THE CHARACTERIZATION BY DIFFERENTIAL THERMAL ANALYSIS OF ORGANIC POLYELECTROLYTES AND FLOCCULATING AGENTS*

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ABSTRACT

Differential Thermal Analysis (DTA) can be used to identify some of the organic polyelectrolytes and polymeric flocculating agents. Results are presented for certain polysaccharides, polyacrylates, and polyacrylamide.

INTRODUCTION

Organic polymers, both ionic and non-ionic, have long been used as flocculating and dispersing agents to control finely divided solids in aqueous suspensions. Uses include stabilization of soils and formations by inhibition of swelling, the removal of unwanted solids in aqueous suspensions by aggregation, and suspension of non-swelling solids by increase of the viscosity of the system.

Most of the useful polymers are readily identified in the pure state by infrared and/or chemical analysis, but the mixtures of polymers with the inorganic solids normally encountered do not lend themselves to analysis by these methods. DTA is very sensitive to organic materials contained in an inorganic matrix. In the concentrations of polymers normally found in such systems (approximately 1%), DTA suffers less from inorganic interferences than do most of the other available methods. Therefore, a study was begun to determine the feasibility of using DTA for the analysis.

The preliminary stage of the investigation was to determine whether the various polymer types could be differentiated from one another by DTA. This report deals with this phase of our study.

EXPERIMENTAL

All DTA curves were obtained on a Robert L. Stone DTA apparatus equipped with the ring thermocouple micro sample holder. The samples were loosely packed in the platinum dishes and heated at 10°C/min in static air at one atmosphere. In most cases the polymers required no prior treatment. The polymer types included

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polyacrylamides, sodium polyacrylate, and polysaccharides such as sodium car-
boxymethylcellulose and starches. Thermogravimetric (TG) curves under static air
atmosphere were obtained for representative samples of each of the polymer groups.
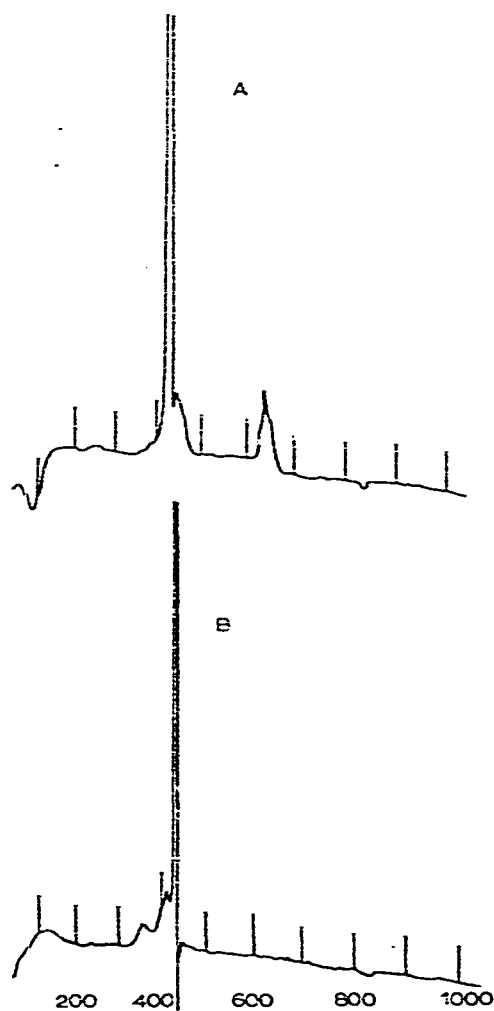

Fig. 1. DTA curves for two sodium polyacrylate samples supplied by A, Minnesota Mining and
Manufacturing Co., and B, Buckman Laboratories.

RESULTS AND DISCUSSION

Sodium polyacrylate. — DTA curves for two typical sodium polyacrylates
(Minnesota Mining and Manufacturing Co. (3M), and Buckman Laboratories) are
shown in Fig. 1. The curves show a small endotherm at about 100°C, which appears
to be a moisture loss, followed by a sharp strong exotherm at 425–450°C that the
TG curve identifies as a sudden pyrolysis with burning of the gaseous products.
The small exotherm at about 650°C in the first sample is probably burning of the
carbon skeleton. The virtual absence of this peak in the curve for the second sample

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seems to indicate the possibility of a lower molecular weight for this sample. The small endotherm at about 830 °C is almost certainly Na_2CO_3 impurity.
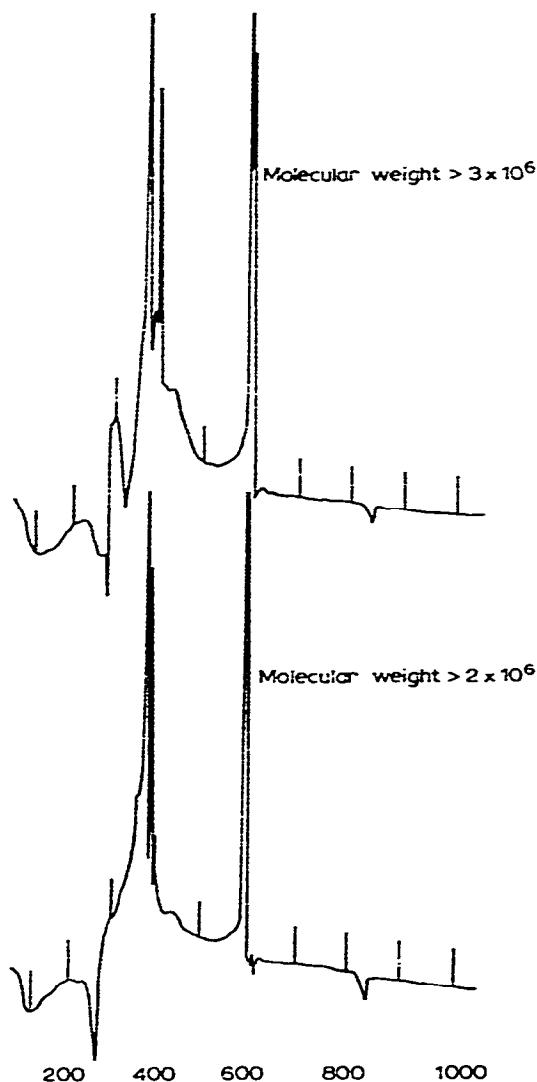

Fig. 2. DTA curves for anionic (partially hydrolyzed) polyacrylamide.

Polyacrylamides. — Both anionic and non-ionic samples (Dow Chemical Co.) were examined. The DTA curves of the polyacrylamides were found to be quite pH sensitive. In general, as shown in Fig. 2, the anionic samples (basic in a 1% aqueous solution) gave a small endotherm due to moisture at about 100°C and a second small endotherm at about 250°C. This second endotherm corresponds to a weight loss on the TG curve. Intense sharp exotherms occur at about 375°C and 575°C. These features are attributed to a rapid pyrolysis with oxidation of the gaseous products. A small endotherm corresponding to the melting of Na_2CO_3 appears at 830°C.
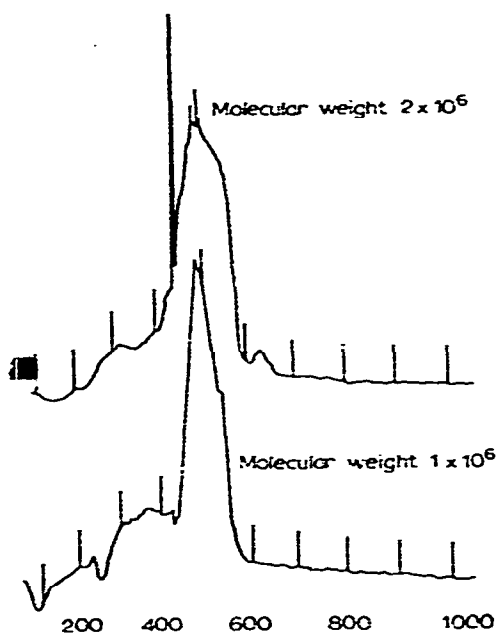
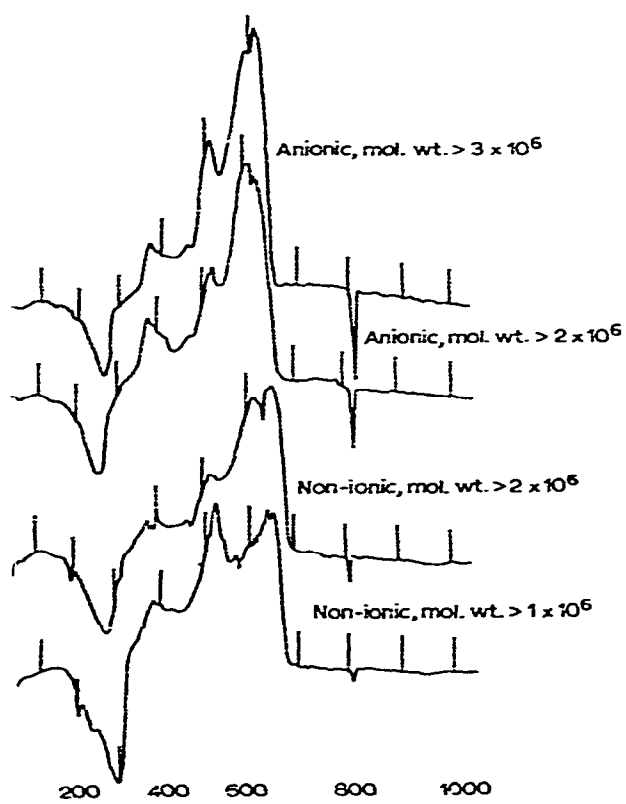Fig. 3. DTA curves for non-ionic polyacrylamide.

Fig. 4. DTA curves for polyacrylamides treated with HCl.

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The most notable DTA feature of the non-ionic polyacrylamides (neutral in a 1% aqueous solution), as shown in Fig. 3, was strong, broad exotherm peaking at about 500°C.

When DTA curves (Fig. 4) were obtained for polyacrylamides that had been made strongly acidic with HCl and evaporated to dryness at 105°C, the patterns became very similar and consisted of a small to medium endotherm at 250°C, followed by three exotherms of increasing intensity at 375–400°C, 500–530°C, and 600–650°C. The sharp endotherm at 810°C indicates the presence of the reaction by-product, NaCl. With the exception of the NaCl these are quite similar to that obtained from polyacrylic acid (Goodrich Chemical) shown in Fig. 5.
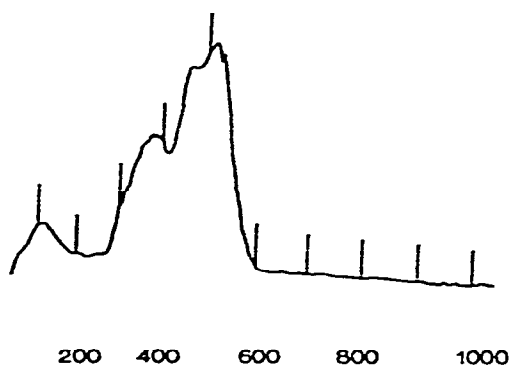

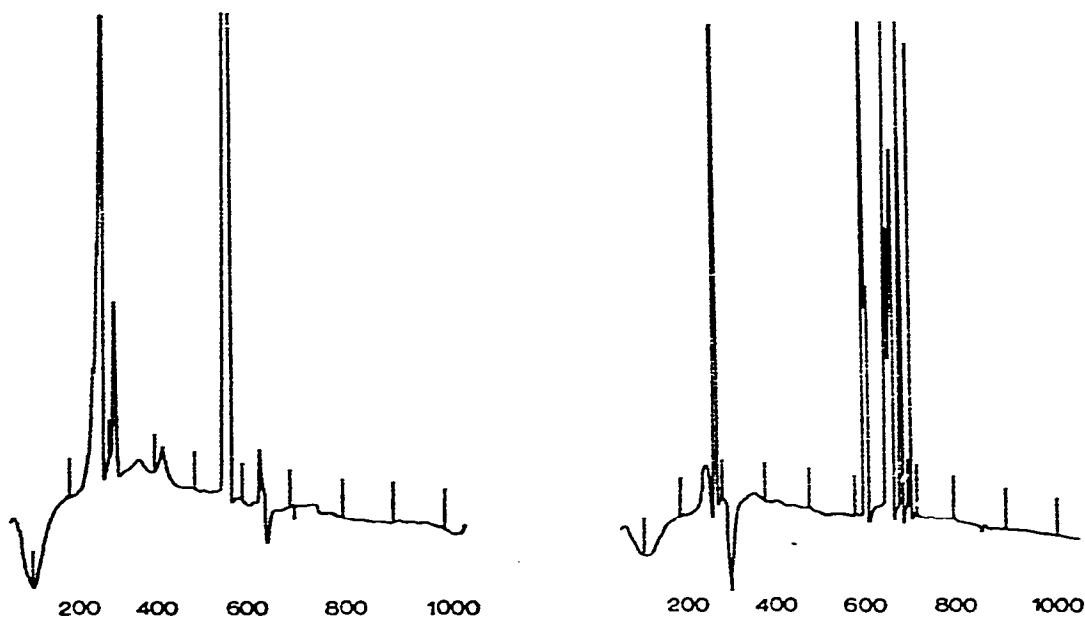Fig. 5. DTA curves for polyacrylic acid.

Fig. 6. DTA curve for technical grade sodium carboxymethylcellulose.

Fig. 7. DTA curve for high grade sodium carboxymethylcellulose.

Sodium carboxymethylcellulose. — The DTA curve shows a weak moisture endotherm at about 100°C. A sharp, strong exotherm appears in the 250–300°C region, followed almost immediately (300–325°C) by a small endotherm with a superimposed exotherm of variable intensity. A family of strong exotherms is observed in the 550–700°C region, with position and complexity apparently dependent on NaCl content. A technical grade sodium CMC (Hercules, Inc.), shown in Fig. 6, with 24% NaCl gave a single exotherm at 550°C. Compare this result to the half-dozen exotherms from 600 to 700°C observed for salt-free, high grade sodium CMC (Hercules, Inc.) as shown in Fig. 7.
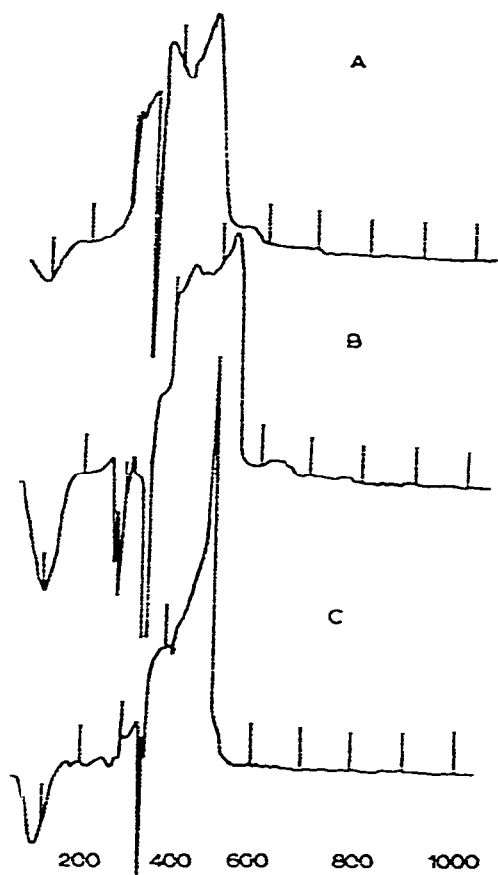

Fig. 8. DTA curves for A, amylopectin starch; B, amylose starch; and C, amylopectin starch containing a small amount of bacteriostat.

Starches. — Starch (Baroid laboratory standard) was generally characterized by a medium to small endotherm at 100°C (moisture loss) followed by a medium to strong (sharp) endotherm at 350°C. This latter feature was followed by a medium to strong double exotherm with peaks at 375–450°C and 450–550°C. The corresponding TG curve indicates that the majority of the weight loss by the sample occurs during the endotherm at 350°C. On some samples an exotherm of varying intensity

is superimposed on the 350°C peak, which suggests that the peak is due to a combined hydroxyl loss and evolution of a combustible material. Other peaks tended to be specific for a particular starch. Fig. 8 contains DTA curves for amylopectin starch, amylose starch, and an amylopectin starch containing a small amount of bacteriostat.

In general, we have found that the DTA results for these polymers are very reproducible, as is evidenced by the curves of two samples of a sodium carboxymethylcellulose which were run three months apart (Fig. 9). We are currently using DTA routinely as one of the methods of identifying polymers of these types, and feel some confidence in our ability to characterize mixtures of these polymers.

Work is continuing on the problem of detecting and identifying these polymers in low concentrations in inorganic solids. To date the results seem to be quite promising.
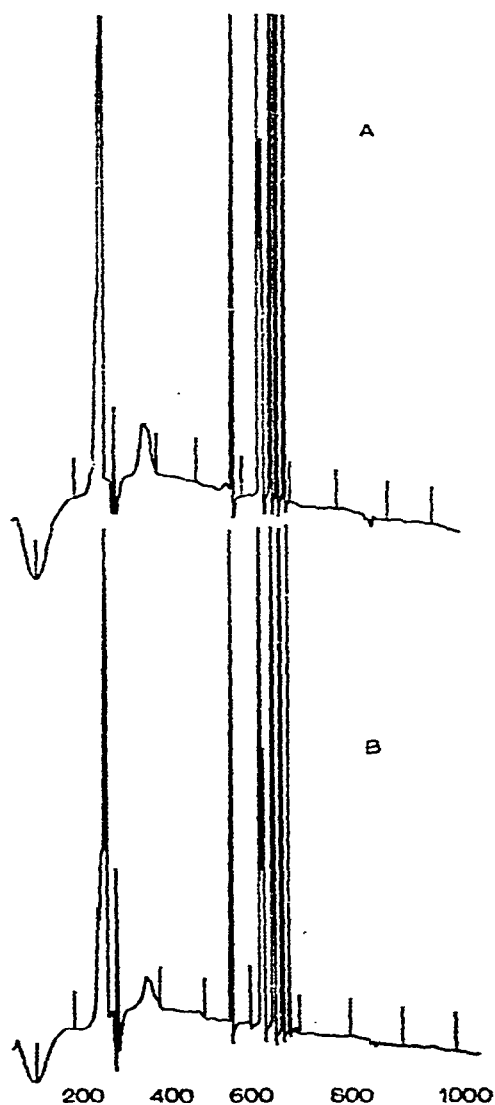

Fig. 9. DTA curves for sodium carboxymethylcellulose analyzed A, in June 1971 and B, in September 1971.