0.30	0.20	0.26	0.46	1.92	50.3	269	805	213	DMSO, NMP
5	HWP	0.30	1.50	0.12	1.29	1.41	2.10	65.7	286	721	163	DMSO, NMP
6	MCC	0.30	0.30	0.13	0.17	0.30	0.97	7.77	15.1	31.2	212	DMSO
7	MCC	1.50	0.30	1.28	0.36	1.64	0.95	41.4	150	411	190	DMSO, NMP
8	HWP	1.50	1.50	1.07	1.71	2.78	1.32	59.1	267	713	161	DMSO, NMP, THF, acetone, HOAc, 2-butanone

[a] MCC = microcrystalline cellulose. HWP = hardwood pulp. [b] Ac = acetyl AA = acetoacetate.

Table 4. Cellulose Acetoacetate Alkanoates

entry	cellulose[a]	anhydride[b] (equiv)	diketene (equiv)	DS[c] alk.	AA	total	IV	GPC(all/1000) M_n	M_w	M_z	T_g	solubility
1	MCC	Pr (1.50)	1.50	1.50	1.40	2.90	1.56	74.4	334	976	150	DMSO, NMP, acetone, HOAc
2	HWP	Pr (1.50)	0.50	1.30	0.35	1.65	2.25	111	460	1370	171	DMSO, NMP
3	HWP	Pr (0.50)	0.50	0.45	0.47	0.92	2.24	57.1	246	706	182	DMSO, NMP
4	MCC	Pr (1.50)	0.50	1.40	0.41	1.81	0.91	60.6	183	434	169	DMSO, NMP, acetone, HOAc, THF
5	HWP	Pr (1.50)	1.50	1.36	1.37	2.73	0.95	73.5	227	419	154	DMSO, NMP, THF
6	MCC	Pr (0.20)	0.40	0.12	0.40	0.52	1.18	29.5	145	511	212	DMSO, NMP, water
7	MCC	Bu (0.90)	0.90	0.85	0.92	1.77	1.44	54.3	247	778	154	DMSO, NMP, HOAc
8	HWP	Bu (0.90)	0.30	0.85	0.26	1.11	1.82	87.4	270	621	177	DMSO, NMP
9	HWP	Bu (0.30)	0.30	0.22	0.24	0.46	2.16	53.7	266	838	209	DMSO, NMP
10	MCC	Bu (0.30)	0.30	0.20	0.24	0.44	1.09	31.4	145	468	>225	DMSO, NMP, water
11	MCC	Bu (0.90)	0.30	0.78	0.15	0.93	1.41	52.9	254	792	176	DMSO, NMP, THF
12	HWP	Bu (0.90)	0.90	0.91	0.92	1.83	1.86	83.9	333	830	156	DMSO, NMP

[a] MCC = microcrystalline cellulose. HWP = hardwood pulp. [b] Bu = butyric. Pr = propionic. [c] Alk. = alkanoate. AA = acetoacetate.

of diketene). Acylations of cellulose with aliphatic anhydrides in commerce and in the literature employ a catalyst, such as pyridine, sulfuric acid, or perchloric acid.[13] The sole exception of which we are aware is the work of Diamantoglou,[10] who achieved only low DS(acetyl) by uncatalyzed reaction of cellulose with acetic anhydride in DMAC/LiCl. We felt that solution acylation without catalyst would be considerably more valuable, since less chain cleavage of cellulose would be observed, the product would be free of catalyst residues, and diketene side reactions would be minimized.

In the event, we found that, by employing the same drying protocol that had been so successful with the CAA's, we could efficiently synthesize mixed esters of cellulose by uncatalyzed reaction with diketene and an aliphatic anhydride (Figure 4). We found that by sequential addition of stoichiometric amounts of acetic anhydride and diketene to a solution of cellulose in DMAC/LiCl, cellulose acetate acetoacetates (CA(AA)'s) were obtained in excellent yield with respect to cellulose and to the acylating agents. The results are summarized in Table 3. It was possible to synthesize examples of the full range of materials, from low-DS materials with some water solubility (total DS 0.46, partly soluble in water) to fully substituted materials with good solubility in solvents such as ethers and ketones. In general, the solubility of these materials is increased versus the CAA's, with a number of materials displaying some solubility in THF, 2-butanone, or acetic acid. Due to some overlap between the methyl regions for the acetates and the acetoacetates in the ^1H NMR spectrum, there is more uncertainty in the DS numbers for CA(AA)'s in Table 3 than for any of the other cellulose esters reported in this work (none of which have similar overlap problems in their spectra).

Even better solubility was observed with cellulose acetoacetate propionates (CAAP's) and cellulose acetoacetate butyrates (CAAB's), synthesized by a similar procedure and exemplified in Table 4. High efficiency with respect to the anhydride and diketene is observed, leading to cellulose esters whose total DS and DS of the particular acyl group may be controlled simply by reaction stoichiometry. The full range of DS is accessible by this method. It is worth noting that we have synthesized fully water-soluble versions of both CAAP and CAAB, each with a total DS in the range 0.44–0.52. Thus, disruption of the hydrogen bonding of cellulose with a small amount of ester substituent, even

Table 5. Cellulose Acetoacetate Alkanoates with High DS: Properties vs DP and Nature and DS of Substituents[a]

				DS[d]				GPC (all/1000)			
entry	cellulose[b]	anhydride[c] (equiv)	diketene (equiv)	alk.	AA	total	IV	M_n	M_w	M_z	T_g
1	HWP	Bu (2.50)	0.50	2.12	0.30	2.42	1.16	75.4	308	768	153
2	MCC	Bu (2.50)	0.50	1.94	0.34	2.28	0.98	36.8	261	692	153
3	HWP	Bu (1.50)	1.50	1.56	1.51	3.07	0.82	42.9	172	440	135
4	MCC	Bu (1.50)	1.50	1.33	1.37	2.70	1.11	47.1	222	617	136
5	HWP	Ac (2.50)	0.50	2.48	0.95	3.43	1.31	61.2	242	607	186
6	MCC	Ac (2.50)	0.50	2.30	0.87	3.17	1.02	51.5	224	643	183
7	HWP	Ac (1.50)	1.50	1.07	1.71	2.78	1.32	59.0	267	713	161
8	MCC	Ac (1.50)	1.50	1.42	1.72	3.14	1.10	37.6	200	616	162

[a] All products were soluble in DMSO, NMP, acetone, and acetic acid and soluble or mostly soluble in dichloromethane and THF. [b] HWP = hardwood pulp. MCC = microcrystalline cellulose. [c] Bu = butyric. Ac = acetic. [d] AA = acetoacetate. Alk. = alkanoate.

Table 6. Cellulose Acetate Acetoacetate: Effect of Order of Addition[a]

				DS[b]				GPC(all/1000)				
entry	Ac_2O (equiv)	diketene (equiv)	order of addition	Ac	AA	total	IV	M_n	M_w	M_z	T_g	solubility
1	1.50	0.30	Ac_2O, then diketene	1.28	0.36	1.64	0.95	41.4	150	411	190	DMSO, NMP
2	1.50	0.30	diketene, then Ac_2O	1.37	0.41	1.78	1.08	42.9	201	639	204	DMSO, NMP
3	1.50	0.30	premixed solution	1.37	0.43	1.80	1.01	40.1	160	486	194	DMSO, NMP

[a] All runs used MCC (microcrystalline cellulose). [b] Ac = acetyl. AA = acetoacetate.

if that substituent is as hydrophobic as a butyryl or acetoacetyl group, will render the resulting cellulose derivative soluble in water.

We have studied the effects of cellulose DP and proportion and type of ester groups on T_g and other properties of fully or nearly fully substituted cellulose acetoacetate alkanoates made by these solution techniques. The results are displayed in Table 5. The results show rather conclusively that T_g is quite sensitive to ester type (and, *vide supra*, to DS) but insensitive to molecular weight within the range studied. The CA(AA)'s have higher T_g's than CAAB's of similar total DS and DS(acetoacetyl), as one would expect. Among the CA(AA)'s, those with a higher proportion of acetyl substituents have higher T_g. The solubility of these highly substituted esters is uniformly good in solvents of moderate to high polarity. It's interesting to note that GPC M_n of the cellulose acetoacetate alkanoate product has little or no correlation to the DP of the starting cellulose.

One would predict that, in a direct and essentially irreversible process such as this one, order of addition of the diketene and anhydride would have an impact on the position of substitution and thus on product properties. The reactivity order for cellulosic hydroxyls is generally thought to be 6-OH $\gg$ 2-OH and 3-OH.[14] For the reactions described previously, the anhydride was added first and then diketene. It is reasonable to speculate that those reaction products have higher proportions of alkanoyl at the 6-OH than at the other hydroxyls. We explored the effects of order of addition in the series of experiments whose results are compiled in Table 6. We examined both sequences of addition as well as addition of a premixed solution for the acetic anhydride/diketene combination. Distinct differences were seen in the acetoacetyl methyl region (δ 2.05–2.45) of the ^{1}H NMR spectrum for the materials prepared by the three addition protocols (Figure 5); a broad singlet at δ 2.20 is largest when acetic anhydride is added first, moderately large when the reagents are premixed and added together, and much smaller when diketene is added first. We have not yet been able to fully assign the peaks in these spectra and so will not speculate on the exact positional selectivity obtained. The spectral differences are reflected in the T_g's of the products, which are highest when diketene is added first (204 °C) and lowest when acetic anhydride is added first (190 °C); we believe that the 14 °C range is significant and reflects the differing substitution pattern of these CA(AA) materials.

Assignment of the ring protons and carbons of CTAA was possible, however, based on results from the DQFCY and HETCOR experiments. In Figure 6 is shown the DQFCY spectrum of CTAA along with ring proton assignments based on standard nomenclature for anhydroglucose residues. These assignments are in agreement with previously published assignments for cellulose triacylates.[15] Proton and carbon-13 NMR chemical shift assignments for the ring and acetoacetate functionalities are shown in Table 7.

In the proton assignments of the acetoacetyl groups, site-specific assignments of the three methylene resonances have not been attempted. The methyl protons of the three acetoacetyl groups exhibit the same chemical shift. Site-specific assignments of the carbons in the acetoacetyl groups have been made based on resonance relative intensities and the assumption that methylene carbons of acetoacetyl groups attached to secondary ring carbons, i.e., the 2- and 3-positions, will have similar chemical shifts while methylene carbons of acetoacetyl groups attached to a primary carbon, i.e., the 6-position, will be different. The resonances at 201.70 and 200.76 ppm are assigned to the ketone carbonyl carbons, while the resonances at 166.76 and 165.85 ppm are assigned to the ester carbonyl carbons.

Cross-Linkable Waterborne Coatings. The fact that some of these cellulose derivatives are water-soluble, and contain the reactive acetoacetate functionality, raises the possibility that they might be useful resins for various types of waterborne coatings. An indication of this potential is given by the experiments summarized in Table 8. In these experiments, a CAA (DS = 0.4) prepared as described in this work was dissolved in water, along with a cross-linker such as hexakis(methoxymethyl)melamine or an α,ω-bis(amine)-capped poly(oxypropylene). In the melamine case an acid (*p*-toluenesulfonic acid) catalyst was added. The resulting solution was coated on steel panels and cured. The resulting cross-linked films were thin, had excellent color, high hardness, and were exceptionally solvent resistant; the films all survived a standard rubbing test with 2-butanone with no damage and, in fact, were not

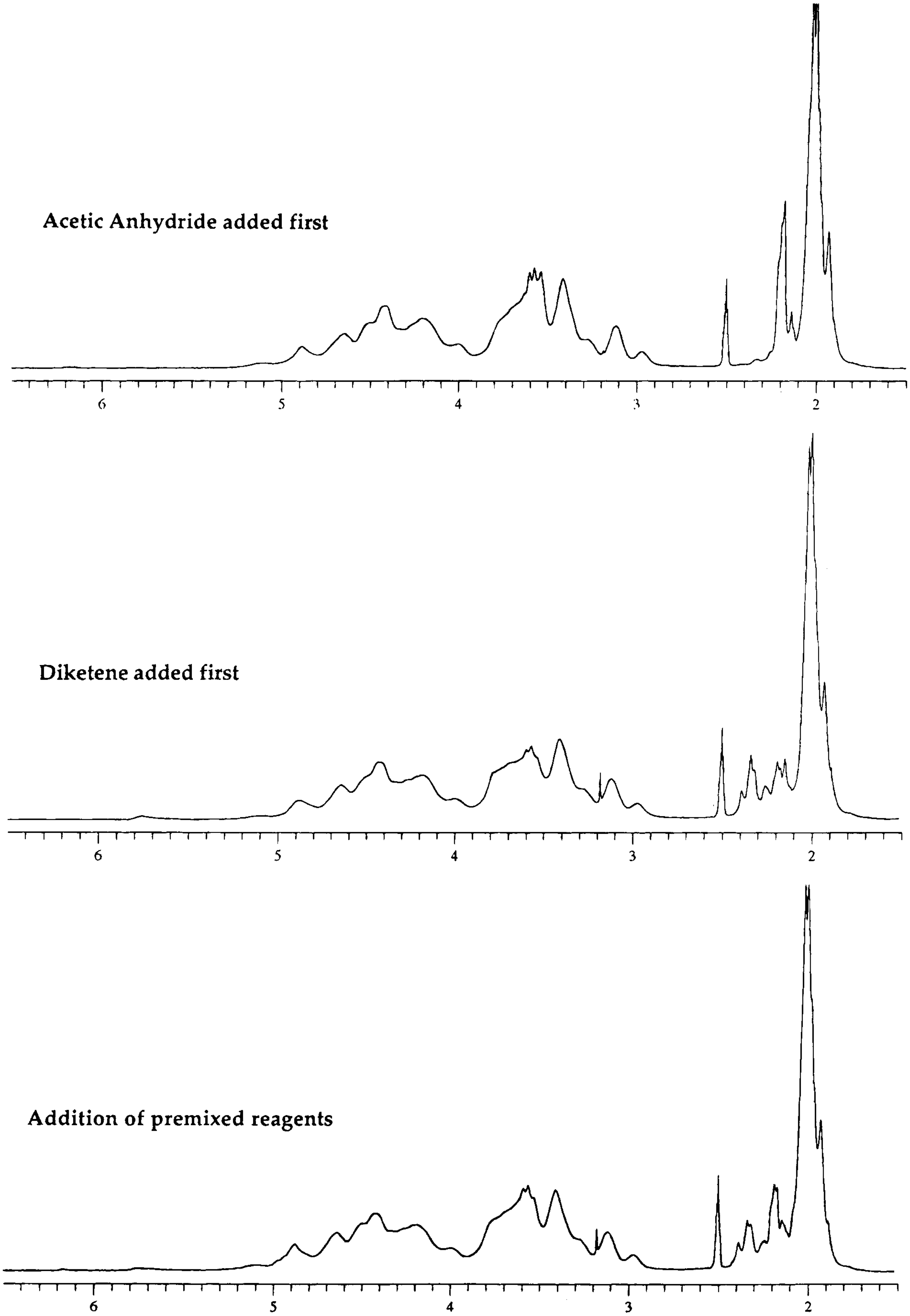

Figure 5. ^{1}H NMR spectra in DMSO-d_6 of cellulose acetate acetoacetates prepared by different orders of addition of diketene and acetic anhydride.

affected even by the same test using DMF! The films were thin because the particular CAA used had high molecular weight, thickened the aqueous coating solution very effectively, and thus limited the amount of solid coating delivered per mil of film laid down. Nonetheless, these results demonstrate considerable

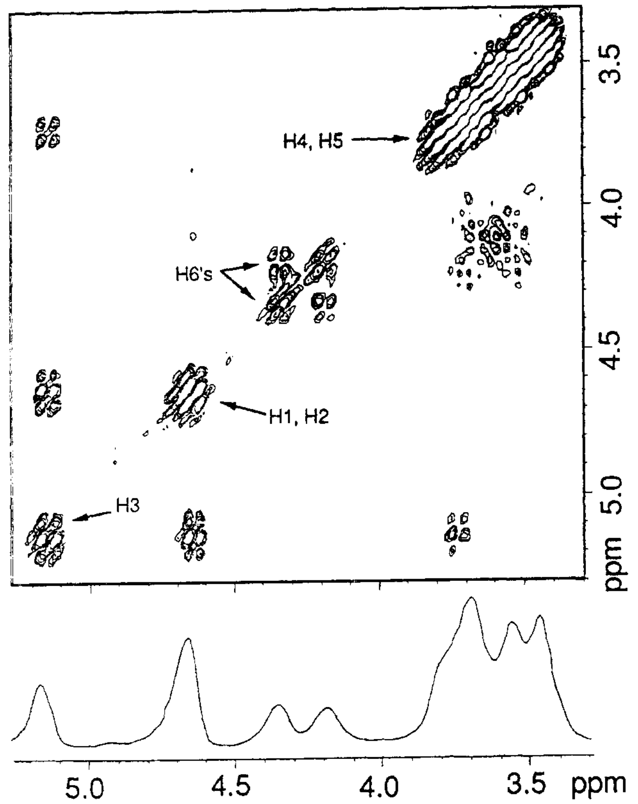

Figure 6. DQF-COSY spectrum of CTAA in DMSO-d_6 at 80 °C.

Table 7. NMR Chemical Shift Assignments for Cellulose Tris(acetoacetate)

	Proton (80 °C in DMSO-d_6)		
H1	4.64	H4	3.72
H2	4.64	H5	3.72
H3	5.14	H6	4.33 4.17
acetoacetates			
methylenes: 3.68, 3.55, 3.46			
methyls: 2.17			
	Carbon (40 °C in DMSO-d_6)		
C1	98.82	C4	75.14
C2	70.74	C5	71.41
C3	71.92	C6	62.06
acetoacetates			
methylenes	49.31 (C6)		48.76 (C2, C3)
methyls	29.63 (C6)		29.88 (C2, C3)
carbonyls	201.70 (C6) 166.76 (C6)		200.76 (C2, C3) 165.85 (C2, C3)

promise for these polymers in thermoset coating applications.

Table 8. Thermoset Coatings from Aqueous Solutions of CAA[a]

entry	cellulosic resin[b]	cross-linker[c]	cell.:XL[d]	% PTSA[e]	resistance[f] MEK	DMF
1	CAA	melamine	75:25	0.3	yes	yes
2	CAA	melamine	65:35	0.3	yes	yes
3	CAA	diamine	74:26	0	yes	yes
4	CAA	diamine	81:19	0	yes	yes
5	HPMC	melamine	70:30	0.3	yes	yes
6	HPMC	diamine	77:23	0	yes	no

[a] All dry films were 0.3 mil in thickness. All solutions of cellulosic resin in water were 500 cP viscosity. [b] CAA = cellulose acetoacetate (DS = 0.4). HPMC = [(hydroxypropyl)methyl]cellulose. [c] melamine = hexakis(methoxymethyl)melamine. diamine = α,ω-bis(amino)poly(oxypropylene). [d] Cell.:XL = weight ratio of cellulosic resin to cross-linker. [e] PTSA = *p*-toluenesulfonic acid. [f] MEK = 2-butanone. DMF = *N,N*-dimethylformamide.

Conclusion

We have discovered a novel method for acetoacetylation of cellulose, involving reaction with diketene or *tert*-butyl acetoacetate in solution in DMAC/LiCl or NMP/LiCl. This method affords access to cellulose acetoacetates across the entire DS range, with good efficiency with respect to both diketene and cellulose. The materials produced are amorphous, have high T_g's, and have more restricted solubility than conventionally prepared cellulose esters. We have also discovered that it is possible to acylate cellulose efficiently with alkanoic anhydrides, *without any catalyst*, under the same solution reaction conditions. This discovery allows us to prepare mixed esters of cellulose such as cellulose acetate acetoacetate, cellulose acetoacetate propionate, and cellulose acetoacetate butyrate. This process allows access to materials across the entire range of total DS and of alkanoate/acetoacetate ratio. These mixed esters have increased solubility with respect to cellulose acetoacetate but more restricted solubility with respect to mixed esters such as cellulose acetate butyrate of similar total DS made by conventional means. One can use the total DS and the ratio of substituents to adjust physical properties such as T_g and solubility; the order of addition also appears to be an inexpensive and somewhat effective way to adjust properties. Water-soluble cellulose acetoacetates made using this technology can be easily cross-linked, using (methoxymethyl)-melamine or bis(amine) resins, to films which are very hard and extremely solvent resistant; these cellulose acetoacetates are therefore promising materials for coating applications.

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