

Crystallinity in Secondary Cellulose Esters

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Synopsis

Cellulose esters which have a high degree of esterification are readily crystallizable by simple heat treatments. Such esters include cellulose triacetate, cellulose tripropionate, and mixed cellulose triesters. X-ray diffraction analysis shows distinct crystal patterns for these crystalline cellulose esters, and differential thermal analysis shows strong melting peaks. X-ray diffraction analysis of secondary cellulose esters, that is, esters having a substantially lower degree of esterification, shows very diffuse patterns which are only slightly indicative of crystalline structure. Differential thermal analysis, on the other hand, shows strong endothermic peaks which appear to indicate melting of crystalline material. Once melted, secondary cellulose esters cannot be recrystallized easily by simple heat treatments, but it has been found that treatment with certain solvents will induce crystallization. For instance, precipitation of secondary cellulose acetate from acetic acid gave a material which showed two melting peaks by differential thermal analysis, and precipitation from acetone gave a material which showed a single melting peak. A secondary mixed ester, cellulose acetate butyrate, precipitated from acetone had three melting peaks. The coincidence of two of the peak temperatures of this ester with those of the separate triesters of acetic and butyric acids indicated a block rather than a random substitution into the cellulose chain.

INTRODUCTION

Highly substituted cellulose esters, such as cellulose triacetate, cellulose tripropionate, and mixed cellulose triesters, are known to crystallize easily. Methods of crystallization as well as rate studies have been made on the triesters of acetic, propionic, and butyric acids. Secondary cellulose esters that have been hydrolyzed to substantially lower degrees of esterification are usually considered to be noncrystallizable.

This paper contains evidence which shows that these secondary esters, if given proper treatment, can be induced to crystallize. The principal evidence for this was obtained by differential thermal analysis. A comparison of differential thermograms shows that both triesters and secondary esters have similar thermal transitions. Even secondary mixed esters can exhibit marked crystallinity in a differential thermogram. The x-ray diffraction patterns show a much lower degree of crystallinity in these secondary esters.

EXPERIMENTAL

Apparatus

The differential thermal analysis apparatus used in this work consisted of several parts. The samples were held in glass sample tubes whose design permitted the sample to be kept in a vacuum or under any desired atmosphere (Fig. 1). Each sample tube contained a carefully positioned,

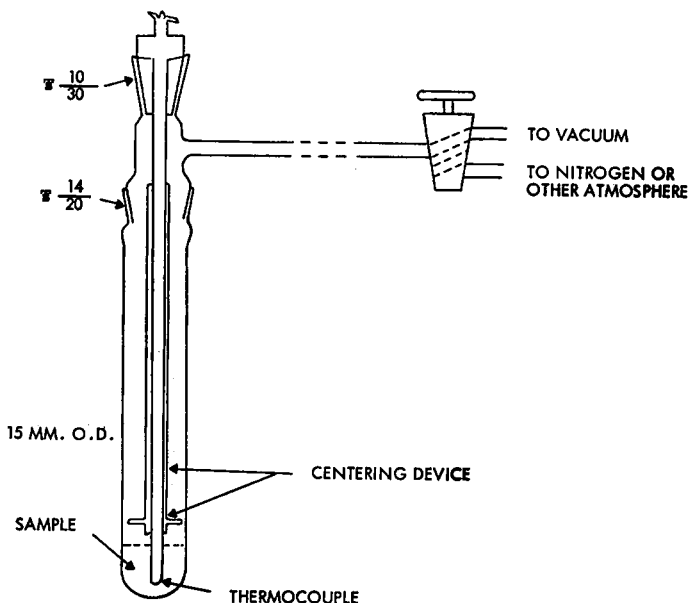


Fig. 1. DTA sample tube.

stainless steel-sheathed thermocouple ($\frac{1}{16}$ in. diameter) whose sensitive tip was buried in the sample. A tubular glass centering device was used to hold the sensitive tip in the proper location, and the overall length of the sample tubes was closely controlled. One sample tube contained the reference material, which was dried sea sand.

The sample tube holder was an electrically heated, cylindrical aluminum block (Fig. 2). A cooling coil ran from end to end in the center of the block, and it was connected to a water injector and a source of compressed air. Nine sample holes and nine holes for cartridge heaters were placed symmetrically in two concentric circles around the cooling coil. The block was jacketed by insulation 4 in. thick. The 200-w. cartridge heaters used varied less than 2.5% to ensure uniform heating. One sample hole was filled with an aluminum plug containing an iron-constantan thermocouple which was used for temperature programming.

The electrical input to the heaters was controlled by a temperature-programming device which consisted of a Speedomax recorder with a pro-

portioning band from a Leeds and Northrup pneumatic controller. This in turn activated the pneumatic Conomotor drive of a continuously variable transformer. By changing the rate at which the recorder controller point was driven, it was possible to vary the heating rate from 0.1 to 15°C./min.

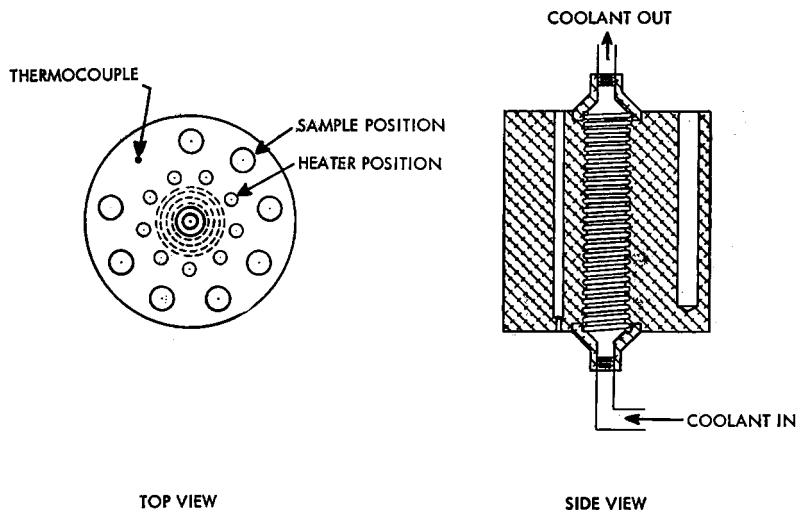


Fig. 2. DTA heat block.

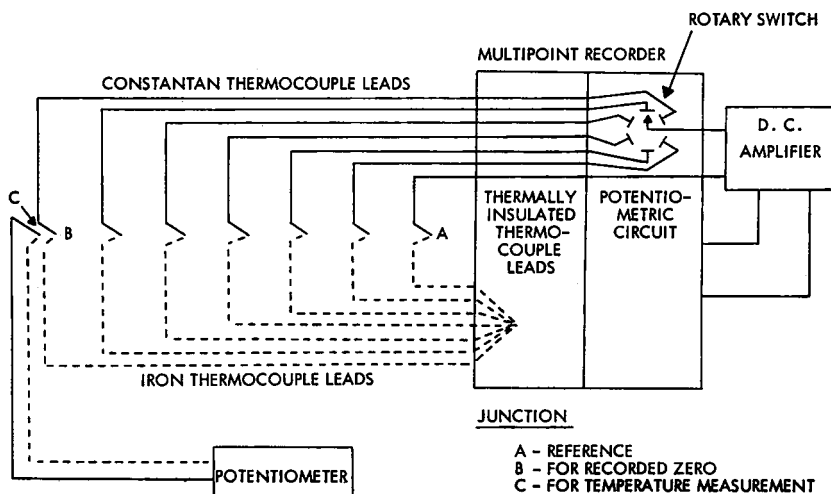


Fig. 3. DTA multipoint circuit.

When it was desired to run an analysis by lowering the temperature, the direction of the controller point drive was reversed and the cooling system was turned on. Water cooling was found to be too erratic, and air cooling was not sufficient. By using an oil-line lubricator to inject a water mist into the cooling air, it was possible to get uniform cooling controlled by the

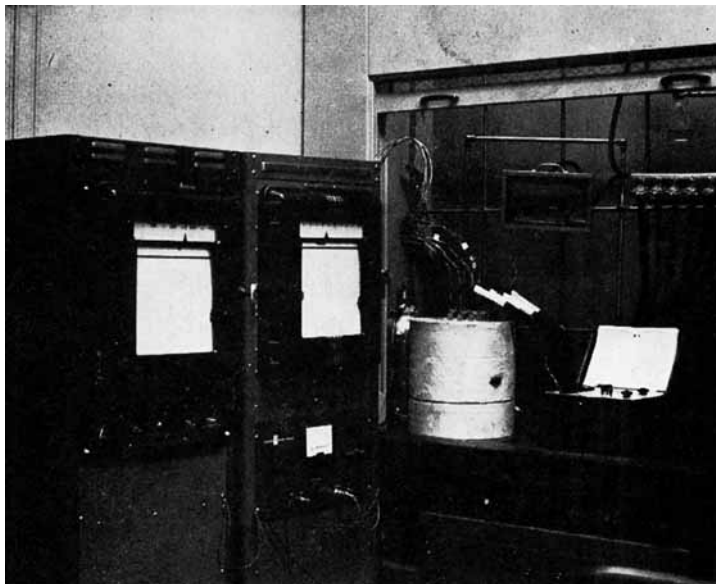


Fig. 4. Photograph of complete DTA apparatus.

heating system. The mist-injection system permitted cooling rates from 0.1 to 15°C./min. to be used.

The differential temperature was measured by use of miniature, stainless steel-sheathed thermocouples whose output, after passing through the rotary switch of the recorder, passed to a Leeds and Northrup stabilized d.c. microvolt amplifier No. 9835-A (Fig. 3). The amplified signals were received on a Speedomax model G, six-point recorder which had been modified to facilitate shifting of the zero. It was found that junctions of thermocouple wire with recorder leads had to be kept in close proximity and thermally insulated from the environment. It was also helpful to make the junctions with a special low-thermal-emf solder. One of the differential thermocouples had a second stainless steel-sheathed thermocouple brazed to it. The sensitive tip of this unit was buried in the same material as the reference. The differential thermocouple part of this unit plotted a base line which located the recorder zero. The temperature was measured by the output of the other thermocouple in this unit, and it was manually plotted on the recorder chart.

The complete apparatus is shown in Figure 4. Any desired atmosphere including vacuum was maintained through the manifold.

Interpretation of Recorder Charts

The recorder chart (Fig. 5) when correctly interpreted gives the temperature of transitions. The nearly straight vertical line is the base line plotted by the recorder. The curved lines are plots of sample behavior at the crystalline melting point. The straight sloping line is a manual

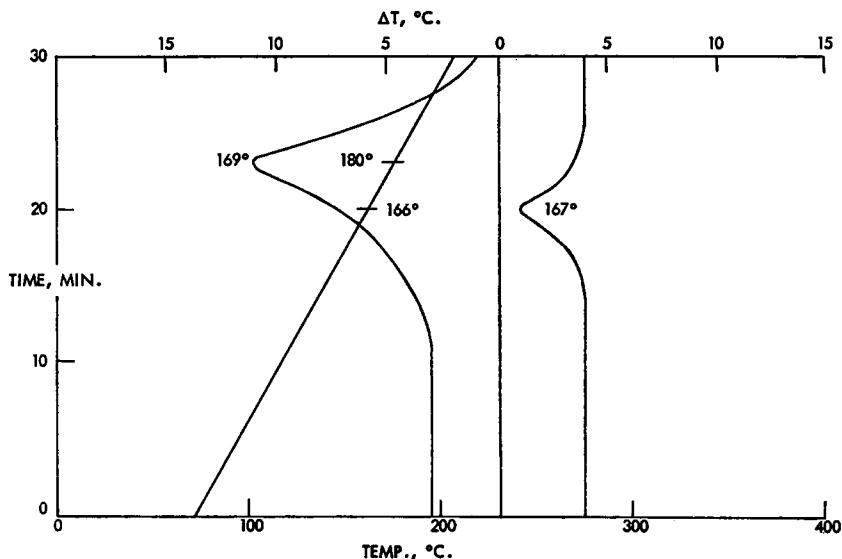


Fig. 5. Measurement of peak temperatures.

plot of temperature. The temperature at which a peak occurs on a sample plot may be determined by (1) drawing a horizontal line through the peak and across the temperature and baseline plots, (2) reading the temperature at the intersection with the temperature plot, and (3) applying a correction to this temperature. The correction to be applied depends upon the distance between the peak and the base line, the amplification used, and the emf for full-scale deflection of the recorder.

As stated before, the curved lines are plots of sample behavior at the melting point. Plots of sample behavior at the crystallization point are very similar to those of melting, but since they are exothermic instead of endothermic their direction is opposite to those of melting.

Second-order transitions or glass transitions are observed as a shift or displacement of the polymer base line. The displacement is in the endothermic direction. In our work we report the temperature observed at the beginning of the displacement.

Materials

The typical composition of several of the cellulose esters manufactured at Tennessee Eastman Company is shown in Table I. The acetyl, propionyl, and butyryl contents, as well as the free hydroxy content, are shown. The melting peak temperature observed by differential thermal analysis is shown on the bottom line of the table.

It will be helpful as we study future figures to know the significance of the ester-type designations. The first letter designates the type of precipitation, E being powder and A being flake. If no other letter precedes

TABLE I
Composition of Cellulose Esters

	E-432 ^a	E-394 ^a	A-394 ^a	EAB-381 ^a	EAP-482 ^a
Acetyl, %	43.5	39.4	39.4	13	2.5
Propionyl, %	—	—	—	—	45
Butyryl, %	—	—	—	37	—
OH, %	1.0	3.7	3.9	2.0	0.07
DTA melting peak, °C.	290	238	230 269	164 238 299	241 253

^a Tennessee Eastman Company designation.

the number, the ester is that of acetic acid. AB indicates acetate butyrate ester, and AP indicates acetate propionate ester. The number, with a decimal inserted, gives the approximate acetyl, propionyl, or butyryl content. In the case of mixed esters, the number represents the percentage of the major ester group substituted in the cellulose chain.

RESULTS AND DISCUSSION

The highly esterified E-432 cellulose acetate melted at 290°C. A cellulose acetate, E-394, which had a lower degree of esterification than E-432 melted at a lower temperature, namely, 238°C. A sample, similar to E-394, as shown by acetyl and free hydroxy contents, which had been manufactured by a slightly different process had two melting peaks. Two melting peaks were also observed for EAP-482 cellulose acetate propionate, and three melting peaks were observed for EAB-381 cellulose acetate butyrate. E-432 can be recrystallized very easily by cooling it from the melt. The acetate propionate can also be recrystallized from the melt, but the acetate butyrate has thus far resisted recrystallization attempts by any cooling rates tried.

Much of the data presented in this paper is in the form of differential thermograms such as the typical one seen in Figure 6. The lower portion of the figure represents transitions which are endothermic in nature or which change the differential between the reference and the sample. The upper portion of the figure represents transitions which are exothermic. Thus we see the glass transition as only a shift in the base line, since it is neither exothermic nor endothermic but is a change in the specific heat. Crystallization and melting are observed as major changes in the differential temperature. The thermogram also shows oxidation and decomposition reactions.

Differential thermograms of two crystallizable cellulose esters are shown in Figure 7. E-432 shows a very strong melting peak at 290°C., and EAP-482 shows a strong melting peak at 241°C. and a weaker peak at 253°C. Recycling, i.e., cooling and reheating in the differential thermal analysis apparatus, gives thermograms that are similar to those in the figure.

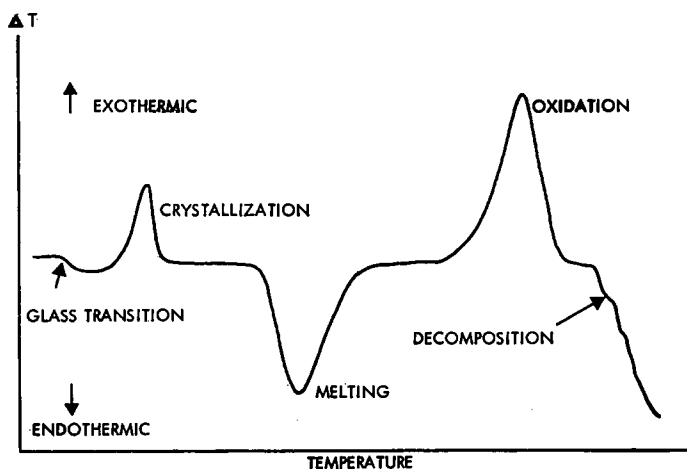


Fig. 6. Typical differential thermogram.

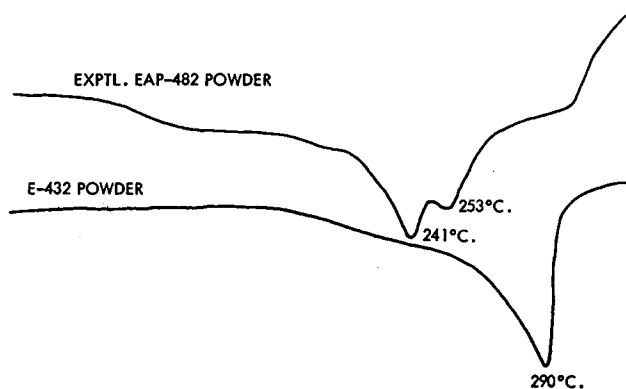


Fig. 7. Thermograms of crystallizable cellulose esters.

The melting temperatures may be changed or one peak may be eliminated by variations in the cooling rate. The melting temperature is greatly affected by the hydroxy content. As the hydroxy content decreases, the melting temperature increases. The presence of crystallinity in these esters is further evidenced by their x-ray diffraction patterns, which show a high degree of crystallinity. A comparison of these thermograms with ones to follow will show similar endothermic transitions in secondary cellulose esters.

Figure 8 contains a thermogram of E-394, a powder-precipitated cellulose acetate. It exhibited a definite melting peak at 238°C. While this endotherm is not so pronounced as those in Figure 7, there is no doubt of its existence. The smaller endotherm may indicate fewer crystalline blocks or perhaps a lower degree of perfection of the crystalline structure. The other thermogram was obtained from a film that had been compression-

molded from E-394 powder and rapidly cooled. Under these conditions a triester would have shown a crystallization peak followed by a melting peak. We observed neither for this material, but two breaks in the base line were found. One was at 181°C., and the other was at 214°C. At present there is no explanation for these phenomena.

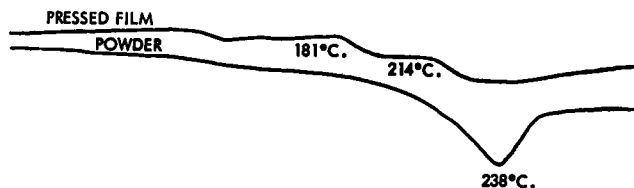


Fig. 8. Thermograms of cellulose acetate, E-394.

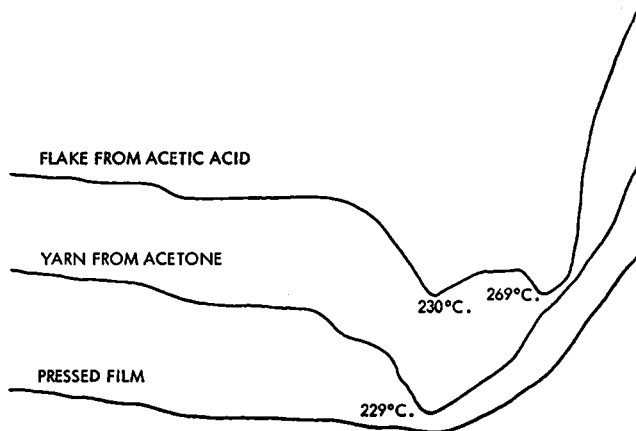


Fig. 9. Thermograms of cellulose acetate, A-394.

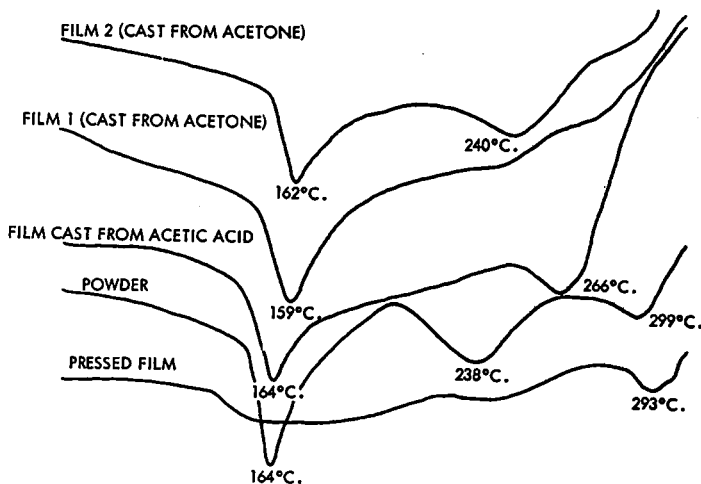


Fig. 10. Thermograms of cellulose acetate butyrate, EAB-381.

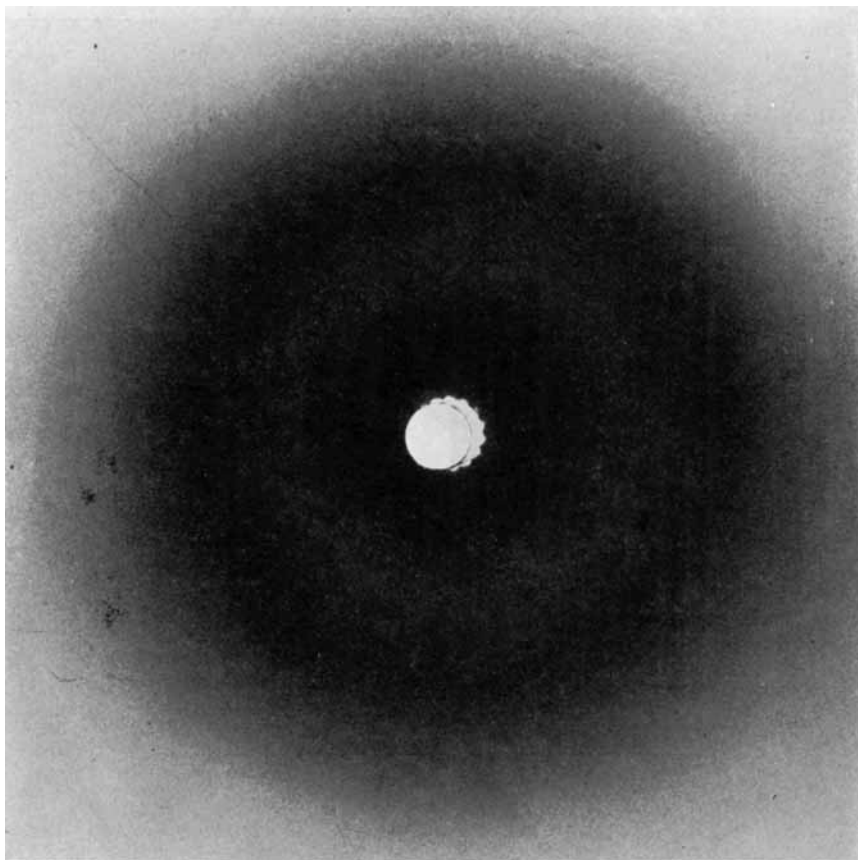


Fig. 11. X-ray diffraction pattern of EAB-381 pressed, quenched film.

The thermograms in Figure 9 were obtained from A-394 cellulose acetate (flake from acetic acid), which in many respects is quite similar to the E-394 ester (powder from acetone) of Figure 8. The differential thermograms of the two esters point out the dissimilarity of the materials. The E-type ester had a single melting peak, whereas the A-type had two melting peaks, at 230°C. and 269°C. The principal difference between these two esters lies in the medium from which each was precipitated. Acetic acid was used as the solvent for the A-type ester, which had the two peaks, whereas acetone was used as the solvent for the E-type ester, which had the one peak. This relation of acetone and acetic acid solvents to the number of peaks found applies only to the cellulose acetates of approximately 38–40% acetyl content. For instance, the acetate propionate shown in Figure 7 had two melting peaks and was precipitated from acetone. The A-type acetic ester, which had the two melting peaks, can be converted readily to the E-type, which had the single peak, by redissolving the ester in acetone and then precipitating it. The thermogram shown in Figure 9 for the A-394 yarn spun from acetone illustrates this point. The amount

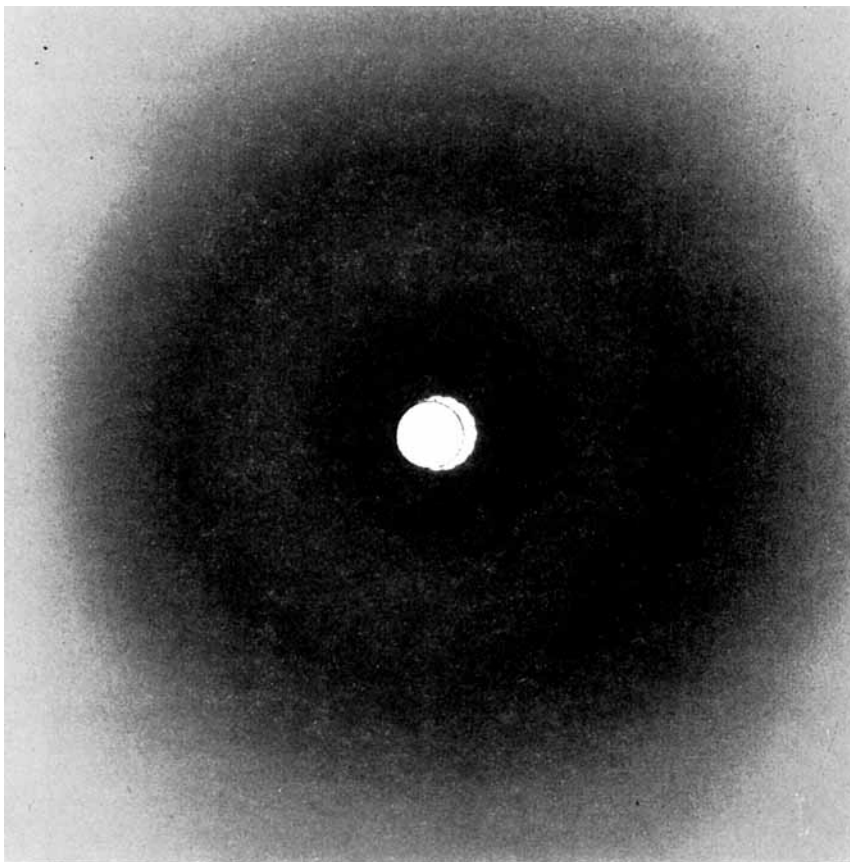


Fig. 12. X-ray diffraction pattern of EAB-381 film from acetone dope.

of crystallization from solution appears to be much greater than that obtained by heat treatment. The lowest thermogram is that of a compression-molded and quenched film. It indicates neither crystallization nor melting during the programmed heating at 5°C./min . This failure of heat treatment to produce crystallinity is characteristic not only of this particular type of cellulose acetate but also of other acetates having substantially less than maximum esterification. Mixed esters such as EAB-500, which has about 48% butyryl content and 6% acetyl content, or EAB-381, which has about 37% butyryl content and 13% acetyl content, also have this characteristic.

Figure 10 shows five differential thermograms obtained on an EAB-381 ester, a mixed acetate butyrate. Various treatments were used to obtain the five thermograms. The thermogram of EAB-381 powder shows three distinct melting peaks, one at 164°C ., a second at 238°C ., and a third at 299°C . As observed earlier, compression molding and quenching eliminates any evidence of crystallization. This may be seen in the lowest thermo-

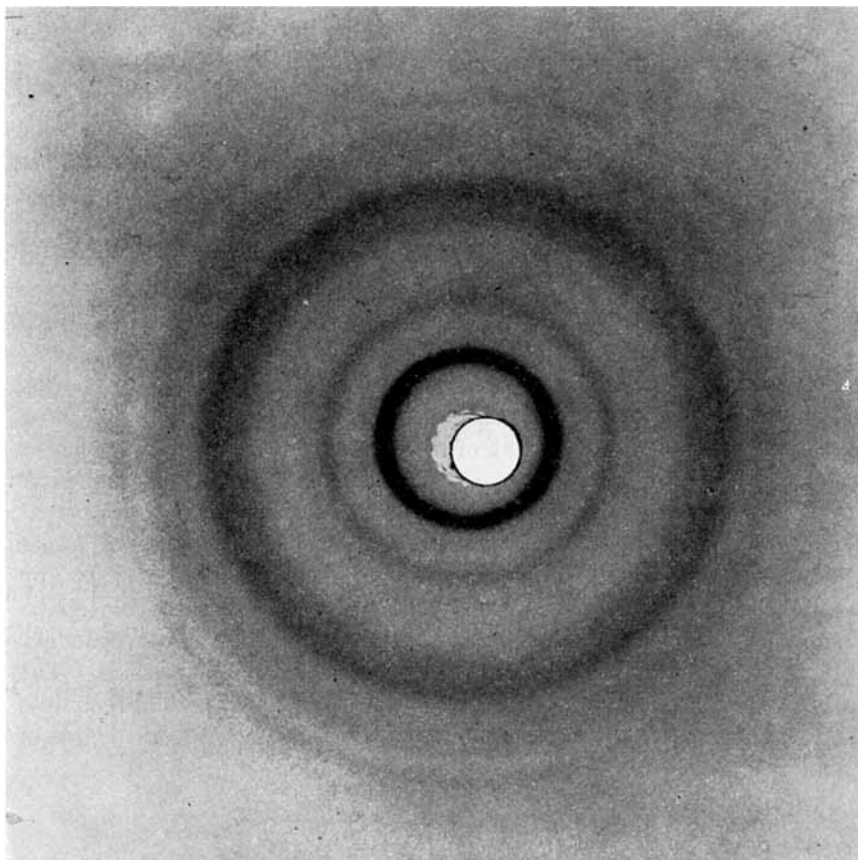


Fig. 13. X-ray diffraction pattern of cellulose tributyrate.

gram. The molding temperature was only 260°C .; therefore, the higher melting material was not destroyed although its melting temperature was changed. The 260°C . molding temperature was apparently not high enough or held long enough to completely destroy all of the crystalline material of the intermediate range, as shown by the slight deviation of the curve in the endothermic direction. The curve at about 155°C . and above may also indicate some residual crystallinity. When this compression-molded film was dissolved in acetone and cast as a film, that film had a strong melting peak at 159°C . (film 1, Fig. 10). A very small melting peak may exist near 240°C .

X-ray diffraction analysis of the pressed and quenched film shows essentially an amorphous pattern which agrees well with the findings by differential thermal analysis. The film cast from acetone also showed an essentially amorphous pattern by x-ray diffraction even though a strong melting peak had been found by differential thermal analysis. These x-ray patterns and one of cellulose tributyrate are shown in Figures 11-13.

Another film in Figure 10, film 2, was made by dissolving some of the original powdered ester in acetone and casting. Differential thermal analysis of that film gave a thermogram which shows melting peaks at 162°C. and 240°C. Similarly, a film cast from acetic acid gave two melting peaks, one at 164°C. and one at 266°C. Thus we see that precipitation from acetone or acetic acid promotes crystallization of esters that could not be crystallized by heat treatment. Comparison of the thermograms of film 2, cast from acetone, and the film cast from acetic acid shows the difference between the effects of the two solvents. Very little difference was observed at the lower melting range, but acetic acid raised the upper melting range about 25°C.

In the thermogram of the EAB-381 powder (Fig. 10), the highest melting peak was nearly coincident with the melting peak of cellulose triacetate. The lowest peak is close to that of cellulose tributyrate. This suggests that acetic and butyric acids react with the cellulose in block sequences rather than in a random fashion. The intermediate peak is close to that observed for secondary cellulose acetate. This may indicate the presence of some material of this composition in the EAB-381 powder. At any rate it is obvious that EAB-381 powder is a rather heterogeneous material.

Differential thermal analysis has shown conclusively that secondary cellulose esters, when heated, pass through endothermic transitions. The similarity of the transitions to the melting transitions of crystalline cellulose triesters leaves no doubt that secondary esters possess a greater degree of crystallinity than x-ray diffraction patterns indicate.

Résumé

Les esters de cellulose qui ont un degré d'estérification élevé sont facilement cristallisables par de simples traitements thermiques. De tels esters comprennent le triacétate de cellulose, le propionate de cellulose et les triesters cellulosiques mixtes. L'analyse de diffraction aux rayons-X montre des réseaux cristallins distincts pour ces esters cristallins cellulosiques, et l'analyse thermique différentielle montre des pics de fusion nets. L'analyse par diffraction de rayons-X des esters de cellulose secondaires, c'est-à-dire des esters ayant un degré d'estérification notablement plus bas, montre des réseaux très diffus qui ne sont qu'une faible indication d'une structure cristalline. L'analyse thermique différentielle par ailleurs montre des pics fortement endothermiques qui indiquent la fusion d'un matériau cristallin. Une fois fondus, les esters cellulosiques secondaires ne peuvent pas recristalliser aisément par simple traitement thermique mais on a trouvé que le traitement avec certains solvants induit la cristallisation. Par exemple, la précipitation de l'acétate de cellulose secondaire par de l'acide acétique fournit un matériau qui montre deux pics de fusion à l'analyse thermique différentielle, et la précipitation au départ de l'acétone fournit un matériau qui montre un seul pic de fusion. Un ester secondaire mixte, l'acétobutyrate de cellulose précipité par la solution acétonique a trois pics de fusion. La coincidence des températures des pics de ces esters avec celles des triesters séparés des acides acétiques et butyriques indique une substitution dans la chaîne cellulosique plutôt séquentielle que simplement statistique.

Zusammenfassung

Celluloseester mit hohem Veresterungsgrad kristallisieren durch einfache Wärmebehandlung leicht. Dazu gehören Cellulosetriacetate, Cellulosetributyronat und gemischte

Cellulose-triester. Die Röntgenbeugungsanalyse zeigt für diese kristallinen Celluloseester deutliche Kristalldiagramme und die Differentialthermoanalyse liefert starke Schmelzmaxima. Die Röntgenbeugungsanalyse sekundärer Celluloseester, also von Estern mit wesentlich niedrigerem Veresterungsgrad, ergibt sehr diffuse Diagramme, die nur schwache Hinweise auf eine kristalline Struktur enthalten. Andererseits zeigt die Differentialthermoanalyse starke endotherme Maxima, die für ein Schmelzen kristallinen Materials zu sprechen scheinen. Nach dem Schmelzen können sekundäre Celluloseester durch einfache Wärmebehandlung nicht leicht wieder zur Kristallisation gebracht werden; es wurde aber gefunden, dass die Kristallisation durch Behandlung mit gewissen Lösungsmitteln induziert wird. So lieferte zum Beispiel die Fällung von sekundärem Celluloseacetat aus Essigsäure ein Material mit zwei Schmelzmaxima bei der Differentialthermoanalyse und die Fällung aus Aceton ein solches mit nur einem Schmelzmaximum. Ein gemischter sekundärer Ester, Celluloseacetatbutyrat, besaß bei Fällung aus Aceton drei Schmelzmaxima. Das Zusammenfallen zweier Maxima-Temperaturen dieses Esters mit denjenigen der einzelnen Triester von Essig- und Buttersäure spricht für eine Blockstruktur und nicht für eine statistische Substitution der Cellulosekette.

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