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Publisher *Taylor & Francis*

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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Tang, Lie-Gui , Hon, David N. -S. and Zhu, Yu-Qin(1996) 'Polymorphic Transformations of Cellulose Acetates Prepared by Solution Acetylation at an Elevated Temperature', Journal of Macromolecular Science, Part A, 33: 2, 203 – 208

To link to this Article: DOI: 10.1080/10601329608010863

URL: <http://dx.doi.org/10.1080/10601329608010863>

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POLYMORPHIC TRANSFORMATIONS OF CELLULOSE ACETATES PREPARED BY SOLUTION ACETYLATION AT AN ELEVATED TEMPERATURE

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ABSTRACT

Transformations of cellulose acetates having different bound acids at an elevated temperature were studied. The experimental conformity between DSC and x-ray diffraction results indicated that amorphous polymers were obtained by a solution acetylating process at an elevated temperature. No glass transitions in DSC curves were found, and all samples exhibiting a cellulose acetate II type of crystal structures were substantiated by x-ray diffractograms.

INTRODUCTION

Cellulose acetate is by far the most important cellulose derivative owing to its broad applications in plastics and fibers, particularly for making cigarette tow. With the exception of fibrous triacetate, practically all cellulose acetate is manufactured by a solution process using a suitable catalyst and a solvent such as acetic

acid. The esterification of cellulose is a heterogeneous topochemical reaction. It is an exothermic reaction; the temperature is controlled at 40–50°C to minimize cellulose degradation. Several methods have been developed to acetylate cellulose at temperatures between 50 and 85°C [1–4] and above 90°C [5, 6].

The thermal transitions of cellulose acetates have been the subject of vigorous studies since the 1960s [7–9]. Most of the information is based on studies focused on the acetylation of fiber in a heterogeneous system at low temperature. The existing data on this subject varies greatly with different materials and methods of preparation and analysis. It is generally accepted that two stable polymorphic crystalline structures exist in cellulose triacetate (CTA): CTA I and CTA II [10, 11]. In the late 1950s, Sprague et al. [10] published the x-ray diffraction patterns of CTA I and II and indicated their correlations with celluloses I and II. In their study the CTAs were heat treated in the 210 to 280°C range at times of 1–5 minutes to develop their crystallinity. They found two crystalline structures for CTA, designated CTA I and CTA II. CTA II could be prepared by acetylation of cellulose I or II and then spun into fibers from methylene chloride-methanol. There was no way to convert CTA II to CTA I or to cellulose I. These observations were contradicted in a later x-ray study [12]. The latter showed that CTA I can be formed by the heterogeneous acetylation of cellulose I and II when swelling in the pretreatment media was slight [12]. Saponification of CTA does not change its polymorphic crystalline structure. The transformation of CTA I to CTA II was also obtained by a superheated steam treatment without any dissolving process [13]. Acetylation of cellulose in aprotic solvents has been reported to occur without changes in the original macroscopic structure [14, 15].

In the present work, both thermal and polymorphic structural transformations of cellulose acetates, prepared by a solution process at an elevated-temperature acetylation, are examined by means of differential scanning calorimetry (DSC) and x-ray diffraction.

EXPERIMENTAL

Materials

The specimens of cellulose triacetate (CTA) used in this study were prepared from a purified cotton cellulose by acetylating it in an acetic anhydride–acetic acid–sulfuric acid system at 90°C for an hour. When acetylation is virtually complete, the reaction mixture is highly viscous and clear. The hydrolysis of cellulose triacetate to produce cellulose diacetate (CDA) was conducted at an elevated temperature of about 120°C for about 10–20 minutes.

Methods

DSC Analysis. A Perkin-Elmer DSC-2C was used for thermal analysis. The thermograms of specimens were obtained by using heating rates of 20°C/min in a nitrogen atmosphere.

X-Ray Diffraction. A Rigaku-Rint D/max-1200 diffractometer was used with a $\text{CuK}\alpha$ radiation.

RESULTS AND DISCUSSION

Phase Transitions

In spite of the differences reported in the literature on phase transitions for cellulose acetates, two-phase transitions are generally accepted. From DSC data [8, 16, 17] it has been recognized that two endothermic peaks at 50–80°C and 200–220°C are detected. They may be ascribed respectively to the conformational change in the glucose ring and glass transition.

In this investigation the phase transitions of CDA samples with different bound acids (ba) between 52 and 56% and CTA (ba, 61%) were determined by DSC. Results are shown in Fig. 1. They display all the transition characteristics of cellulose acetates:

1. 340–370 K: endothermic peaks due to the softening and conformational transitions in the glucose ring.
2. 470–480 K: exothermic peaks caused by the crystallization temperature of CTA, T_c .
3. 500–530 K: endothermic peaks caused by the melting temperature, T_m , of CDA.
4. 580–590 K: endothermic peak caused by the melting temperature, T_m , of CTA.
5. 590–620 K: exothermic peaks due to chemical crosslinking, intramolecular chain stiffening, or a breakdown of a new polymer structure formed as a result of thermal transformations [9].

The glass transition, i.e., endothermic peak at 473–493 K, was not detected from the CDA and CTA samples used in this study. Since these samples were prepared by a solution acetylation process at 90°C, it is postulated that most of the crystalline region was destroyed and hence no glass transition peaks were observed [18].

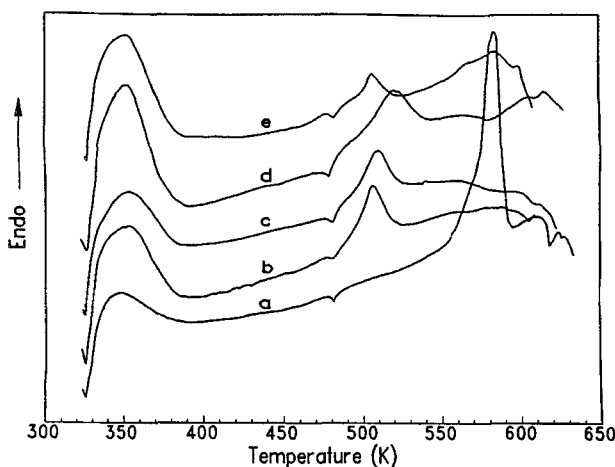


FIG. 1. DSC thermograms of cellulose acetates with various bound acids (in percentage). a, CTA (61%); b, CDA (56.2%); c, CDA (54.8%); d, CDA (54.5%); e, CDA (52.6%).

Interestingly, two DSC exothermic peaks, i.e., 470–480 and 590–620 K, which had not been detected in earlier work, were detected in all the samples in this study. The former peak was due to crystallization. We also performed DSC studies from commercially available CDA as well as CDA from partially and completely hydrolyzed CTA. Their thermograms are shown in Fig. 2. The CDAs of commercial origin and completely hydrolyzed CTA with ba of 51.1% did not display the exothermic peak at 470–480 K; however, the CDA of partially hydrolyzed CTA did display the exothermic peak. These results suggested that only the CTA would exhibit the crystallization phenomenon in DSC. Hence, the detection of the exothermic peak between 476 and 479 K from CDAs was due to the samples containing a certain amount of CTA which was not completely hydrolyzed. Consequently, the exothermic peak at 476–479 K may be used as an indicator for checking the purity of CDA. Moreover, the detection of the exothermic peaks at 590–620 K was due to chemical crosslinking, intramolecular chain stiffening, or degradation of derivatives of cellulose acetate as a consequence of thermal transformations [9, 19].

The endothermic peaks at 500–530 K and 580–590 K were attributed to melting points for CDA and CTA, respectively. The latter is in agreement with the reported value for the melting point of fully substituted CTA [20].

Transformation of Polymorphism

It is well known that two stable polymorphic forms, CTA I and CTA II, exist in CTA and have been identified by x-ray diffractions [10]. X-ray diffractograms of CTAs prepared from various sources in this study indicate that at elevated temperature the crystalline region is destroyed and the polymorphic structure is transformed from I to II (Fig. 3); polymorphic form I was not presented. This differed from the CTAs which were prepared by the heterogeneous process; they contain both

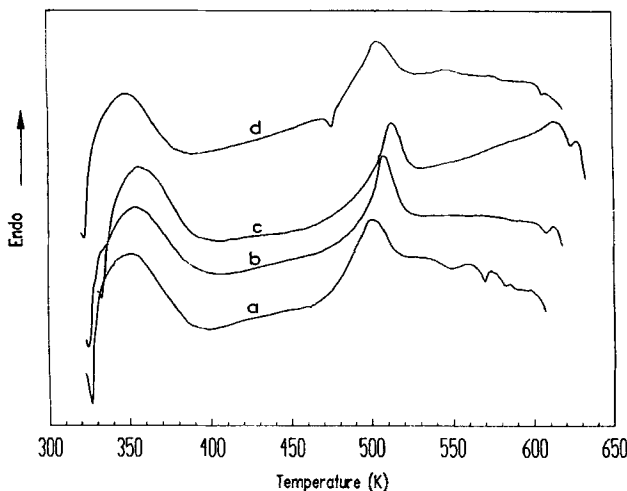


FIG. 2. DSC thermograms of CDA samples prepared in the laboratory (a, 51.6%; d, 54.7%) and commercial products from Daicel (b, 54.5%) and Celanese (c, 54.8%). Percentage denotes bound acid content.

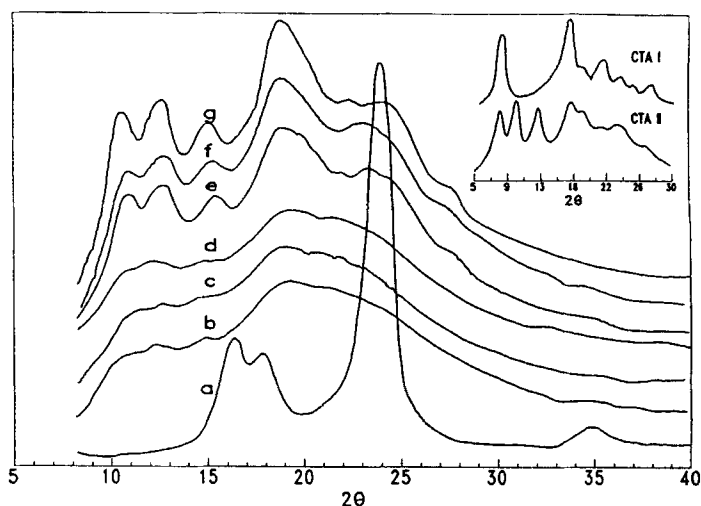


FIG. 3. X-ray diffractograms of cellulose acetates prepared by a solution process at an elevated temperature. a, cellulose; b, wood-CDA; c, commercial CDA; d, cotton-CDA; e, cotton + wood-CTA; f, wood-CTA; g, cotton-CTA.

polymorphic forms of I and II [10]. Moreover, Doyle et al. [21] reported that very high levels of substitution can be achieved using the heterogeneous approach while retaining a high level of ordered structure.

On the other hand, x-ray diffractograms have also proven that CDAs, such as those shown in b, c, and d in Fig. 3, from the hydrolysis of CTA increased their amorphous contents with only a pattern of cellulose II. This result is consistent with the DSC data which substantiated that CTA obtained from the solution process and its hydrolyzed product (CDA) did not display glass transition temperatures and that it is amorphous with the polymorphic structure of II.

ACKNOWLEDGMENTS

This investigation was carried out within a program supported by the State Planning Commission, People's Republic of China.

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Received April 10, 1995

Revision received June 5, 1995