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A PARALLEL STUDY OF PVC DEGRADATION AND STABILIZATION BY Ba/Cd STEARATES USING DIFFERENTIAL SCANNING CALORIMETRY AND MASS SPECTROMETRY

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Abstract—Direct inlet mass spectrometry (DIMS) is used for the interpretation of differential scanning calorimetry (DSC) curves of PVC degradation and stabilization. The samples of PVC had various *k* values, came from different polymerization processes and were used in mixtures with Ba/Cd complex stearates as stabilizer. The effectiveness of DIMS to interpret the multistage processes recorded by DSC is examined. The use of DSC and DIMS to differentiate between various types of PVC is discussed.

INTRODUCTION

Differential scanning calorimetry (DSC) has been used for the study of thermal degradation and stabilization of PVC and its compounds. DSC has been used for the study of the thermal behaviour of PVC, before or after processing, in the presence of stabilizers or additives [1–3]. The interpretation of thermographs is not always clear because of the variety of the constituents of PVC compounds, especially in the case of stabilized polymer.

The combination of thermal methods with gas analysis methods, including mass spectrometry, is a powerful tool for the proper identification of volatile products evolved during thermal treatment [4]. In the present work, direct inlet mass spectometry (DIMS) and DSC are used for parallel studies of various PVCs and PVC mixtures with Ba/Cd complex stearate as stabilizer. DIMS has been previously used for the study of isothermal treatment of PVC and PVC mixtures with stabilizers [5, 6].

EXPERIMENTAL

Materials

The following materials, based on PVC, were used:

A, B—PVC, suspension polymerization, with *k* values 58 and 65 respectively;
C—PVC, mass polymerization, with *k* value 65, containing di-butyl phthalate (DBP) as plasticiser and 2.6 di-butyl-*p*-cresol (DBpC) as antoxidant;
D1, D2—PVC of type B containing 2.5 and 5 parts per hundred (pphr) of Ba/Cd stearates (technical grade) respectively, as well as di-octyl phthalate (DOP). All polymers were in the powdered form.

Instruments

The differential scanning calorimeter used was a Stanton Redcroft instrument, model 1500 and the mass spectrometer was a MAT-44 with electron impact ion source.

Methods

DSC—30 mg of the sample were placed in a Pt crucible and heated at a rate of 5°/min from ambient to 400°. The carrier gas was Ar with a flow rate of 50cm^3/min. Precured a-Al_2O_3 was used as reference material. MS—Approx. 0.5 mg of the sample were brought directly in the ion source where they were heated at a rate of 5°/min from 70° to 400°. Mass spectra were recorded under the following operating conditions: voltage of electrons, 70 V; emission current, 0.7 mA; temperature of source, 220°; scan duration, 1 sec. for mass range 33–349.

In order to monitor the evolution of volatiles, the following masses were used: mass 36 which is attributed to HCl, mass 78 to benzene, mass 91 to compounds of type C_6H_5R, mass 128 to aromatics with 4–5 double bonds and mass 178 to aromatics with 6–7 double bonds. Total ion current (TIC) is used for monitoring the evolution of total volatiles.

RESULTS AND DISCUSSION

Table 1 presents the glass-transition temperatures (T_g), the melting ranges and the temperature of the biggest peaks (T_{max}) measured by DSC. The T_g measured are in the range 78–83°, in good agreement with published values. As shown in the same table, the melting ranges vary from 122° to 210°. These values depend on the presence of additives and the type of polymer (*k* value, polymerization process). It should be noted that T_{max} is shifted towards higher temperatures as *k* values and stabilizer concentration increase.

Study of the mass spectra of various PVC and PVC mixtures with stabilizer leads to the conclusion that there are three temperature ranges of interest, viz. $<150°$ 150°–200° and $>200°$. Below 150° there is an evolution of volatile compounds such as polymerization residuals and volatile additives. In the range 150–200° there is an evolution of mainly HCl,

Table 1. Temperatures measured by DSC, for PVC samples

Sample	T_g(°)	Melting range (°)	T_{max}(°)
A	78	130–194	258
B	83	122–210	270
C	82	126–196	256
D1	82	132–206	276
D2	82	146–206	277

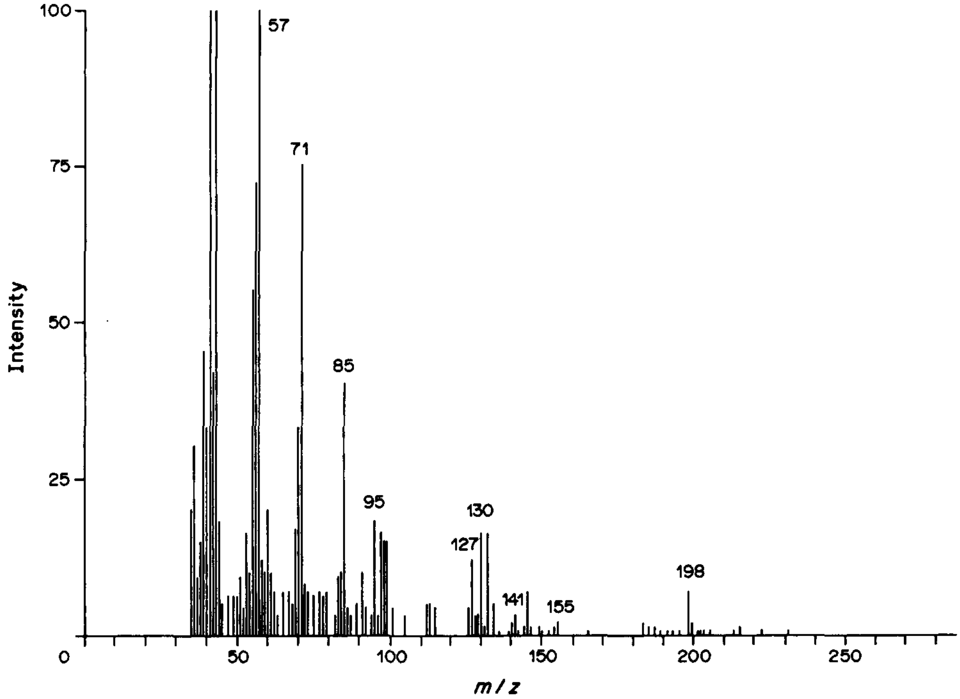

Fig. 1. Mass spectrum of PVC (*k* value 58, suspension polymerization) recorded at 110°.

above 200° HCl and aromatics with 2–4 rings are evolved. The composition of the mixture of volatiles formed above 200° depends mainly on the temperature of treatment [5].

Figure 1 presents the mass spectrum of A recorded at 110°. Masses 136, 134, 132, 130, 99, 97, 95, 62, 60 are attributed to tri-chloro-ethylene, masses 198, 155, 141, 127 to a hydrocarbon of the type $C_{14}H_{30}$, and the remainder are attributed to poly-(vinyl alcohol) residuals. Figure 2 presents the mass spectrum of sample C recorded at 110°. Masses 278, 223, 149 are attributed to DBP while masses 220, 205, 177, 161, 145 are associated with DBpC. Figure 3 presents the mass spectrum of sample D2 recorded at 200°. Masses 36 and 38, attributed to HCl, are absent because of the stabilizer. Masses 60, 73, 129, 143, 157,

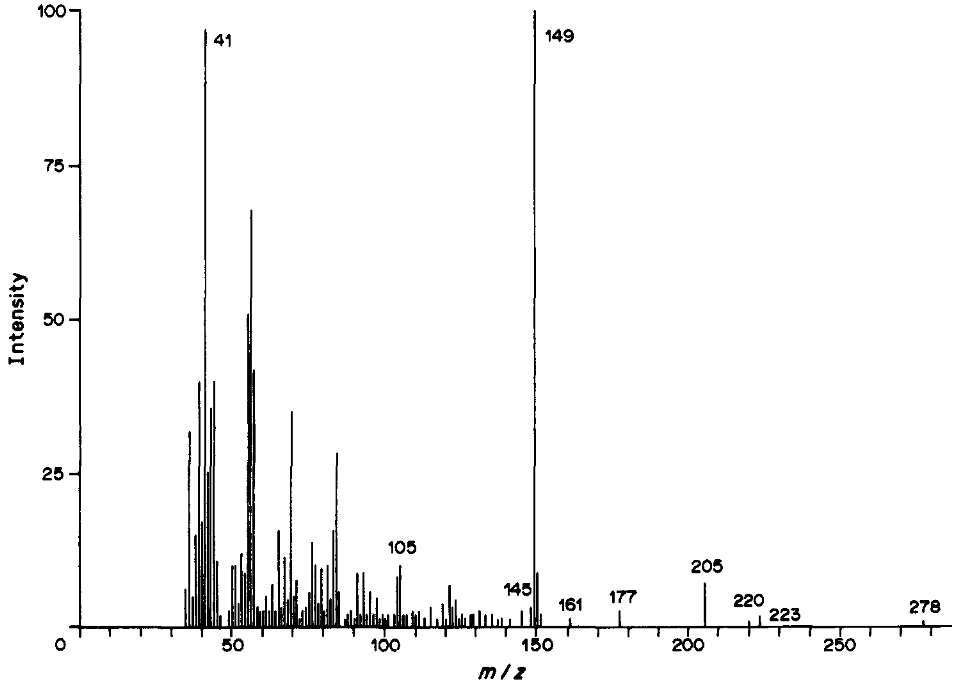

Fig. 2. Mass spectrum of PVC (*k* value 65, mass polymerization) recorded at 110°.

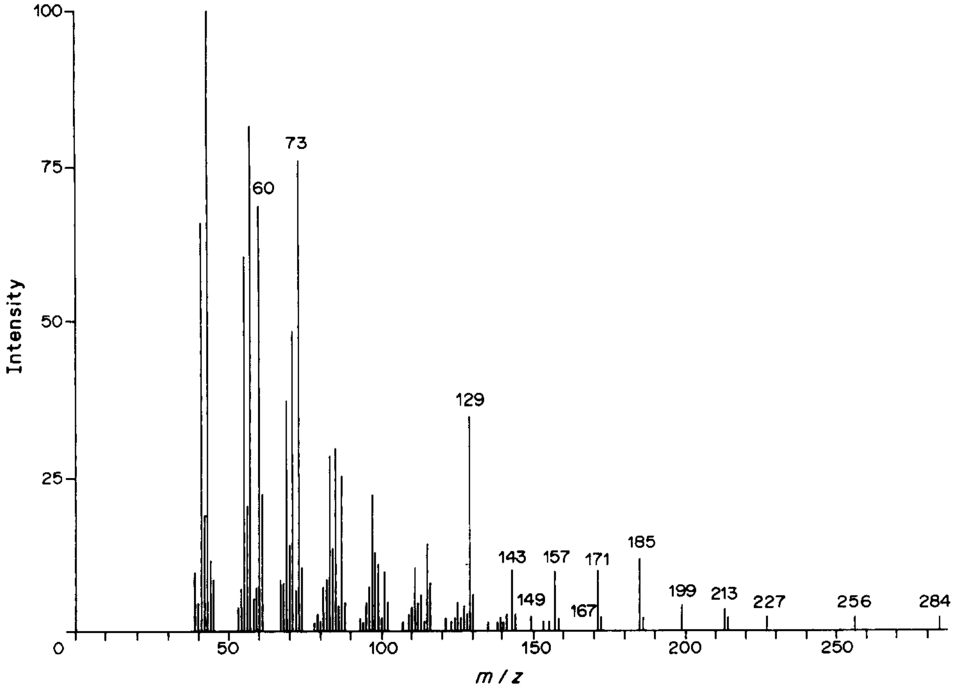

Fig. 3. Mass spectrum of PVC (*k* value 65, suspension polymerization) mixture with 5 pphr Ba/Cd stearates, recorded at 200°.

171, 185 ... 284 are attributed to stearic acid which is a product of the stabilization process while masses 149, 167 are associated with DOP. Figures 4 and 5 show the DSC curves for samples A and B respectively, together with the evolution profiles of volatiles recorded by DIMS.

It should be noted that the increase of TIC value above T_g is connected with the desorption of various volatiles such as polymerization residuals or additives (Fig. 1). HCl is initially observed by DIMS, in the crystallinity range, while DSC is not sensitive enough for this purpose. The T_{max} measured by DSC is

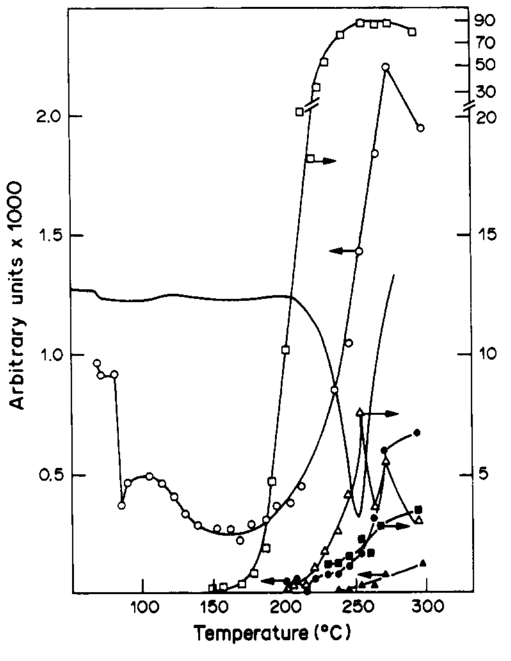

Fig. 4. DSC curve and DIMS evolution rate profiles for sample A (PVC of *k* value 58, suspension polymerization). (○) TIC, (□) HCl, (△) benzene, (●) compounds of the type C_6H_5R, (■) aromatics with 4–5 double bonds, (▲) aromatics with 6–7.

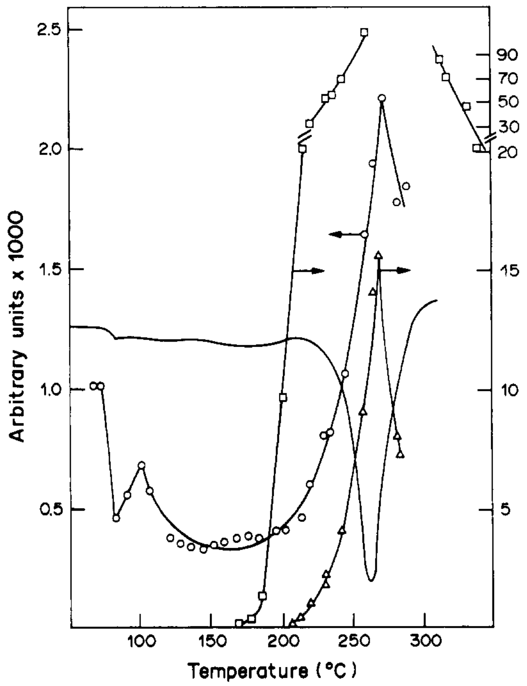

Fig. 5. DSC curve and DIMS evolution rate profiles for sample B (PVC of *k* value 65, suspension polymerization). (○) TIC, (□) HCl, (△) benzene.

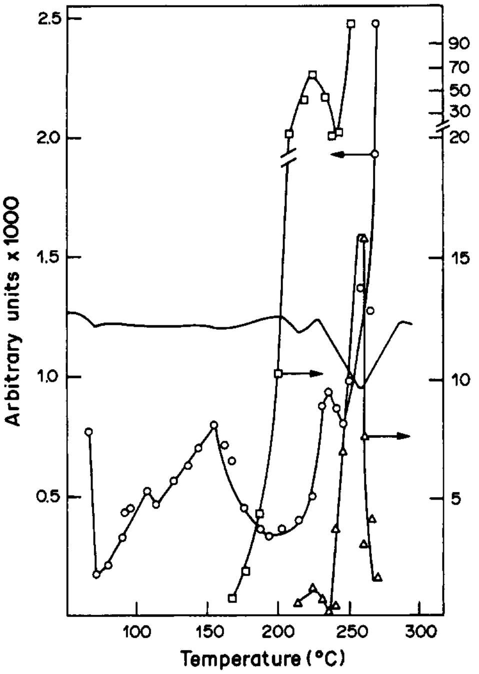

Fig. 6. DSC curve and DIMS evolution rate profiles for sample C (PVC of *k* value 65, mass polymerization). (○) TIC, (□) HCl, (△) benzene.

directly connected with the highest evolution rate of HCl and benzene. Both methods confirm that PVC with the lower *k* value decomposes at lower temperatures. Such a result is consistent with previous work [7].

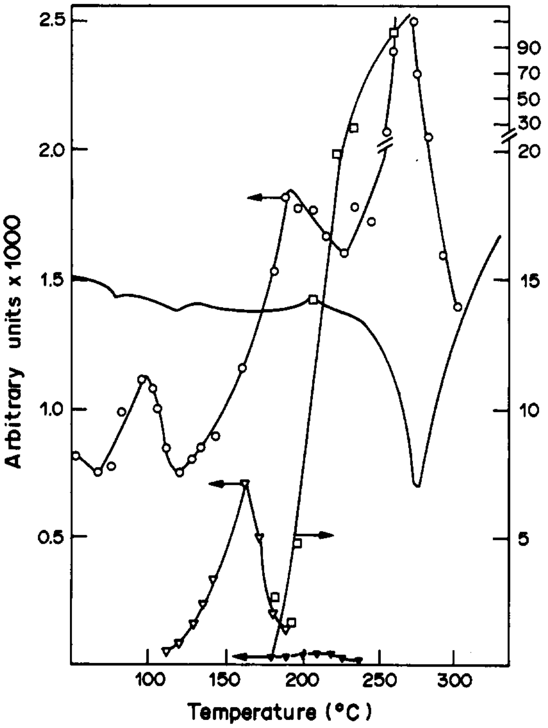

Fig. 7. DSC curve and DIMS evolution rate profiles for sample D1 (PVC of *k* value 65, suspension polymerization in mixture with 2.5 pphr Ba/Cd stearates). (○) TIC, (□) HCl, (▼) stearic acid, (▽) DOP.

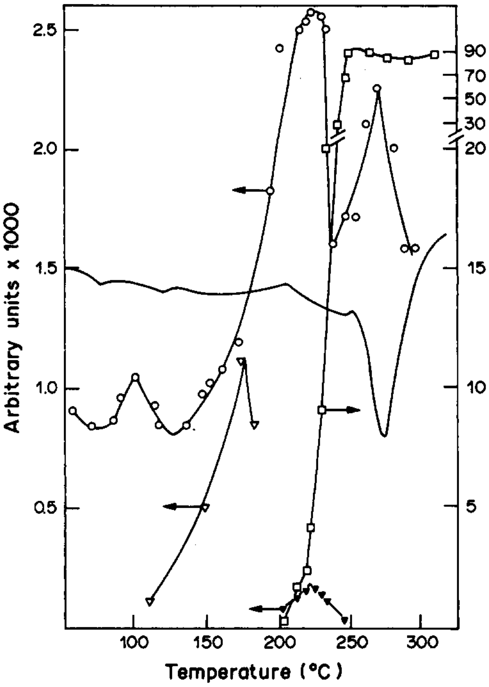

Fig. 8. DSC curve and DIMS evolution rate profiles for sample D2 (PVC of *k* value 65, suspension polymerization in mixture with 5 pphr Ba/Cd stearates). (○) TIC, (□) HCl, (▼) stearic acid, (▽) DOP.

Figure 6 presents the measurements on sample C. The first TIC peak is connected with the partial desorption of the antioxidant while the second TIC peak is attributed to the desorption of the plasticizer (Fig. 2). The presence of antioxidant seems to be responsible for the inhibition of dehydrochlorination observed in the DIMS curves. Figures 7 and 8 present the measurements for samples D1 and D2 respectively. The three maximum values observed for TIC profile are associated with the desorption of polymerization residuals, (Fig. 5), the stabilization process (followed by stearic acid evolution) and with the final degradation process respectively.

The major quantity of plasticizer is given off in the melting range. The evolution of HCl with accelerated rate (T_{ac}) shifts towards higher temperatures due to the action of the stabilizer. The values of T_{ac} measured by DIMS are 160, 180 and 200° for samples B, D1 and D2 respectively, while the same temperatures measured by DSC are 204, 238 and 254° respectively.

CONCLUSIONS

DIMS can be used for detailed insight of the DSC degradation and stabilization curves of the PVC. Since the addition of the stabilizer modifies the degradation profile of PVC at earlier stages, DIMS can be used for interpretation of the multistage processes recorded by DSC. The basic processes that can be recognized are the desorption of additives and the chemical reactions of degradation and stabilization.

The results from the two methods are in good agreeemnt but it should be noted that DIMS is more sensitive in tracing the initial stages of the various reactions. It also should be noted that DSC and DIMS can be used for differentiating PVC from mixtures of the polymer with stabilizers or anti-oxidants, based on the modifications of DSC and DIMS curves. Moreover DIMS can be used for differentiating various types of PVC based on the presence of various volatile polymerization residuals and additives that can be recorded in the mass spectra.

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