

Thermoanalytical Characteristics of Polycarboxylic Acids Investigated as Durable Press Agents for Cotton Textiles*

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SYNOPSIS

Polycarboxylic acids are of great interest to the cotton textile industry as durable press agents because they do not release substances that require mandatory monitoring. Differential scanning calorimetric (DSC), thermogravimetric (TG), and differential thermogravimetric (DTG) techniques were used to study the thermal characteristics of a series of 10 polycarboxylic acids. Samples included di-, tri-, and tetra-functional compounds some of which contained olefinic linkages, hydroxyl substituents, and cyclic structure. Thermogravimetric data at simulated fabric cure temperatures was used to assess the potential of a compound for use as a textile finishing agent. In high-temperature studies the compounds were readily distinguishable in DSC analyses. General characteristics such as increases in total heats of reactions were found to be related to the number of functional groups. These results also provided support for a mechanism for the reaction of polycarboxylic acids with cellulose through an anhydride intermediate.

INTRODUCTION

For years durable press properties have been achieved for cotton fabrics by reaction with agents based on cyclic ureas. Such finishes have excellent smooth drying properties and are durable to repeated laundering. These finishes have disadvantages that include lower fabric strength and some finish hydrolysis with the subsequent liberation of formaldehyde.¹ Recently, there has been renewed interest in the use of carboxylic acids for production of smooth drying cotton fabrics. With a new class of catalysts based on alkali metal salts of phosphorus-containing inorganic acids, more rapid reaction with fabrics has been observed.^{2,3} Durable press (DP) levels of wrinkle resistance and smooth drying properties have been achieved.^{4,5} The polycarboxylic acids (PCA) offer the same advantages as those mentioned above. In addition, they cause somewhat less strength loss and release no formaldehyde.

To achieve smooth drying properties with fabrics of cotton cellulose, chemical crosslinks are necessary throughout the entire fiber matrix. Traditionally, finishes achieved crosslinks through etherification of the cellulose. Reaction of cellulose with the carboxylic acids is achieved by esterification. The proposed mechanism⁴ for this reaction involves formation of an anhydride intermediate that subsequently reacts with a cellulose hydroxyl group to form an ester linkage and a carboxyl group. A schematic drawing of this reaction is shown in Figure 1. Dicarboxylic acids can form only one anhydride group per molecule, therefore no further reaction with cellulose is likely, and few if any crosslinks are achieved. Of interest to the textile industry are those acids with three or more carboxylic acid groups so that formation of at least a second anhydride group is theoretically possible. Such compounds would be capable of crosslinking cellulose. To date the best fabric performance has been achieved with tetracarboxylic acids. Their cost is high; however, the industry interest is so strong that widespread efforts for more economical production are underway.

As research on finishes from these polycarboxylic acids has progressed, we began a complementary study on the thermal characteristics of these compounds. The literature contains scattered references

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FORMATION OF ESTER CROSSLINKS IN COTTON

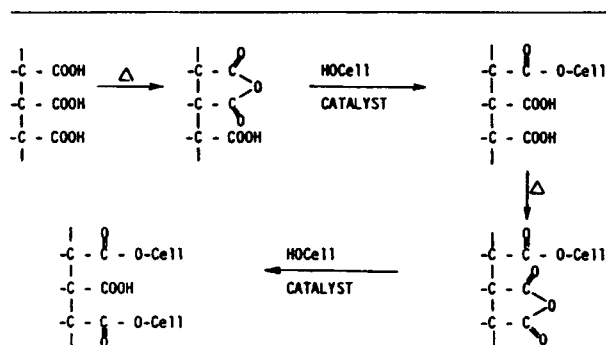


Figure 1 Schematic drawing of theoretical reaction mechanism of polycarboxylic acid with cellulose via an anhydride as a reactive intermediate.

worldwide to thermoanalytical investigations of some of the simple polycarboxylic acids investigated here.⁶⁻¹⁰ Most researchers used differential thermoanalytical (DTA) instruments and different conditions of testing. The simple di- and tri-functional acids are included in this work to present a more complete series of compounds to examine and to supplement the old literature with modern differential scanning calorimetric data. A similar thermoanalytical study was made on a series of cyclic ureas used for DP finishing. This research yielded a thermoanalytical marker for agents capable of releasing formaldehyde.¹¹ The thermoanalytical results of the polycarboxylic acid study will provide more basic information on these compounds so that we can better understand how their thermal characteristics under simulated cure as well as high-temperature conditions can affect their usefulness as DP fabric finishing agents, and may provide evidence to support the proposed anhydride mechanism for crosslinking cellulose.

MATERIALS AND METHODS

A series of 10 commercially available polycarboxylic acids were analyzed. They consist of di-, tri-, and tetra-functional compounds and are listed in Table I with their molecular weights and their manufacturer's supplied melting points.

The thermoanalytical properties were measured with a DuPont* 1090 thermoanalyzer. Differential scanning calorimetric (DSC), thermogravimetric (TG), and differential thermogravimetric (DTG)

analyses were performed. The instrument is equipped with both a 910 DSC and a 951 TGA module. All thermograms were obtained under a dynamic nitrogen atmosphere. DSC sample weights were all normalized to 5 mg.

In the first set of experiments the samples were maintained isothermally at 60°C for 1 min, heated at 25°C/min to the maximum temperature (160, or 180°C), and held 3 min at the maximum. These conditions were set to loosely approximate cure conditions on fabric. Percent residue of these low-temperature runs were measured at the end of each

Table I Polycarboxylic Acids Investigated

Compound	MW	MP (°C)
Dicarboxylic acids		
Succinic	118	187-9
Maleic	116	134-6
DL-Malic	134	131-3
Tricarboxylic acids		
Tricarballic	176	159-62
tr-Aconitic	174	190d
Citric, anhydr	192	152-4
Tetracarboxylic acids		
Butanetetracarboxylic (BTCA)	234	196
Thiodisuccinic	266	196-7
All- <i>cis</i> -cyclopentanetetracarboxylic (CP-TCA)	246	192-5d
Tetrahydrofuranetetracarboxylic (THF-TCA)	248	205d

d = decomposed.

* Names of companies or commercial products are given solely to provide scientific information and do not imply endorsement by the U.S. Department of Agriculture over others not mentioned.

gravimetric analysis. In the second set of experiments, duplicate thermograms were obtained by heating a sample from 50 to 600°C at 15°C/min. Under these circumstances the sample's percent residue was measured at 575°C. The high-temperature study was performed to completely evaluate a compound's reaction to thermal stress.

RESULTS AND DISCUSSION

Simulated Cure Study

As a test of whether or not thermal analyses could be used to quickly assess which agents might be selected or even eliminated as reagents for textile finishing, we performed initial thermal analyses under conditions that would approximate those encountered during textile processing. Thermograms of the samples heated to the maximum of 180 and 160°C were obtained. Two parameters were valuable as predictors of an agent's potential usefulness as a textile finishing reagent: percent residue and maximum rate of weight loss. First, the percentage residue results from the 180 and 160°C programmed

heating results were compared in Figure 2. When heated to a maximum of 180°C, maleic acid lost more than 90% of its sample weight. The scientific explanation, that maleic acid dehydrated to the anhydride rapidly and that the anhydride does not easily decompose but evaporates or sublimates, is known. For the purposes of textile finishing, we assumed a compound would need to be present to react with cellulose. Therefore, by our definition, maleic acid is probably thermally unsuitable. Aconitic and citric acids had lost 40–50% of their weight due to thermal degradation. Their potential usefulness for textile applications was better than that of maleic acid. The remaining acids had all lost less than 15% of their weight and should therefore be available for reaction with cellulose. When the acids were heated to a maximum of 160°C, the percent residue results again showed that only maleic acid was significantly effected. This compound was so thermally degraded that it would apparently be the most inefficient to use as a finishing agent. All the other polycarboxylic acids were thermally stable enough at 160°C to be available for reaction with cellulose. BTCA and the two cyclic tetra-carboxylic acids retained the highest percentage of residue in both instances, and there-

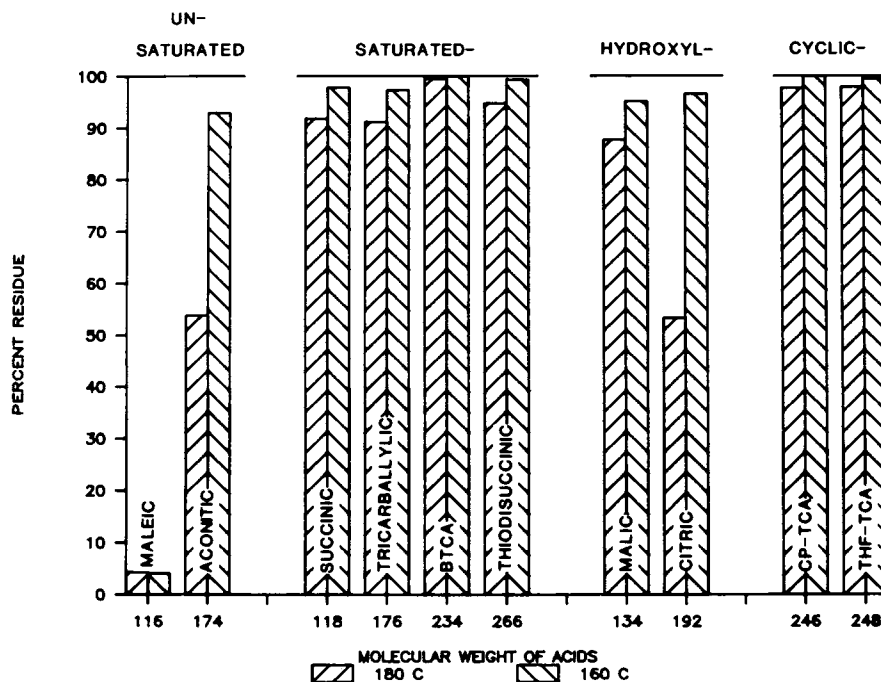


Figure 2 Comparisons of percent residue data from TGA for each polycarboxylic acid. Data are given for two temperatures that represent simulated fabric cure procedures. Residue data were collected at the temperatures indicated. Samples are grouped by structural similarities: unsaturation, saturation, and hydroxyl-substitution of linear PCAs and cyclic PCAs.

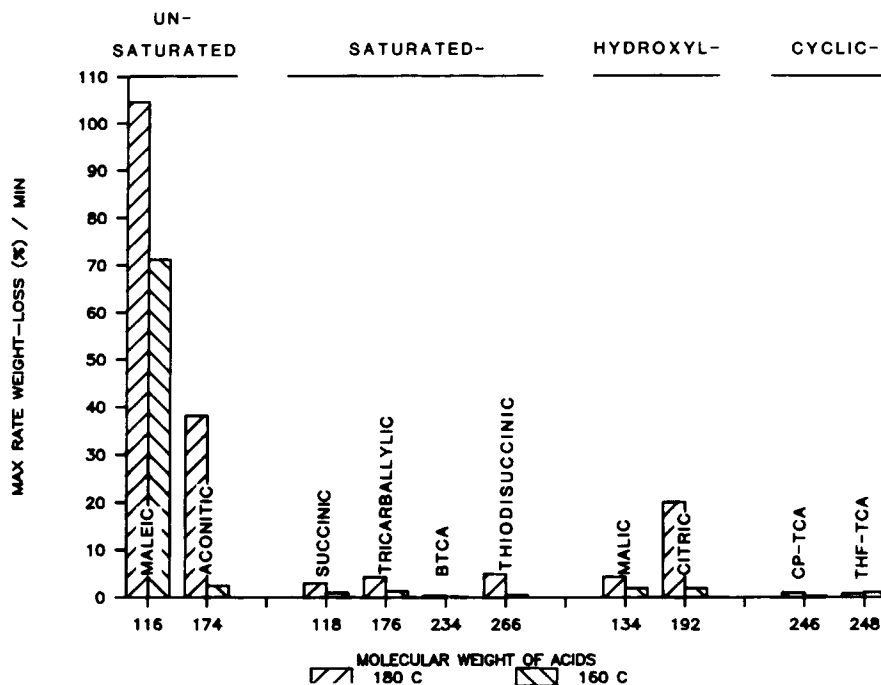


Figure 3 Comparisons of maximum rate of weight loss data from DTG thermograms for each polycarboxylic acid. Data are given for two temperatures that represent simulated fabric cure procedures and were collected during the heating procedures whose maximum temperatures are indicated. Samples are grouped by structural similarities: unsaturation, saturation, and hydroxyl-substitution of linear PCAs and cyclic PCAs.

fore they were presumably present and available for reaction with cellulose at either temperature.

A comparison of maximum rate of weight loss data from DTG thermograms under these same simulated cure temperature conditions are shown in Figure 3. Based on the assumption that a low rate of weight loss is desirable, the results again showed maleic acid, with its rapid loss of weight, to be inappropriate for textile applications at both temperatures. Aconitic and citric acids began to lose weight at intermediate rates with aconitic about twice as active as citric probably due to its unsaturation. The remainder of the compounds should be available for reaction with cellulose. The tetracarboxylic acids have very low rates of weight loss; in reality we have not measured any appreciable thermal activity for the tetracarboxylic acids under either of these simulated curing conditions, and theoretically they would be available for cellulose esterification. BTCA was among the best by this indicator.

General Thermoanalytical Results

The thermograms of the polycarboxylic acids tested at the simulated fabric cure temperatures, below

even the melting points of many of the compounds, were nearly featureless. In order to study the compounds in depth, we generated thermograms that included all thermal activity by heating the samples to 600°C at 15°C/min. The DSC results of each compound are presented in Table II. The onset temperature of the first peak is the melting point as measured by this technique. Unless stated otherwise all DSC peaks in this article are endothermic, i.e., the sample absorbed heat as it was heated. The overall temperature range of thermal activity was listed and was the interval used to calculate the total heat of activity in joules per gram.

The corresponding thermogravimetric data are listed in Table III. The TG peak temperature was defined as the temperature at which the rate of weight loss was maximum for a defined temperature/activity interval. By an expansion of the DTG curve to maximize sensitivity, we were able to perceive the subtle weight loss areas shown in Table III as shoulders. The major peak in the DSC thermogram roughly corresponded to the temperature where the largest weight loss was found to occur.

Thermograms of the 10 compounds heated to 600°C are shown in Figures 4-7. The curves illus-

Table II Differential Scanning Calorimetric Data on Polycarboxylic Acids Heated to 600°C

Compound	Peak Onset		DSC Peak Temperatures			Range Total Activity	Total ΔH (J/g)
	Temperature (°C)						
Dicarboxylic acids							
Succinic	187	191	265			170–285	1354
Maleic	143	145	151s	194		125–205	1261
DL-Malic	131	138	185s	245	284	110–290	1439
Tricarboxylic acids							
Tricarballic	157	163	198	242		130–270	1015
tr-Aconitic	—	191	210s			135–250	932
Citric, anhydr	155	158	228			140–260	1218
Tetracarboxylic acids							
BTCA ^a	195	201	wide	312		175–340	1213
Thiodisuccinic	198	205	220	290		155–340	1186
All- <i>cis</i> -CP-TCA ^a	—	199	294	331		160–370	1143
THF-TCA ^a	—	212	259	299x		155–320	837

^a Abbreviations of compound names defined in Table I.

s = shoulder.

x = exothermic peak.

Table III Thermogravimetric Analyses Data on Polycarboxylic Acids Heated to 600°C

Compound	TGA Peak Temperatures (°C)			Associated Weight Loss (%)		
Dicarboxylic acids						
Succinic	195s	229		7.0	91.1	
Maleic	162s	178		14.8	83.4	
DL-Malic	213s	239	254	13.9	75.1	10.1
Tricarboxylic acids						
Tricarballic	232s	298		10.5	71.7	6.0
tr-Aconitic	197s	212	257	10.9	60.2	13.5
Citric, anhydr	242			95.5		
Tetracarboxylic acids						
BTCA ^a	263	306		14.5	70.7	
Thiodisuccinic	212s	224	298	7.2	22.4	55.6
All- <i>cis</i> -CP-TCA ^a	214	295	387	8.6	44.3	17.7
THF-TCA ^a	237	281		5.7	70.8	

^a Abbreviations of compound names defined in Table I.

s = shoulder.

trated correspond to the data in Tables II and III. Results are presented for initial comparison by number of carboxylic acid groups. Details of the thermal decomposition of the lower molecular weight acids are known. The mechanisms include dehydration, decarboxylation, and in some cases, notably succinic and maleic acids, volatilization/evaporation. For the purposes of this research, an attempt was made to identify only dehydration; other identification of specific decomposition products/steps are beyond the scope of this article.

Dicarboxylic Acids

Figure 4 contains the thermograms of the dicarboxylic acids—succinic, maleic, and malic (MW 118, 116, 134, respectively). These simple acids are included to provide information on saturated, unsaturated, and hydroxyl-substituted acids for comparisons with the larger, potentially more useful polycarboxylic acids.

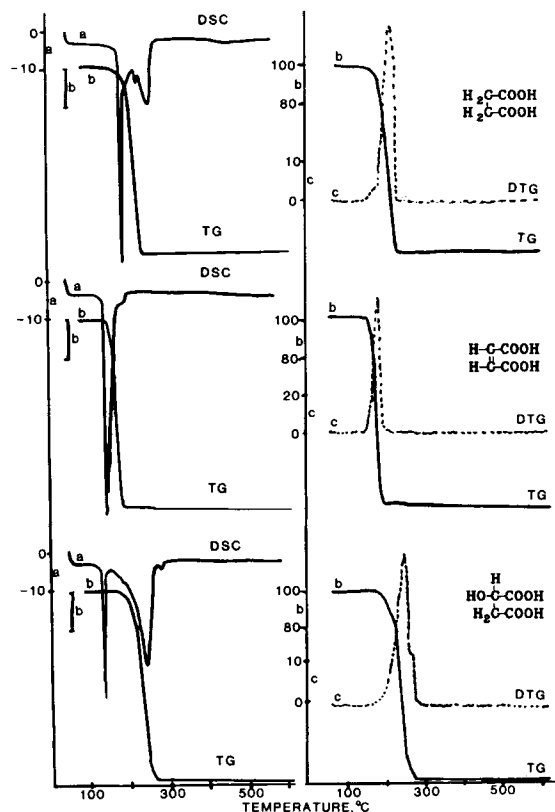


Figure 4 Thermograms of dicarboxylic acids shown. Units are (a) heat flow in mW for DSC curves, (b) weight in % for TG curves, and (c) percent weight loss/min for DTG curves. All curves are plotted vs. temperature.

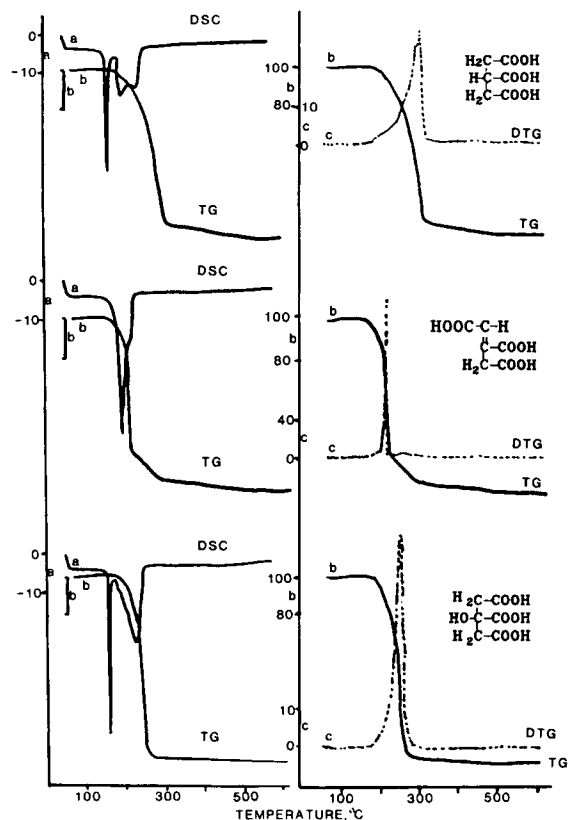


Figure 5 Thermograms of tricarboxylic acids shown. Units are (a) heat flow in mW for DSC curves, (b) weight in % for TG curves, and (c) percent weight loss/min for DTG curves. All curves are plotted vs. temperature.

The DSC thermogram of succinic (butanedioic) acid showed a melting peak followed by decomposition. The TG curve showed an initial small weight loss region, corresponding to approximately 7% sample weight, followed by the major loss of 91% sample weight. Residue remaining at 575°C was low.

Maleic acid or *cis*-1,2-ethylenedicarboxylic acid, containing a double bond, had a DSC thermogram with a melting peak and an almost immediate decomposition peak that were nearly indistinguishable. The curve was simple, i.e., the compound had a narrow temperature range of thermal activity. The TG weight loss curve had a small region corresponding to approximately 15% weight loss followed by sample decomposition that caused nearly total weight loss. Evaporation, distillation, or sublimation is probably responsible for final weight loss of both succinic and maleic acid.

Malic acid or hydroxysuccinic acid had a complex thermogram. A sharp melting peak was followed by a broader decomposition range and a final small

peak. This thermogram covered a broader temperature range than the other dicarboxylic acids. The corresponding TG weight loss appeared to occur in one step and the sample left little residue. DTG scale expansion allowed subtle differences to be recognized.

Tricarboxylic Acids

The thermograms of the tricarboxylic acids are found in Figure 5. Tricarboxylic acids are those with the lowest allowable functionality if an anhydride mechanism is operative in polycarboxylic acid crosslinking of cellulose. They include tricarballylic, aconitic, and citric acids (MW 176, 174, and 192, respectively) and correspond in structure to the previous dicarboxylic acids, i.e., saturated, unsaturated, and hydroxyl-substituted structures.

The saturated trifunctional compound was tricarballylic acid or 1,2,3-propanetricarboxylic acid. Its DSC thermogram showed the compound melting and decomposing in two peaks. The corresponding TG curve had associated weight losses of 11 and 72%, respectively, and left a moderate amount of residue.

Trans-aconitic acid (1,2,3-propenetricarboxylic

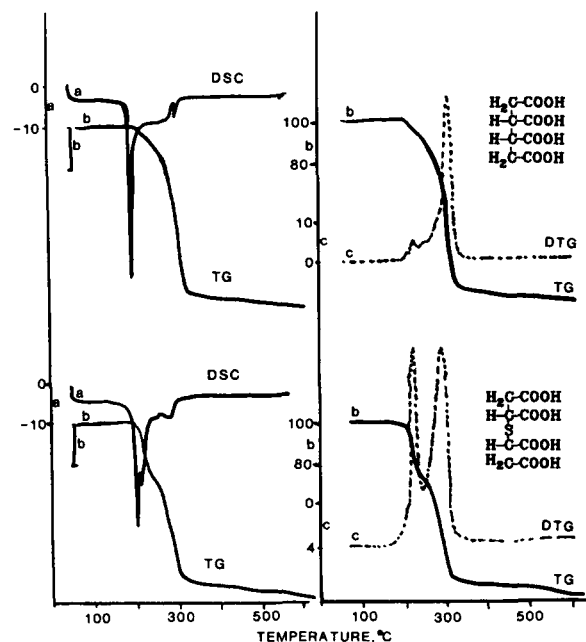


Figure 6 Thermograms of tetracarboxylic acids shown. Units are (a) heat flow in mW for DSC curves, (b) weight in % for TG curves, and (c) percent weight loss/min for DTG curves. All curves are plotted vs. temperature.

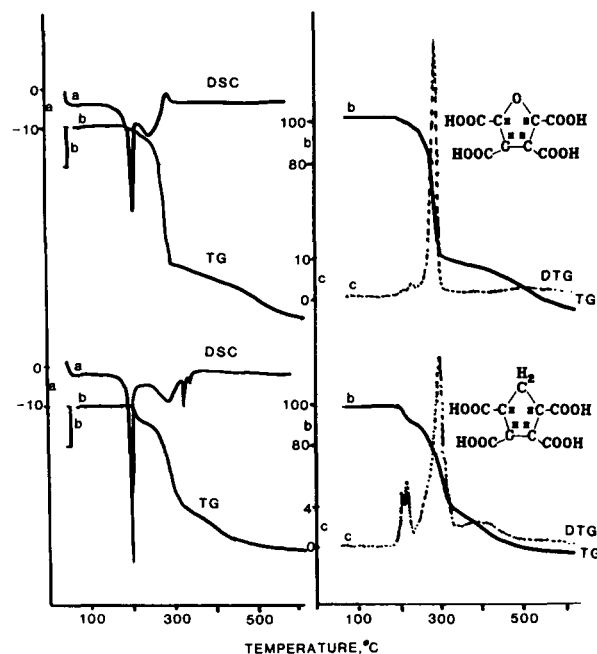


Figure 7 Thermograms of tetracarboxylic acids shown. Units are (a) heat flow in mW for DSC curves, (b) weight in % for TG curves, and (c) percent weight loss/min for DTG curves. All curves are plotted vs. temperature.

acid) contains an olefinic linkage. This compound's DSC curve was simple, as was the curve of the unsaturated dicarboxylic acid. Aconitic acid melted/decomposed in a single peak at 191°C. There was a small area of weight loss that preceded the major weight loss region that involved 60% of the sample. There was a final slow loss corresponding to an additional 14% weight loss. The residue amount at 575°C was similar to that left by tricarballylic acid.

Anhydrous citric acid (2-hydroxy-1,2,3-propanetricarboxylic acid) with its single hydroxyl group melted and then decomposed in an apparent single peak. This occurred at approximately the same temperature as was observed with malic acid. Citric acid's major weight loss region was responsible for 96% of the sample size. The residue at 575°C was low.

Citric and aconitic acids reacted in a manner intermediate between maleic acid and the remainder of the compounds when they were tested at the lower temperatures. These two compounds appear related. Usolitseva et al.⁸ claimed citric acid decomposed to aconitic at 150°C. However, that is where we found melting to occur. While citric acid probably dehydrates to aconitic acid under thermal stress, the evidence is not clear among our data.

Tetracarboxylic Acids

The results of four tetracarboxylic acids are examined in Figures 6 and 7. Curves for the linear compounds, 1,2,3,4-butanetetracarboxylic acid (BTCA) and thiodisuccinic acid (MW 234 and 266, respectively), are given in Figure 6.

The BTCA compound melted and had a broad decomposition temperature range; the activity range extended above 300°C. Its TG curve showed some weight loss as a shoulder preceding the major weight loss of 71%. The residue at 575°C was moderate.

Thiodisuccinic acid is another linear, tetra-functional compound, and its DSC thermogram consisted of a melting point peak followed by decomposition in the form of a shoulder peak and a broad area of activity. The gravimetric data from thiodisuccinic acid was unique. The TG curve showed the clearest example of a compound with two distinct weight loss regions representing 30 and 56% weight loss, respectively. This thermogram might indicate a two-step thermal degradation where the compound breaks in mercaptosuccinic and maleic acids. The sample retained residue at 575°C in an amount similar to the other linear tetra-functional acid, BTCA.

In Figure 7 are presented the thermoanalytical

results of two cyclic, tetracarboxylic acids that were also studied. All-*cis*-1,2,3,4-cyclopentane-tetracarboxylic acid (CP-TCA) (MW 246) had a large range of thermal activity. The compound did not simply melt. The DSC thermogram began with a sharp peak that resembled a melting peak, but had significant decomposition weight loss associated with it. This is an instance where the melting peak was probably superimposed on a decomposition peak. Two or three other peaks followed, and the activity range extended above 300°C. The weight loss of this compound was in multiple steps also. The final residue for this sample was the highest of all the compounds.

Tetrahydrofuran-2,3,4,5-tetracarboxylic acid (THF-TCA), a heterocyclic compound (MW 248) with an oxygen atom in its ring structure, also decomposed without a distinct melting peak. The DSC thermogram of THF-TCA was the only one of this series to show some exothermic activity peaking at approximately 299°C. The gravimetric data showed two small areas of weight loss totaling 6% and one major region accounting for 71% of the sample. The residue at 575°C was modest.

In Table IV are presented the remaining thermoanalytical data from the 600°C series of tests. The samples are arranged for easy comparison of

Table IV Additional Thermal Properties Arranged by Structure of the Polycarboxylic Acids (600°C)

Compounds	DSC Total Heat of Reaction (kJ/mol)	Percent Residue at 575°C	Max. Rate Wt Loss (%/min)
		Unsaturated	
Maleic	146.3	0.5	69.8
tr-Aconitic	162.2	9.5	165.5
		Saturated	
Succinic	159.7	1.6	53.6
Tricarballic	178.6	8.5	26.6
BTCA*	283.8	10.8	43.9
Thiodisuccinic	315.5	13.5	20.2
		Hydroxyl	
Malic	192.8	1.1	38.6
Citric, anhydr	233.9	5.3	58.6
		Cyclic	
<i>cis</i> -CP-TCA*	281.2	26.5	20.9
THF-TCA*	207.6	11.2	57.3

* Abbreviations of compound names defined in Table I.

the effects of di-, tri-, and tetra-functionality. The total heat of reaction of each sample was recalculated taking molecular weight into account, and the values are reported here in kJ/mol. The following relationships were found. The total heat of reaction values increased with functionality within comparable structural series. BTCA and thiodisuccinic acid are saturated, linear compounds and had the greatest thermal activity as measured by molar ΔH values. Within the di- and tri-functional series, the unsaturated compounds had slightly lower molar heats of reaction corresponding to their simpler curves, while the acids with a hydroxyl group had slightly higher ΔH values corresponding to their more complex thermograms when compared to the saturated agents.

The tetracarboxylic acids, cyclic CP-TCA and heterocyclic THF-TCA, were also among the most active; the presence of the oxygen in the furan ring may have destabilized that compound because the molar ΔH was the lowest of all the tetra-functional agents. It is tempting to propose that high total heats of reactivity would be a good predictor of usefulness as a textile finishing agent; textile finishing data are needed to support such a theory.

The percent residue at 575°C and the maximum rate of weight loss are also given in Table IV. Percent residue increased with functionality. However, the previous relationship between structural features was not present. The general conclusion reached from these data is that compounds apparently grouped into three levels of residue production, with the tetracarboxylic acids producing the greatest quantity. The maximum rate of weight loss data clearly showed that the unsaturated compounds were the least stable to thermal stress.

Thermoanalytical data of the polycarboxylic acids at high temperature are valuable. With these distinctive thermograms we were able to distinguish among the acids. High-temperature analyses also provided the information to support our theoretical mechanism for reaction with cellulose.

Thermoanalytical Support for Proposed Textile Reaction Mechanism

A major objective of this research was to gather thermal data to support the proposed mechanism for PCA reaction with cellulose via acid anhydride formation.³ Early thermoanalysis references claim their formation^{6,12,13}; however, only Meirovics et al.¹² showed water loss with GC and IR data. Without an instrumental interface to analyze the gases given

off during heating, our search for anhydride formation was confined to comparisons of theoretical water loss and measurable initial weight loss regions. Our results were based upon examinations of DTG thermograms generated from the high-temperature (600°C) analyses. The early portions of the DTG curves were expanded to provide maximum sensitivity. We sought a point on the curve to indicate a change in thermal activity that may account for a change in reaction—i.e., end of water loss to beginning of decomposition. The results are discussed but not shown for the di- and tri-functional compounds. Succinic acid produced a clear shoulder that was approximately equivalent to the theoretical loss of 0.5 mol water. At that temperature (230°C) the sample began to lose weight rapidly. Whether succinic acid/anhydride sublimates or distills is uncertain but likely. During treatments of fabrics at cure temperatures, succinic acid samples give off white vapors/smoke. Gal et al.⁶ reported 77% anhydride formation under their test conditions. Of the remaining di- and tri-carboxylic acids studied, only the unsaturated acids, maleic and aconitic, had recognizable weight loss regions that could represent water loss. The theoretical vs. actual percent weight losses were 15.5 : 14.8 and 10.3 : 10.9. The DTG curves of malic, citric, and tricarballic acids all had shoulders that could account for a mole of water, but none were as clearly defined as those of the unsaturated acids.

The expanded DTG thermograms of the four tetracarboxylic acids are plotted in Figure 8. The sample of all-*cis*-CP-TCA produced the best defined single weight loss region that could correspond to loss of one mole water. A second mole of water loss could have occurred as the shoulder on the major peak. The second cyclic compound, THF-TCA, produced a DTG curve that supports one mole of water loss. There is no clear shoulder at which, theoretically, another mole of water would be lost. The arrangement of the four carboxyl groups in the THF-TCA molecule may prevent formation of a second anhydride linkage.

Both linear tetracarboxylic acids are spatially free to produce two anhydride structures. Thiodisuccinic's DTG thermogram produced one clear shoulder that probably corresponded to loss of one mole of water. Loss of the second mole would be highly speculative. However, the DTG curve for BTCA showed weight loss activity that probably corresponded to early loss of two moles of water. These data provided the best thermal evidence that BTCA and all-*cis*-CP-TCA are probably capable of forming a dianhydride to crosslink with cellulose.

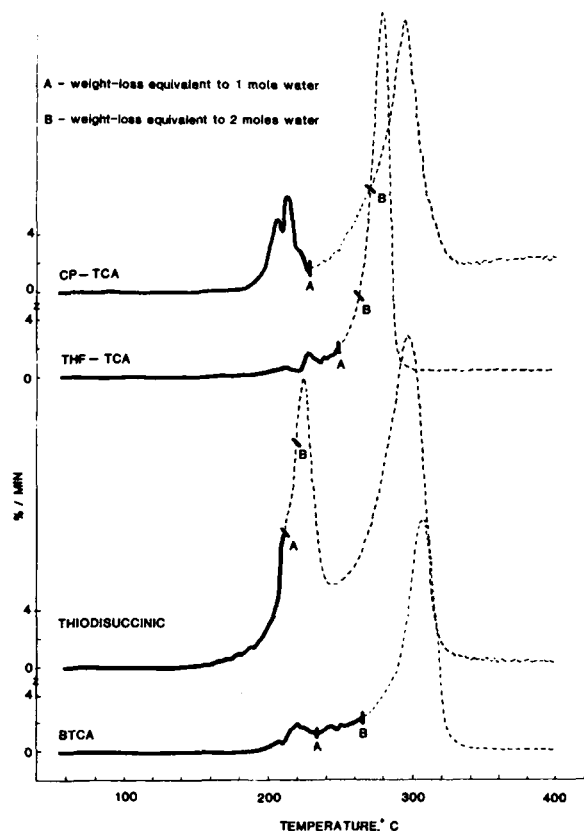


Figure 8 Expanded DTG thermograms for the tetra-carboxylic acids showing the points on each that correspond to the theoretical loss of one mole of water. Evidence of the loss of two moles of water is best for CP-TCA and BTCA.

SUMMARY AND CONCLUSIONS

Ten di-, tri-, and tetra-functional, polycarboxylic acids were examined with thermoanalytical techniques. When percent residue values at simulated cure temperatures were analyzed along with the corresponding rates of weight loss, we were able to make a preliminary assessment of a compound's potential usefulness as a textile finishing agent. If a sample combined high residue, indicating that it would be present to react with cellulose, with a reasonable rate of weight loss, suggesting that it would not decompose or vaporize so rapidly that it would be removed from the proximity of the cellulose, then we concluded an acid would be worth further investigation as a possible textile finishing agent. Due to the excessive and rapid weight loss by maleic acid under thermal stress, this compound would be the least likely to perform well as a cellulose DP reagent. However, these same properties appear to be better

balanced with the tetra-functional compounds, especially with all-*cis*-CP-TCA and BTCA.

Thermograms from ambient to 600°C agreed well with melting point data and, when combined with the peak temperatures and profiles, could be used to distinguish among the compounds. Thermal parameters were found useful in describing fundamental relationships among the samples as well as providing practical information of interest to the textile industry.

Total heats of reactions generally increased as the number of functional groups increased. In addition, the polycarboxylic acids with the olefinic linkages had smaller total heat values than did their corresponding hydroxyl-substituted acids. Percent residue values generally increased as the carboxyl content of these acids increased.

Evidence was found to support the proposed mechanism of PCA's reaction with cellulose by way of an anhydride as a reactive intermediate. Thermoanalytical data indicated that water loss occurred with the acids containing an olefinic linkage or especially with the larger compounds. Evidence of possible dianhydride formation was found with all-*cis*-CP-TCA and BTCA. To date, finishes from BTCA have performed best in textile finishing applications.

The search for water in mass spectrometric data on these same acids should help us understand whether water loss and anhydride formation occurs stepwise or continuously. In addition, there is a strong possibility that instrumental techniques can be used to find good acid/catalyst/cure condition combinations, i.e., those conditions where the acid has dehydrated sufficiently to produce enough anhydride to cause reaction with cellulose to occur. When combined with the thermoanalytical data presented here, our knowledge of polycarboxylic acids and their potential as durable press reagents for cotton textiles will be significantly advanced.

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