# STUDY OF OVERLAPPING TRANSITIONS IN POLYMERS BY COMBINED DIFFERENTIAL SCANNING CALORIMETRY AND THERMAL OPTICAL ANALYSIS METHODS*

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ABSTRACT

In some polymers, thermal transitions and molecular relaxation processes may be situated closely together on the temperature scale or may actually overlap. In such cases, observations by differential scanning calorimetry (DSC) may lead to ambiguous results or to erroneous conclusions. In many instances, the ambiguity can be removed by making additional measurements at the same scanning rate on polymer samples of similar past history by thermal optical analysis (TOA). The combined use of these two types of measurements, DSC and TOA, is here applied to a study of transitions and structural changes in several types of cellulose acetate. From the results obtained, it is possible to resolve and identify various overlapping thermal processes such as the glass transition of the polymer chains, subsequent crystallization, melting of ordered phases and thermal degradation.

INTRODUCTION

Differential thermal analysis (DTA) and differential scanning calorimetry (DSC) are exceedingly useful tools for studying thermally induced transitions in polymers[1-7]. In some polymers, however, molecular processes that give rise to endothermic effects, such as melting of a crystalline phase or thermal degradation, frequently overlap other processes, such as crystallization giving rise to exothermic effects. Such overlapping can easily occur in those polymers where the glass transition temperature and the melting temperature are close together and the ratio of $T_g$ to $T_m$ is much higher than normal values[8-10]. It is also possible that exothermic reactions occurring above $T_g$, as a result of the greater molecular mobility of chains in the amorphous phase, may overlap both the amorphous softening process and the start of crystalline melting[9,11]. All of these possibilities can lead to ambiguous results and to the drawing of erroneous conclusions. Other difficulties, such as baseline curvature, thermal gradients, and thermal lag in the apparatus may also lead to inaccurate values for DSC transition temperatures, and various methods for dealing with such situations have been described in the literature[12-16].

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Our principal concern is with polymers in which there is definite overlapping between different molecular processes each of which—if it could be examined separately—would give an identifiable change in the DTA and DSC temperature scan.

The ambiguity caused by overlapping of transitions can sometimes be removed by separating the competing processes. An example would be to broaden the temperature range between $T_g$ and $T_m$ by adding a plasticizer that had little effect on the crystalline phase but which shifted $T_g$ of the amorphous phase to lower values. In other instances, where several competing processes are involved it may not be possible to separate the transitions, or in doing so, undesirable structural or chemical changes may occur.

In this latter type of situation, resolution and identification of thermally induced overlapping transitions can frequently be made by combined use of TOA and DSC. In the TOA method the intensity, $I$, of plane polarized light transmitted through the polymer sample (powder or film) and observed between crossed polarizers is monitored as a function of temperature. The sample is located in an appropriate hot stage and the scanning rate set to the desired value. The method cannot be applied to isotropic samples, as then the transmitted intensity is zero. However, most polymer film samples, and even many polymer powders, will show some anisotropy and some birefringence; and, even when they do not, a scratch made on the sample will provide sufficient local orientation to make the method feasible[17-18].

The TOA method has not been widely used to date. It has been applied by Wilkes and Lehr[19] to study molecular aggregation in the amorphous and molten states of poly-4-methylpentene-1 and by Magill[20] to study rates of crystallization in nylon. In this latter case, the temperature was held constant at different values and the intensity of the transmitted light monitored as a function of time at temperature. The TOA method was also used by Schultz and Gendron[18] to study glass transition phenomena in amorphous blends, and by Ameri and Sauer[9] to study the possible effects of ordering and disordering phenomena that occur in cellulose triacetate and cellulose acetate films. An excellent discussion of the TOA method, including experimental artifacts that may affect the results, has been given by Kovacs and Hubbs[17] and $I$ vs. $T$ profiles are presented for various amorphous and partially crystalline polymers.

In the present study, combined DSC and TOA techniques are used to help resolve the nature of molecular processes occurring in secondary cellulose acetates. It is known that in cellulose acetates there can be marked overlapping of the $T_g$ transition—located usually in the 190–200°C range for dry materials—and of exothermic effects, possibly arising from onset of crystallization or from recrystallization. These may, in turn, overlap disordering effects associated with melting of ordered phases, and of thermal changes associated with degradation[7,9,11,21]. Some preliminary results of the application of combined DSC and TOA techniques to an understanding of molecular processes in various cellulose acetates has been given[9] but a more thorough analysis, especially of a secondary cellulose acetate film, prepared from CA 394-60, is given here.

EXPERIMENTAL

Tests have been carried out of three types of cellulose acetate: CA 398-3 (MW = 35,100; D.S. = 2.44); CA 398-10 (MW = 44,800; D.S. = 2.44); and CA 394-60 (MW = 59,400; D.S. = 2.42). In addition some test data have been acquired on cellulose triacetate flakes (D.S. = 2.83), on a commercial CTA film containing plasticizer and on biaxially oriented films of an amorphous polymer, polystyrene (PS), and of a crystalline polymer, polypropylene (PP).

Dense films were prepared from the CA powders by dissolving the material in acetone (25% solution) and casting on clear glass plates with a Gardner knife. The acetone was allowed to completely evaporate.

DSC tests were made on a Perkin-Elmer Model DSC-1B using a sample weighing 7.5 mg unless otherwise noted. The samples were placed in aluminum pans with crimped covers. All tests were run in a nitrogen atmosphere. The scanning speed was generally maintained at $10°C \ min^{-1}$.

TOA measurements were made with a Zeiss polarizing microscope and a Mettler hot stage, FP-5/52, having controlled heating and cooling rates. The intensity of the light transmitted through the specimen and the crossed polars was monitored by means of a Mettler photorecorder. Measurements of intensity, $I$, as a function of temperature were usually taken at a scan speed of $10°C \ min^{-1}$ and recorded directly on a chart. Sample areas were generally kept smaller than the video area of the hot stage to avoid extra material coming into the video area due to sample shrinkage at elevated temperatures.

For a few samples, the above tests were supplemented by thermogravimetric analysis (TG) in order to determine the amount of weight loss upon exposure to elevated temperature. These tests were performed with a Mettler Thermoanalyzer, Model 1, at a constant $N_2$ flow-rate of $10 \ ml \ min^{-1}$ and at a scanning rate of $10°C \ min^{-1}$.

RESULTS AND DISCUSSION

DSC scans of both powder and film samples of all three types of cellulose acetate are shown in Fig. 1 for the temperature region from about 150°C to about 250°C. In the powder samples, degradation effects are very severe and they mask other processes that may be occurring in the same temperature range. This thermal degradation leads to a very broad endothermic peak which extends from about 220°C to above 300°C[9] Only in the CA 394-60 powder sample can one discern what appears to be a small endothermic melting peak, near 235°C, that is superimposed on the broad degradation peak. In the cast film samples, degradation is not so severe. For these samples, as Fig. 1 shows, one can detect a small baseline shift in the data for CA 394-60 and CA 398-3 in the 190-200°C range and at higher temperatures endothermic melting peaks in the CA 398-3 and CA 398-10 samples. The importance of solvent in development of ordered morphologies is evident from the results ob-
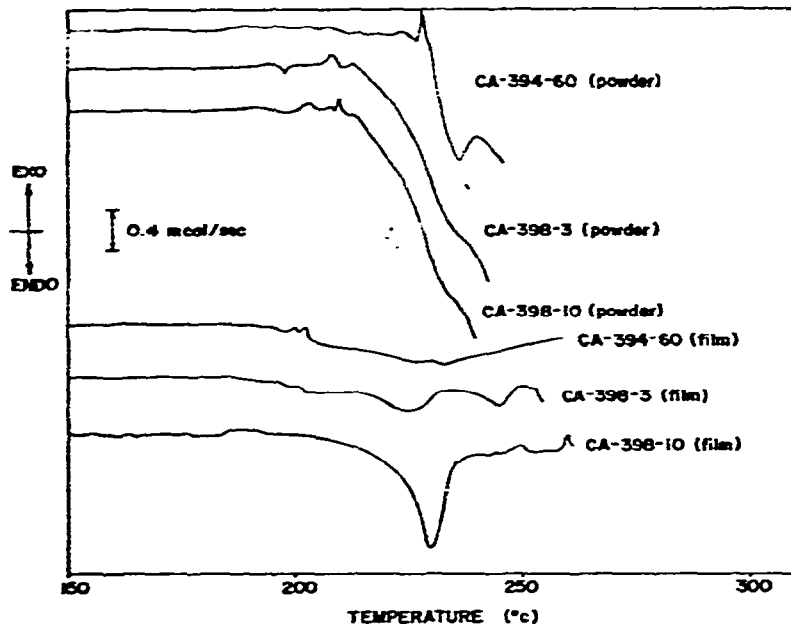
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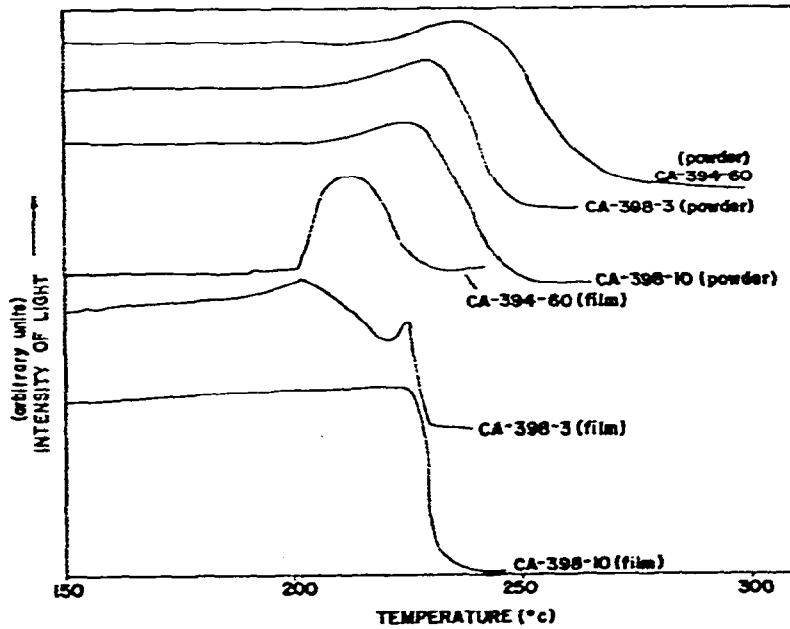Fig. 1. DSC scans of powder and film samples of CA 394-60, CA 398-3 and CA 398-10.



Fig. 2. TOA scans of powder and film samples of CA 394-60, CA 398-3 and CA 398-10.

tained on CA 394-60. This polymer shows the largest melting endotherm in powder form but the smallest one when cast from acetone solution. The CA 398-10 polymer, on the other hand, shows the opposite behavior. The significant role played by the solvent, as well as by the type of acetate used, in developing an ordered phase has been noted by several investigators[21-23].

TOA data on both powder and film samples of each of the CA's are shown in Fig. 2. The intensity of the transmitted light, a measure of the amount of orientation present in the sample, is not very sensitive to degradation effects. Figure 2 shows that, in the powder samples, there is a slight rise in intensity in the $200-230\,^\circ C$ range. This is attributed to onset of crystallization once $T_g$ is passed. This rise is then followed by a marked decrease in intensity as the ordered phase present in the sample melts and orientation is lost.

In the film samples, the CA 398-10 material shows the least rise in intensity due to annealing during the test run and the sharpest intensity drop in the vicinity of $230\,^\circ C$. These effects would indicate that the CA 398-10 sample had the highest initial degree of crystallinity when cast from acetone solution. The CA 394-60 material, which gave the least indication of the presence of an ordered phase by DSC, shows in TOA a rather large rise in intensity, from an initially low level, once the temperature exceeds $T_g$. This is indicative of some crystallization occurring during the test run once the chains acquire sufficient mobility. The ordered phase that develops is probably a defect one as the intensity, after rising, falls again to low values in the $220-230\,^\circ C$ range; for the same material in powder form the intensity did not fall until temperatures of $240\,^\circ C$ or so were reached.

In all of the test specimens there is no appreciable drop in intensity in the $T_g$ region ($190-200\,^\circ C$). This would indicate that the orientation which is present and which further develops during the test run is probably predominantly associated with the crystalline phase. Rises in intensity above $T_g$ can sometimes develop even in fully amorphous polymers due to dimensional changes that occur in oriented samples when temperatures reach and exceed the $T_g$ range.

To investigate the possible effects of specimen shrinkage additional TOA tests were carried out on CA 394-60 film samples, and on film samples of biaxially oriented polystyrene and biaxially oriented polypropylene. The results of these tests are presented in Fig. 3. The curves marked A were obtained on samples whose sizes were larger than the video area. In these tests when film shrinkage occurs it brings new material into the video area. The curves marked B were obtained for samples whose sizes were smaller than the video area.

Figure 3a shows that for the oriented polystyrene B sample there is a large drop in intensity in the $110\,^\circ C$ region and then little change thereafter. The drop is associated with the $T_g$ transition and with loss of amorphous orientation as the chains acquire Brownian motion. For sample A, a drop in intensity in the $T_g$ region is also present but specimen shrinkage now brings new material not yet disoriented into the video area. This produces a rather sharp rise in intensity which is not related to onset of any ordered or crystalline phase but is simply a result of film shrinkage.
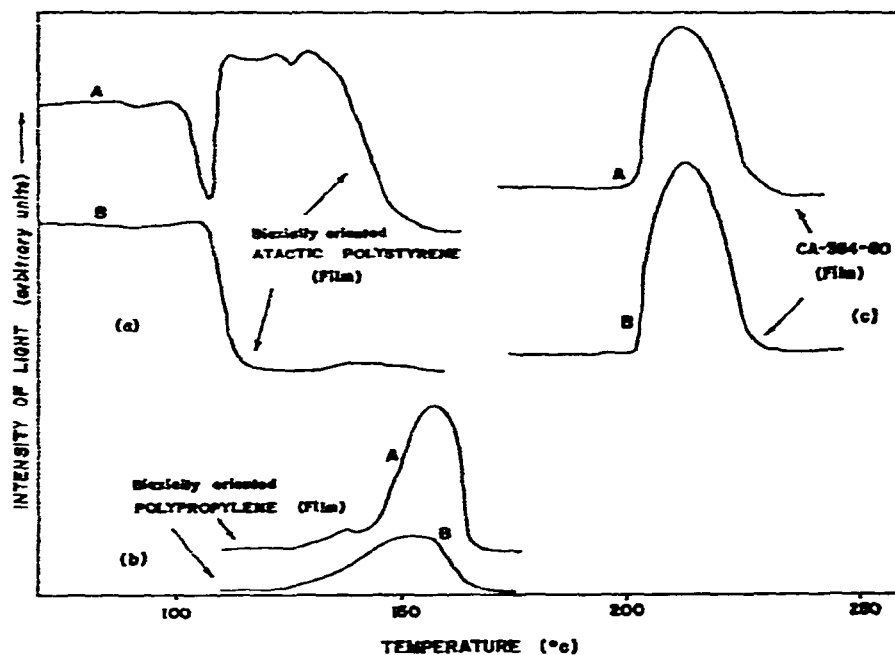
Fig. 3. TOA scans. (a) Biaxially oriented atactic polystyrene film. (b) Biaxially oriented isotatic polypropylene film. (c) CA 394-60 film. Curves marked: (A) = sample size larger than video area; (B) = samples size smaller than video area.

Figure 3b shows, for the biaxially oriented PP specimens, an increase in intensity in the temperature range 140-160°C for both samples. Since this occurs in the B sample, it may be related to additional crystallization occurring during the test run. The transmitted light intensity falls in both samples when temperatures near 160°C are reached. This is a result of melting of the ordered or crystalline phase.

Figure 3c shows that for the CA 394-60 samples, there is essentially no change in the $I$ vs. $T$ profile for samples A and B. Thus, the observed increase in birefringence in the 200-215°C region is not a result of film shrinkage but rather of an ordering or crystallization occurring during the test run. The subsequent drop in intensity in the 220-225°C region is then a result of the melting or disordering of the ordered phase. These two processes, one crystallization, and the other melting are not clearly revealed on the DSC scan (Fig. 1) because the first is exothermic and the second is endothermic. Since these two processes overlap there is a tendency for the two effects to annul one another insofar as DSC detection is concerned. However, in the more sensitive TOA method both processes are evident, even through the scanning rate was maintained at the same value in both tests.

Further insight into the nature of these ordering and disordering processes is obtained by running TOA and DSC tests at lower scan rates. Figure 4 shows data obtained on CA 394-60 film. Figure 4a shows TOA results obtained at a scan rate of 10°C min$^{-1}$ on first heating to 213°C, subsequent cooling and then reheating while

Fig. 4b shows results obtained by simply heating the specimen at $2\,^{\circ}C\ min^{-1}$. At this slower speed, annealing during the test run is more pronounced. A slight drop in $I$ is noted in the 190–200°C region and this is attributed to some loss of orientation in the amorphous phase as $T_g$ is passe⁻. Also the rise in $I$ at 200°C, associated with increasing crystallinity, is now more clearly separated from the subsequent drop in $I$ at 225°C that is associated with disordering and melting.
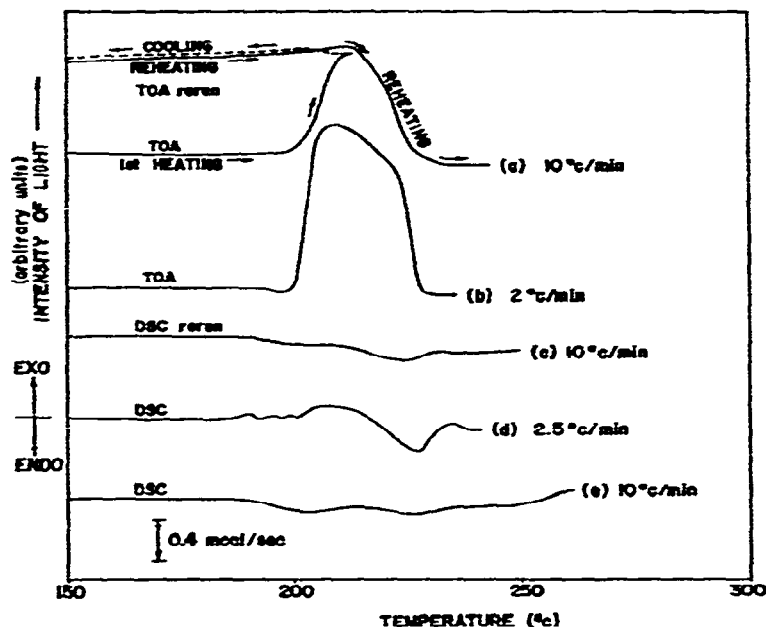


Fig. 4. TOA and DSC scans on CA 394-60 film. (a) TOA scan during first heating to 213°C, subsequent cooling, and then reheating. Scan rate $10\,^{\circ}C\ min^{-1}$. (b) TOA scan of unannealed sample. Scan rate $2\,^{\circ}C\ min^{-1}$. (c) DSC scan after first heating to 213°C, subsequent cooling, and then reheating. Scan rate $10\,^{\circ}C\ min^{-1}$. Sample weight 3.75 mg. (d) DSC scan of unannealed sample. Scan rate $2.5\,^{\circ}C\ min^{-1}$. Sample weight 3.75 mg. (e) DSC scan of unannealed sample. Scan rate $10\,^{\circ}C\ min^{-1}$. Sample weight 3.75 mg.

Figure 4c shows DSC results obtained at a scan speed of $10°C\ min^{-1}$ after first heating to 213°C, subsequent cooling, and then reheating while Fig. 4d shows the DSC scan that is obtained at the slower scan rate of $2.5°C\ min^{-1}$. It is clear from comparison of the data for Figs. 4d and 4e (scan rate $10°C\ min^{-1}$) that the slower speed of scanning has led to a clearly identifiable exothermic peak in the 200–210°C range, associated with crystallization, and to a definite endothermic peak at 227°C, associated with melting of the ordered phase.

An endothermic peak near 225°C can also be developed and made distinguishable, even at a $10°C\ min^{-1}$ scan, if the specimen is first run to 213°C, then cooled down and rerun. This is shown by the data of Fig. 4c. Note that for this sample, the $T_g$ baseline shift in the 190–200°C region is still discernible but is reduced

in magnitude compared to the nonheat-treated sample. This effect arises because of the annealing effects occurring during the first test run.

The effects of preheating to 213 °C, cooling and rerunning, are also evident from the TOA scan taken at 10 °C min$^{-1}$ and shown in Fig. 4a. Note that the rise in $I$ between 200–215 °C, observed in the first heating, is not as great as for the sample tested at 2 °C min$^{-1}$ (Fig. 4b). This effect supports the hypothesis that the rise in $I$ is caused by an increase in crystallization resulting from thermal annealing during the test run. Note also that after heating and cooling the $I$ vs. $T$ profile remains essentially constant, or only slightly increases, with increasing temperature until temperatures of 215 °C are reached. Melting of the defect ordered phase then commences and as this phase disorders, the intensity falls to low values.

The combined DSC and TOA data thus strongly support the presence in CA 394-60 of at least two overlapping transitions; one occurring mostly in the 200–215 °C region and associated with improved chain packing and ordering and one occurring mostly in the 220–230 °C range and associated with onset of melting and loss of orientation of the ordered phase. Degradation effects are not significant in this temperature range for film type samples and for the scan rates utilized. In fact TG data indicate that severe weight loss only occurs when temperatures exceed 250 °C or so[9]. However, there is some indication in the various tests of a $T_g$, or glass–rubber transition of the amorphous phase, centered in the 190–200 °C range. This transition thus overlaps the crystallization transition which we have noted above generally falls in the 200–215 °C range. It is this overlapping of transitions, and some cancelling of DSC effects, that cause some ambiguity in the DSC test results obtained on secondary cellulose acetates and some uncertainty in the location of $T_g$.

To resolve the uncertainty in $T_g$, two additional types of tests have been carried out. In the first method, TOA scans are made of the light transmitted only through the cut edge of a film sample. Cutting of the film causes some orientation of the amorphous phase near the cut edge and makes detection of amorphous orientation changes easier. This test is thus somewhat akin to that of using TOA-temperature observations on scratched isotropic films[17,18] to detect thermal transitions. The second method is to make observations on quenched samples so as to increase the amount of amorphous or disordered material in the samples. Each of these methods will now be discussed in turn.

TOA temperature profiles of two different cut-edge samples of CA 394-60 are shown in Figs. 5a and 5b. In both instances, the $T_g$ transition is clearly revealed by a large drop in intensity on the 190 °C temperature range. In many cut-edge samples, this drop in intensity was followed by a subsequent rise in the 210 °C range, and then another drop in intensity near 220 °C (Fig. 5b). These effects are thought to arise if in viewing the cut-edge, one also picks up some transmitted light from nearby, but not yet disoriented bulk material. Nevertheless, it is clear that observations of the oriented cut-edge material give more definite and clearcut indication of the presence of the $T_g$ transition than observations taken over a large area of the bulk cast film. The $T_g$ of the CA 394-60 cellulose acetate material may be placed at $188 \pm 2$ °C, if we

define $T_g$ as the temperature at which the transmitted light begins to fall. This value is in good agreement with DSC estimates[9] and with other reported values based on various techniques[24,25].
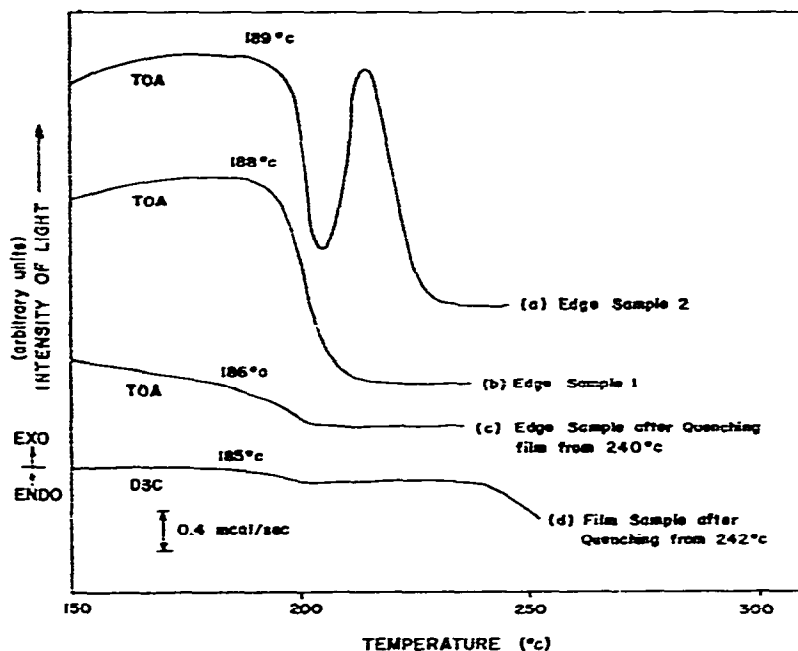


Fig. 5. TOA and DSC scans of CA 394-60 at temperatures near $T_g$. (a) TOA scan-edge sample No. 2. (b) TOA scan-edge sample No. 1. (c) TOA scan-edge sample—after quenching film from 240°C. (d) DSC scan-film sample—after quenching film from 242°C.

The use of quenching to improve sensitivity of DSC detection of the $T_g$ transition in cellulose acetates has recently been utilized by Arneri and Sauer[9]. They have shown that rapid quenching of secondary cellulose acetate samples from 250°C will decrease the intensity of the DSC detected ordering or melting peak observed near 235 K. Hence, it will also noticeably increase the amount of amorphous or disordered material present in the samples. Results of DSC and TOA tests, on CA 394-60 film samples quenched from 240°C or so, are shown in Figs. 5c and 5d. The $T_g$ baseline shift is clearly apparent in the DSC scan. It begins at about 185°C and extends to about 200°C. The TOA scan, by itself does not provide as definite an indication of the $T_g$ relaxation but the onset of a more rapidly decreasing light intensity is evident at 186°C, in good agreement with the $T_g$ value from the DSC data.

Another indication of the effectiveness of combined measurements of both TOA and DSC to help resolve overlapping processes is shown by the data of Figs.6 and 7. The data of Fig. 6 were obtained on samples of a commercial CTA film (TA 401) containing plasticizer. The DSC run on a sample of this film as received gives the results shown (Fig. 6c). There is no indication of a melting process but only a
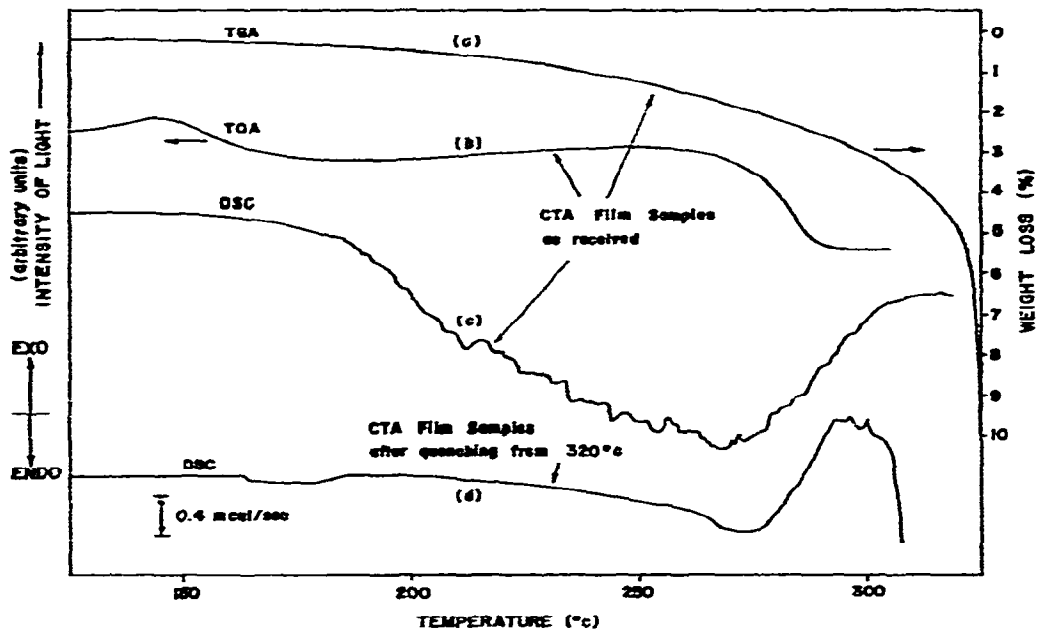
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Fig. 6. TG, TOA and DSC scans of CTA (TA 401) film samples. (a) TG scan of as-received material. (b) TOA scan of as-received material. (c) DSC scan of as-received material. (d) DSC scan of sample after quenching from 320 °C.
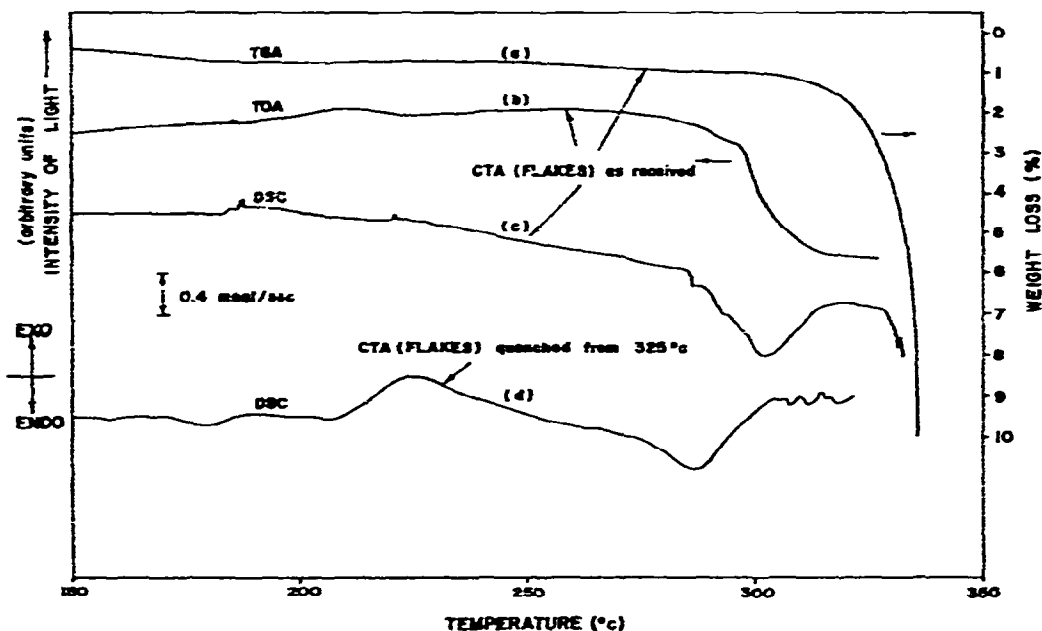


Fig. 7. TG, TOA and DSC scans of CTA flakes. (a) TG scan of as-received flakes. (b) TOA scan of as-received flakes. (c) DSC scan of as-received flakes. (d) DSC scan of sample quenched from 325 °C.

very broad and large endotherm extending from about 180°C to past 300°C. It was conjectured that this endotherm probably was itself a combined result of plasticizer evaporation and thermal degradation. To obtain additional information, it was decided to run both TG and TOA data on samples of the same material. The TG scan (Fig. 6a) shows there is a constantly increasing percent weight loss as the temperature nears and passes 200°C. By contrast with similar results on CTA flakes (no plasticizer) and shown in Fig. 7a, it may be inferred that most of the weight loss occurring between 200 and 300°C is caused by loss of plasticizer. However, the effect of this process on the DSC results is to mask other effects due to the presence of crystallinity.

The TOA temperature profile of the plasticized CTA film sample (Fig. 6b) is quite interesting as it appears to be little affected by the accompanying degradation or loss of plasticizer. The intensity shows a pronounced drop in the 280–290°C region, indicative of intensity changes occurring upon melting of an ordered phase. This melting presumably also occurred during the DSC run but its effect was masked by the effects due to plasticizer evaporation. In further support of this statement, we obtained the DSC data, shown in Fig. 6d, when a sample, quenched from 320°C, was rerun. Since much of the plasticizer has already been removed by the prior heating, the large broad endotherm, which previously extended from 200–300°C, is now essentially missing. Instead we note an endothermic peak, characteristic of the melting of an ordered phase, in the 275° region. Quenching tends to lead to more imperfect crystallites and the 10–15°C shift to lower temperatures between the temperature location of the TOA intensity drop and the DSC peak is attributed to this factor.

Somewhat similar tests, to those outlined, have also been made on CTA flakes, in which no plasticizer was present. In this case, as Fig. 7c shows, the DSC data on the as-received sample shows a definite melting endotherm near 300°C and the TOA data (Fig. 7b) shows a marked intensity drop in the same temperature region. Thus the as-received CTA flakes are quite crystalline and while the melting transition is clearly revealed the $T_g$ transition is not readily detectable from either the DSC or the TOA scan. However, if we quench the CTA sample from 325°C (just before the start of extensive degradation as revealed by the TG curve (Fig. 7a) on this sample), then we obtain on the subsequent DSC run the results shown in Fig. 7d. There is now a $T_g$ baseline shift starting at about 170°C. Hence, our results show that the $T_g$ for CTA is about 15°C lower than the $T_g$ for CA. This is in accord with results of previous studies[9,11,24,26]. Evidently the substitution of polar hydroxyl groups for more flexible acetate side groups raises the interaction energy and shifts $T_g$ to higher temperatures. We also see, from the DSC results obtained on the quenched CTA sample that there now is a sizable exothermic peak in the 225°C range that can be associated with recrystallization during the test run. The melting peak is present at about 285°C and it has been shifted about 15°C to lower temperatures as a result of the quenching operation. It also appears that the area under the melting peak, a measure of the heat of fusion, is about the same as the area under the crystallization exotherm. Thus, most of the crystallinity that is present in the quenched samples, and

which is manifested by the endotherm at 285°C, has developed from crystallization during the test run.

## CONCLUSIONS

(1) DSC is sensitive to glass transition changes, onset of crystallization, and melting but if these various processes overlap one another or other processes, such as degradation, as they do in the cellulose acetates, then DSC results are frequently ambiguous.

(2) The TOA method is a sensitive one for observing thermally induced changes in orientation, whether this is a loss of orientation due to $T_g$ or $T_m$ transitions, or a gain in the amount of oriented material due to a crystallization process.

(3) Combined use of DSC and TOA methods, especially when run at comparable scan rates, and on polymer samples of comparable past history, frequently allows most of the ambiguity to be removed.

(4) Quenched samples of CA and CTA, as well as of other polymers can readily be annealed during normal DSC or TOA tests and hence observations indicating melting of ordered phases will not reflect the morphology of the initial samples, but only of those having the specific past history characteristic of the scan rate used. Crystallization occurring during the test run is revealed both by exothermic peaks in the DSC record and by intensity rises in the TOA scans. Therefore, conventional quantitative methods for measuring the initial degree of crystallinity by DSC or DTA methods for materials of this type would give ambiguous results.

## REFERENCES

1 J. Chia (Ed.), *Polymer Characterization by Thermal Methods of Analysis* papers presented at *Symposium at ACS, Detroit Meeting 1973*, 1974.
2 R. C. MacKenzie (Ed.), *Differential Thermal Analysis* Academic Press, 1970.
3 C. E. Wilkes and C. S. Yusek, *J. Macromol. Sci. Phys.* B, 7 (1973) 157.
4 B. Wunderlich, *J. Therm. Anal.*, 5 (1973) 117.
5 G. M. Bartenev and Yu. V. Zelenev, *Mech. Polymerov.* 1 (1969) 30.
6 W. G. Harland, M. M. Khado and R. H. Peters, *Polymer*, 13 (1972) 13.
7 J. K. Gillham and R. F. Schwenker, Jr., *Appl. Polym. Symp.* 2 (1966) 59.
8 A. A. Askadskii, *Polym. Sci., USSR*, 16 (1974) 495.
9 G. Arneri and J. A. Sauer, presented at *IV Inter-American Conference on Materials Technology, Caracas, Venezuela, July 1975, Polym. Eng. Sci.*, 15 (1975) 795.
10 A. F. Klarman, A. V. Galanti and L. H. Sperling, *J. Polym. Sci., Part A-2*, 7 (1969) 1513.
11 K. Dimov, Chr. Betchev and V. Sarmadgieva, *J. Therm. Anal.*, 5 (1973) 397.
12 K. H. Illers, *Eur. Polym. J.*, 10 (1974) 911.
13 M. J. Richardson and P. Burrington, *J. Therm. Anal.*, 6 (1974) 345.
14 D. Vucelic, A. Stamatorie and U. Todovic, *J. Therm. Anal.*, 4 (1972) 479.
15 E. M. Barrall II and Barbara Dawson, *Thermochim. Acta*, 8 (1974) 83.
16 S. Strella and P. F. Erhardt, *J. Appl. Polym. Sci.*, 13 (1969) 1373.
17 A. J. Kovacs and S. Y. Hubbs, *J. Appl. Polym. Sci.*, 16 (1972) 301.
18 A. R. Schultz and B. M. Gendron, *J. Appl. Polym. Sci.*, 16 (1972) 461, *ACS Polym. Preprints*, 14 (1973) 571.
19 C. E. Wilkes and M. H. Lehr, *J. Macromol. Sci. Phys.* B, 7 (1973) 225.
20 J. H. Magill, *Polymer*, 2 (1961) 221.

21 A. S. Buntjakov and V. M. Averyanova, *J. Polym. Sci. Part C*, 38 (1972) 109.

22 R. E. Boy. Jr., R. M. Schulken, Jr. and J. W. Tamblyn, *J. Appl. Polym. Sci.*, 11 (1967) 2453.

23 E. Ott, H. M. Spurlin and M. W. Grafflin, *Cellulose and Cellulose Derivatives*, Parts 1 and II, Interscience. New York, 1954.

24 J. Dickson, in K. D. Pae, D. R. Morrow and Yu Chen (Eds.), *Advances in Polymer Science and Engineering*. Plenum Press. New York, 1972, p. 307.

25 D. R. Morrow and J. A. Sauer, *OSW Reports*, Grant 14-01-0001-2130, Aug. (1969), Sept. (1970).

26 J. Russel and R. G. Van Kerpel, *J. Polym. Sci.*, 25 (1957) 77.