

# Thermal Properties of Cellulose Triacetate as Prepared from Low-Grade Dissolving Pulp

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## SYNOPSIS

Because cellulose triacetate is prepared from low-grade dissolving pulp, a considerable amount of the insoluble residue was present in the acetylation medium of the acetic acid/acetic anhydride/sulfuric acid system. To reduce the insoluble residues, a solvent, such as nitromethane, nitroethane, or dichloroacetic acid, added to the acetylation medium was found to be very effective for its reduction. By exploring the optimum conditions for acetylation with these solvents, nitromethane added and dichloroacetic acid added systems with solvent/acetic acid = 3/7 (v/v) were found to have a particularly high transmittance at  $\lambda = 670$  nm in their acetylation solution with a low insoluble residue. The obtained acetates revealed good thermal properties similar to that from high-grade dissolving pulps. Therefore, a high quality cellulose triacetate can be manufactured from acetylation systems with even low-grade dissolving pulps with an appropriate solvent added. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Cellulose acetate is one of the most important cellulose derivatives in the fiber and textile industries and is usually manufactured from cotton linters or high quality wood dissolving pulps.<sup>1</sup> This is because low-grade dissolving pulps contain hemicelluloses; and hemicellulose acetates behave differently in the solution, resulting in industrial problems such as filterability, turbidity, and false viscosity.<sup>2-10</sup>

In spite of these problems, it is still beneficial economically and technically for low-grade dissolving pulps to be used as raw materials for cellulose acetate production. Therefore, cellulose triacetate (CTA) was prepared from low-grade sulfite softwood dissolving pulp in an acetic acid/acetic anhydride/sulfuric acid system. However, a substantial amount of insoluble residues was found in its system; and through a characterization of the insoluble residue,<sup>11</sup> it was found to be composed of CTA and glucomannan triacetate (GTA) in aggregate with each other in the acetylation medium by their compatible nature.

Therefore, some trials were made to reduce such residues. As one of the trials, the pretreatment of the low-grade dissolving pulps with mixtures of acetic acid and sulfuric acid was found to reduce the amount of insolubles, due perhaps to selective degradation by hydrolysis or acidolysis of glucomannan without degrading cellulose. Furthermore, the use of a higher amount of sulfuric acid as a catalyst was also found to reduce the insoluble residues formed.<sup>12</sup> As another trial, the effect of the addition of a solvent to the acetylation medium on the reduction of the insoluble residues was studied. As a result, some solvents such as nitromethane, nitroethane, or dichloroacetic acid were found to be effective in reducing the insoluble residues.<sup>13</sup>

In this study, therefore, the optimum conditions for acetylation with these solvents were studied for low-grade dissolving pulps to prepare CTA as high in quality as that from high-grade dissolving pulps, particularly for its thermal properties.

## EXPERIMENTAL

### Materials and Methods

One part of well-defibered, sulfite softwood low-grade dissolving pulps with  $\alpha$ -cellulose content of

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87.5% (Table I) was first activated by stirring with a mixture of a solvent, such as nitromethane, nitroethane, or dichloroacetic acid, with acetic acid with varying volumetric ratios of 0/10, 1/9, 2/8, 3/7, and 5/5 (totally 160 parts) solvent/acetic acid (v/v) for 20 min at 40°C. Subsequently, the activated pulps were acetylated with a mixture of acetic anhydride (7 parts) and sulfuric acid (0.1 part) for 3 h at 40°C, followed by stirring overnight at 20°C. In a similar way, the medium-grade and high-grade dissolving pulps in Table I were also acetylated, for comparison, without adding the solvent.

The reaction solution obtained was then spun in a centrifuge at 7,000 rpm for 30 min. After the tubes were removed carefully, the supernatants were pipetted away and the precipitated substances were washed repeatedly with fresh acetic acid by centrifugation to obtain the insoluble portions. All supernatants collected were concentrated and poured into deionized water to precipitate the soluble portions. The soluble and insoluble portions were washed with saturated NaCl solutions 3 times for stabilization, and the remaining NaCl was washed away thoroughly with deionized water. These were successively washed with ethanol and dried under a vacuum for more than 12 h, and then studied by differential scanning calorimetry (DSC) and thermogravimetry (TG) with Shimadzu DSC-50 and TGA-50 instruments with a flow of nitrogen gas at 30 mL/min. The temperature was raised from 350 to 600 K at a heating rate of 5 K/min. The GTA prepared in a previous work<sup>11</sup> was also studied by DSC and TG, just for comparison.

The obtained reaction solutions just after 3-h acetylation and after overnight stirring were subject to a photometric analysis to determine the degree of transmittance of the solution by the formula below with a monochromatic light of 670-nm wavelength on a Shimadzu recording spectrophotometer, UV-365.

$$\text{transmittance (\%)} = (I_{\text{solution}}/I_{\text{medium}}) \times 100 (\%),$$

where  $I_{\text{solution}}$  and  $I_{\text{medium}}$  refer to the transmittances of the reaction solution and the acetylation medium without CTA, respectively.

The neutral sugar compositions were determined by an alditol-acetate procedure<sup>14</sup> with a Shimadzu GC-7A gas chromatograph to which a 10% Silar-10C column (2 m) was attached. The carrier gas used was helium with a flow rate of 40 mL/min. An injection temperature of 260°C was set with a column temperature of 230°C.

## RESULTS AND DISCUSSION

### CTA in Solvent-Added Acetylation Medium

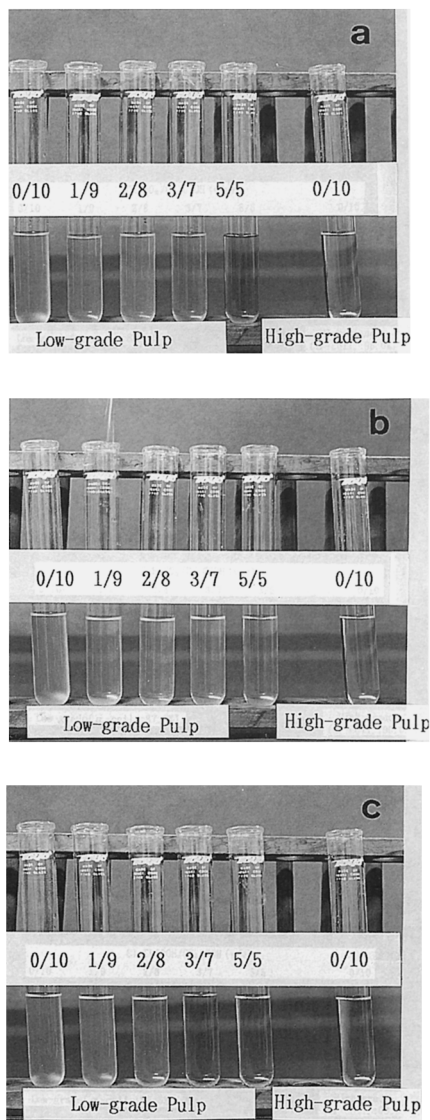
It was known from our previous work<sup>11</sup> that when CTA is prepared from sulfite low-grade dissolving pulp, a substantial amount of insoluble residues (13–15 in wt %) is present in the acetylation medium of the acetic acid/acetic anhydride/sulfuric acid system. However, these insoluble residues are fully acetylated, keeping the fiber structure in a swollen form.

As one of the remedies for reducing these insoluble residues, a solvent was added to the acetylation medium. Among 17 different solvents investigated, nitromethane, nitroethane, and dichloroacetic acid were found to be very effective for its reduction in the acetylation medium at 0.6, 3.0, and 0.8% insoluble residue content, respectively.<sup>13</sup> In this study, therefore, the optimum conditions for acetylation with these solvents were studied for low-grade dissolving pulps to prepare CTA, and thermal properties of prepared CTA were evaluated.

Figure 1 shows comparisons of reaction solutions of low-grade dissolving pulps acetylated in the acetylation medium with an addition of various amounts of nitromethane, nitroethane, or dichloroacetic acid with volumetric ratios of 0/10, 1/9, 2/8, 3/7, and 5/5 to acetic acid [solvent/acetic acid (v/v)]. Just for comparison, the reaction solution of acetylated high-grade dissolving pulps is also shown. Prior to evaluation for transmittance,

**Table I** Chemical Compositions of Original Pulps Used for Acetylation

Pulps	$\alpha$ -Cellulose Contents (wt %)	Chemical Compositions (mol %)		
		Glucose	Mannose	Xylose
High grade	96.0	96.2	0.7	1.1
Medium grade	93.2	93.2	3.0	3.7
Low grade	87.5	90.4	7.0	2.6



**Figure 1** Comparisons of reaction solutions of low-grade dissolving pulps acetylated in the acetylation medium with an addition of various amounts of (a) nitromethane, (b) nitroethane, or (c) dichloroacetic acid. The reaction solution of acetylated high-grade dissolving pulps is also shown for comparison.

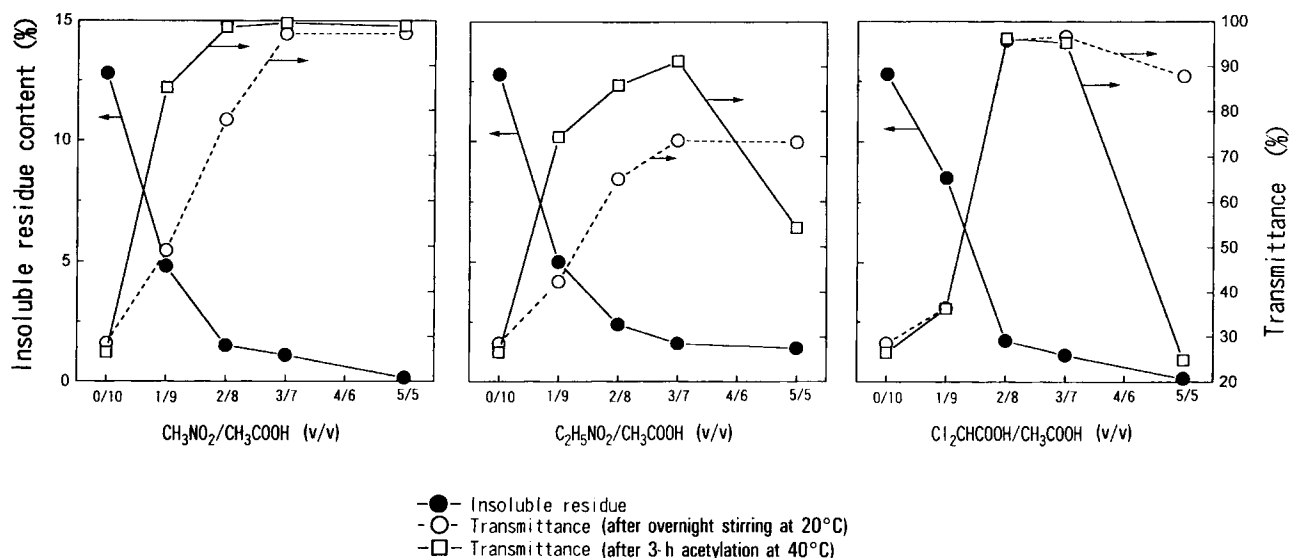
no absorbance was ensured for not only CTA and GTA molecules, but also acetylation mediums with and without the three different solvents added, at 670-nm wavelength monochromatic light. Therefore, the degree of the transmittance obtained is inversely dependent upon the light scattering by the insoluble residues in the solution. It is quite apparent that with an increased amount of the solvent added, the solutions were becoming more transparent to a level of that from high-grade dis-

solving pulp. This is due perhaps to an increased solubility of the insoluble residues in the solution by the addition of the solvent.

Figure 2 shows the relationship between the insoluble residue content and the transmittance at a wavelength of 670 nm in various acetylation solutions with nitromethane, nitroethane, or dichloroacetic acid. A transmitting trend that could be observed in Figure 1 can be quantitatively visualized; and with an increase in the amount of the solvent added, the degree of transmittance was generally improved. However, a closer inspection clearly indicates that in nitromethane and nitroethane added systems, the solutions after 3-h acetylation at 40°C were mostly reduced in their transmittances after overnight stirring at 20°C. In the dichloroacetic acid added system, however, the transmittances were not changed except for the 5/5 solution. For the insoluble residue content, it has a direct correlation with the transmittance; and it is apparent that, as overall transmittance is improved, the insoluble residue content is decreased.

It was demonstrated in our previous work<sup>11</sup> that the insoluble residue is composed of CTA and GTA in aggregate with each other at the molecular level by their mutual interactions, and that GTA is involved in the formation of the insoluble residue to a great extent. Therefore, a decrease in transmittance after overnight stirring (Fig. 2) would suggest that after CTA and GTA molecules are dissolved in the acetylation medium, they meet and aggregate with each other, which would have resulted in a decrease in the transmittance. However, in solutions with the increased amount of the solvent added, as seen for the 3/7 and 5/5 solutions of nitromethane, a complete solubilization of CTA and GTA, even after 3-h acetylation, would be made by releasing molecular aggregation of these two kinds of macromolecules.

Based on the results of Figure 2, the relationship between the insoluble residue content and the transmittance of the acetylation solution was studied as in Figure 3. Just for comparison, the results from three different dissolving pulps in Table I acetylated without any solvent added were also included as shown by the filled circles. It is quite apparent that with a decrease of the insoluble residue content, the degree of transmittance was improved and that 3/7 and 5/5 solutions of nitromethane added systems, and 2/8 and 3/7 solutions of dichloroacetic acid added systems revealed a transmittance as high as that from the high-grade dissolving pulp.



**Figure 2** Relationship between insoluble residue content and transmittance at  $\lambda = 670$  nm in various acetylation solutions with nitromethane, nitroethane, or dichloroacetic acid, as described by the volumetric ratios to acetic acid.

### Thermal Properties of Soluble Portion and Insoluble Residue in Acetylation Medium

Figure 4(a) shows the DSC thermograms, under a flow of nitrogen, of the soluble portion and insoluble residue of the CTA prepared in an acetylation medium without a solvent added. The DSC thermograms of pure CTA prepared from cotton linters and GTA are also shown in Figure 4(b,c). From these results it is clear that the soluble portion reveals a similar pattern to that of CTA. Therefore, an exothermic peak at about 475 K and an endothermic peak at 575 K respectively correspond to peaks of crystallization and melting as in the literature,<sup>15</sup> whereas the insoluble residue reveals neither of them for the soluble portion.

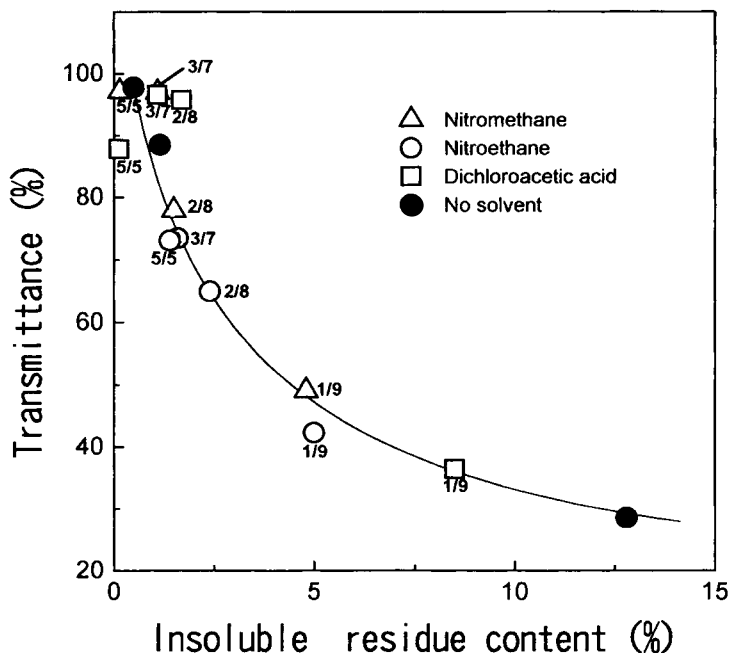
For the TG thermograms in Figure 4 the soluble portion was fairly stable against a temperature rise up to about 580 K, but the insoluble residue revealed some weight decrease started from about 495 K. It is reported that when the polymer molecules are pyrolyzed, the TG thermogram reveals some weight decrease due to its pyrolysis; and correspondingly, the DSC thermogram reveals an endothermic peak.<sup>16</sup> Therefore, the peak at about 510 K observed in the DSC thermogram of the insoluble residue would be due to its pyrolysis. Because GTA is rather thermally stable as in Figure 4(c), the observed degradation by pyrolysis would be due to that of CTA molecules.

Although the insoluble residue is composed of CTA and GTA, its DSC thermogram did not reveal a feature of CTA molecules, as observed in the sol-

uble portion. Because the CTA and GTA molecules of the insoluble residue are in molecular aggregate with each other, its residue cannot act as CTA by itself. This would be a reason why the CTA molecules in the insoluble residue are thermally degraded. Therefore, when the weight decrease is observed in the TG thermograms, special care must be taken for the assignment of the DSC thermograms.

Figure 5 shows one example of the DSC thermogram of the soluble portion prepared in 1/9 nitromethane added acetylation medium. As the TG thermogram shows, the soluble portion is thermally degraded from about 470 K. Therefore, a corresponding endothermic peak must be at about 495 K in the DSC thermogram. In addition to this peak, the exothermic and endothermic peaks are present at temperatures of about 480 and 560 K, respectively. These seem to correspond to temperatures of cold crystallization and melting of the CTA. Therefore, it would be appropriate to consider that the two DSC thermograms shown by the dotted lines would overlap and result in the DSC thermogram shown by the solid line in Figure 5.

Based on this assignment, Figure 6 shows the DSC and TG thermograms of the soluble portion prepared in various nitromethane added acetylation mediums in which the solid line of the DSC thermogram shows the observed DSC curve and the dotted lines are two estimated individual curves. As observed in Figures 2 and 3, with an increase of the amount of nitromethane added, the transmittance

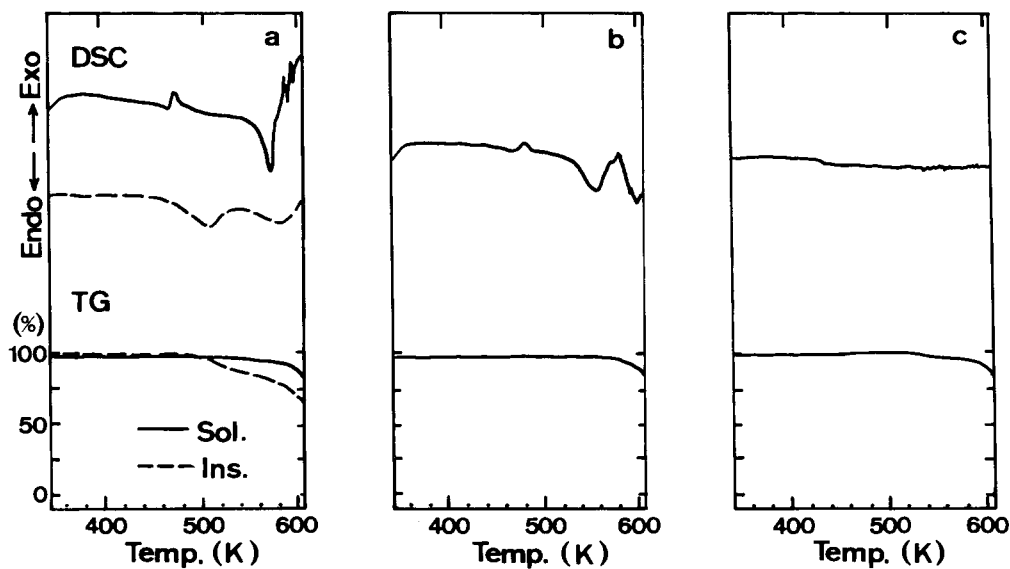


**Figure 3** Relationship between the insoluble residue content and the transmittance at  $\lambda = 670$  nm of the acetylation solution. Numbers of each plot show the volumetric ratio of the solvent to acetic acid in the acetylation medium.

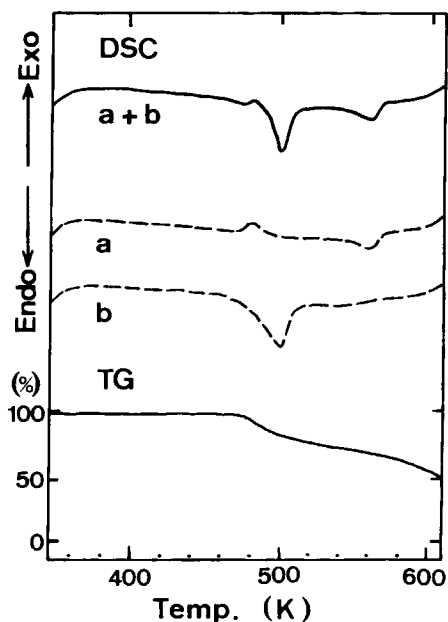
is improved and the insoluble residue content is decreased. It is very interesting, concomitantly, that the soluble portion becomes more stable, as observed in the TG thermograms, with its increase in transmittance.

Because there exists a large difference in the thermal properties among three different nitrome-

thane added acetylation systems, chemical compositions of these soluble portions were determined as shown in Table II. However, the results are very similar to that of the original low-grade dissolving pulp. This indicates that the improved properties are not due to the removal of the hemicellulose acetates from the acetylation system, but due to sol-



**Figure 4** The DSC and TG thermograms of (a) soluble portion (Sol.) and insoluble residue (Ins.), (b) CTA, and (c) GTA.



**Figure 5** The DSC and TG thermograms of the soluble portion prepared in 1/9 nitromethane added acetylation medium. The DSC thermogram was assigned to two individual DSC curves shown by the dotted lines.

vation of the GTA molecules with the solvent-added acetylation medium.

As the results are shown in Table III, a similar trend was obtained for the nitroethane added and dichloroacetic acid added acetylation systems.

**Table II** Chemical Compositions of Each Soluble Portion Prepared from Various Nitromethane Added Acetylation Systems

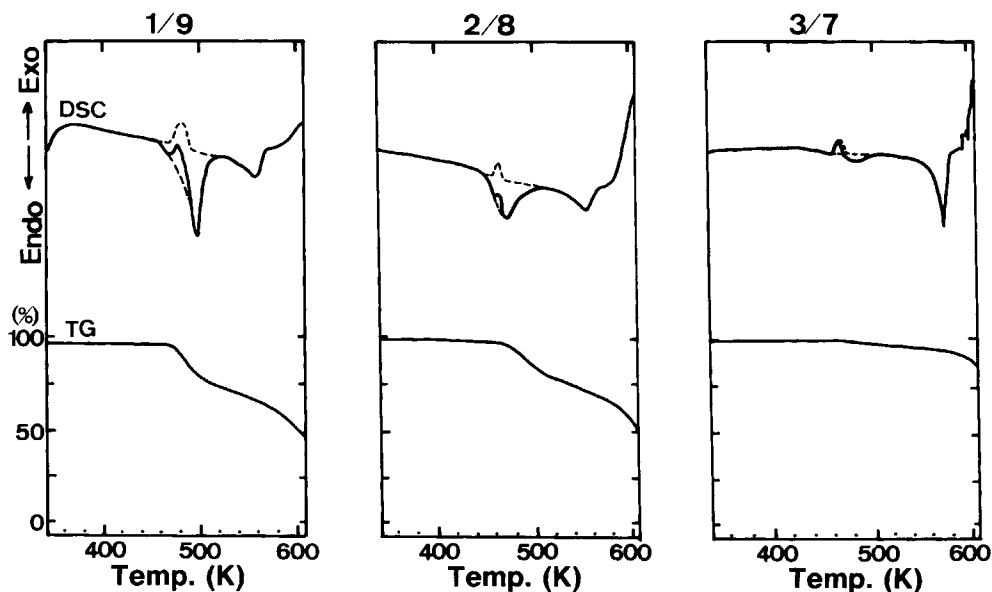
Samples	Chemical Compositions (mol %)		
	Glucose	Mannose	Xylose
Low-grade pulp	90.4	7.0	2.6
Sol. [1/9 (v/v)]	92.8	6.0	1.2
Sol. [2/8 (v/v)]	86.9	9.3	3.7
Sol. [3/7 (v/v)]	92.4	6.9	0.8

Therefore, basically the same phenomenon also occurred in these systems.

### Mechanism of Enhanced Thermal Properties Achieved for CTA Prepared from Low-Grade Dissolving Pulp

For these observed results, a mechanism is proposed in Figure 7 in which molecular arrangements are demonstrated of CTA and GTA in an acetylation medium with and without a solvent added.

Acetic acid, a major part of the acetylation medium, is known not to be a good solvent for either CTA or GTA.<sup>6</sup> In particular, GTA, different from CTA in consisting of only glucose residues, contains mannose residues with a cis configuration of hydroxyl groups in the C<sub>2</sub> and C<sub>3</sub> positions. Therefore,



**Figure 6** DSC and TG thermograms of soluble portions prepared in nitromethane added acetylation mediums with varying volumetric ratios of nitromethane to acetic acid (1/9, 2/8, and 3/7) in which the solid line of the DSC thermogram shows an observed curve while the dotted lines are two estimated individual DSC curves.

**Table III Overall Evaluation of Prepared CTA in Acetylation Medium with Designated Solvent Added**

Cellulose Samples	Solvents	Acetylation Mediums Solvent/AcOH (v/v)	Insoluble Residues (wt %)	Transmittance <sup>a</sup> (%)		Thermal Analyses of Soluble Portion	
				40°C, 3-h Acetylation	Overnight Stirring	Residue at 580 K (wt %)	<i>T<sub>m</sub></i> <sup>b</sup>
Low-grade pulp	—	0/10	12.8	26.5	28.5	95	EE
	CH <sub>3</sub> NO <sub>2</sub>	1/9	4.8	85.0	49.0	64	E
	CH <sub>3</sub> NO <sub>2</sub>	2/8	1.5	98.5	77.9	67	E
	CH <sub>3</sub> NO <sub>2</sub>	3/7	1.1	99.4	97.0	93	EE
	C <sub>2</sub> H <sub>5</sub> NO <sub>2</sub>	1/9	5.0	74.2	42.3	70	E
	C <sub>2</sub> H <sub>5</sub> NO <sub>2</sub>	2/8	2.4	85.8	65.0	63	NE
	C <sub>2</sub> H <sub>5</sub> NO <sub>2</sub>	3/7	1.6	91.2	73.5	79	E
	Cl <sub>2</sub> CHCOOH	1/9	8.5	36.2	36.4	75	E
	Cl <sub>2</sub> CHCOOH	2/8	1.7	96.1	95.8	79	E
	Cl <sub>2</sub> CHCOOH	3/7	1.1	95.2	96.6	86	EE
Medium-grade pulp	—	0/10	0.8	—	88.5	—	EE
High-grade pulp	—	0/10	0.5	87.2	97.8	99	EE

EE, extremely evident; E, evident; NE, not evident.

<sup>a</sup> Transmittance of the reaction solution at  $\lambda = 670$  nm.

<sup>b</sup> *T<sub>m</sub>*, Melting temperature of CTA.

GTA molecules must be a little more difficult in solvation than CTA molecules. The molecules of GTA would therefore be aggregated with each other or aggregated with CTA molecules in the acetylation medium as in Figure 7(a). On the other hand, in the acetylation medium with an appropriate solvent added such as nitromethane, nitroethane, or dichloroacetic acid, CTA and GTA molecules are solubilized as in Figure 7(b), with releasing the molecular aggregation. Therefore, when macromolecules different in structure as in Figure 7(a,b) are precipitated, the precipitates must be different in their properties. In Figure 7(a) these two kinds of molecules are molecularly aggregated so that they are physicochemically interacted. Thus, molecules are not reflected in the CTA structure. However, in Figure 7(b) molecules are just physically mixed for precipitation without any molecular interactions. In this particular case, the CTA molecules can act as themselves so that a characteristic structure of CTA would be reflected by their thermal analysis.

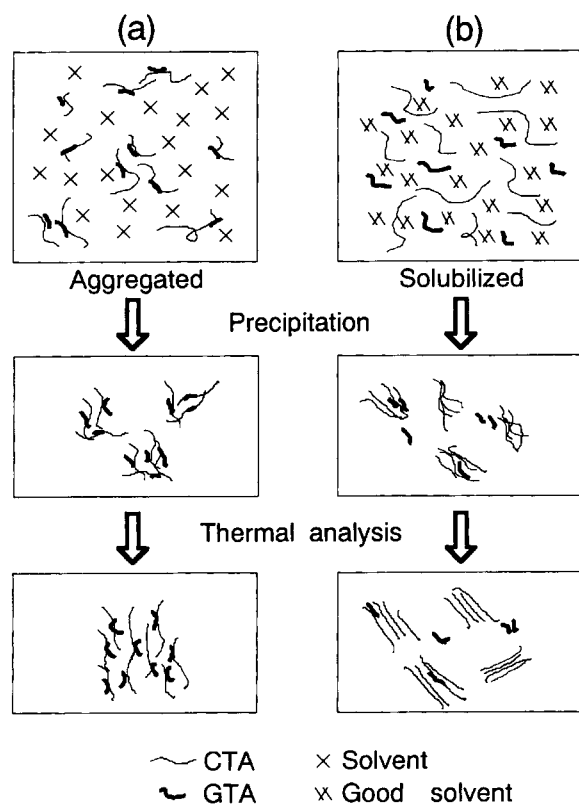
## CONCLUSION

For all nitromethane, nitroethane, and dichloroacetic acid added acetylation mediums, insoluble residues were decreased with an increase of the amount of the solvent added; and a transmittance at  $\lambda = 670$

nm was higher in the reaction solutions in which the less insoluble residues were present.

The thermal properties were better in acetates prepared in the reaction solutions with the higher transmittances; and such acetates revealed, without any degradation, an evident endothermic peak in the DSC curve due to the melting of CTA. The better thermal properties obtained were assumed to be due to the fact that CTA and GTA are not molecularly aggregated in highly transmitted reaction solutions. CTA and GTA obtained from such solutions are only physically mixed, thus reflected in the crystallized CTA molecules at an elevated temperature whereas molecularly aggregated CTA and GTA in poorly transmitted solutions are such that CTA molecules in the aggregates cannot act as themselves, which resulted in an absence of CTA melting and their thermal degradation during thermal analyses.

Based on these results, we may conclude that, even from low-grade dissolving pulps, CTA can be manufactured with a similar quality to that from high-grade dissolving pulp. Such acetates must be physically mixed with GTA but not molecularly aggregated with each other to reveal good thermal properties. It may therefore be concluded that such a new acetylation system with an appropriate solvent can provide a clue to an industrial use of the low-grade dissolving pulps for cellulose acetate production.



**Figure 7** Molecular arrangements of CTA and GTA in (a) an acetylation medium and (b) an acetylation medium with a good solvent added. (a) CTA and GTA are molecularly aggregated. (b) CTA and GTA are completely soluble. After precipitation, (a) aggregated molecules of CTA and GTA are such that no evidence can be achieved on CTA structure, but (b) physically mixed molecules would result in a characteristic structure of CTA by their thermal analysis.

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