COORDINATION POLYMERS. IX.

STUDIES ON THE THERMAL BEHAVIOUR OF IONIC POLYESTERS

I. Vancsó-Szmercsányi and Á. Szilágyi

Research Institute for the Plastics Industry, Budapest, Hungary

Poly-(butanediol-1,4-adipate) and poly-(diethyleneglycol-succinate) polyesters and their "ionized" derivatives, containing Mg^{2+} and Zn^{2+} ions with different stoichiometric ratios to the chain-end COOH groups of the polyesters have been investigated by derivatograph.

The thermal decompositions of the metal-containing polyesters differ significantly from those of the unionized polyesters. These differences are connected with the chemical repeating unit of the polyesters and the chemical nature of the metal ions, and proportional to the amount of the latter.

An explanation is given of the catalytic effect of metal ions on the process of decomposition of the polyesters.

In the late sixties, systematic investigations were started on the products of the interactions between various organic polymers (or monomers) and ions (especially metal ions), i.e. on ion-containing polymers. These new products were denoted as coordination or ionic polymers.

The expression ionic polymers refers to a wide variety of such systems [1], namely, all polymeric systems including ionic associates or ionic dipolar associates. It is reasonable to distinguish a subdivision denoted as coordination polymers, where the repetitive units in the molecule are linked by coordinate bonds. These repetitive units are generally organic atomic groups, linked mainly through metal ions. In this way, quite complicated systems are formed since, in most cases, composite multidentate ligands represent the organic units, and they undergo both intermolecular and intramolecular interactions of several kinds and different strengths with counter-ions.

Their variants of the highest industrial importance are metal derivatives of polymers containing COOH groups or COO^- ions, such as zinc-polycarboxylate cements [2], ionomers [3], carboxylic elastomers [4], etc.

In these cases, COOH groups as ligands are located rather periodically along the polymer chain (such as in polymers or copolymers of methacrylic acid). There are, however, systems having carboxyl groups as terminals, such as polyesters and polyamides.

Carboxylic or alcoholic OH end-groups of polyesters based on dicarboxylic acids and diols act as ligands in their complexes with metal ions [5, 6]. Because of their polarized nature, $C = O$ groups of ester bonds in the polyester molecule can also coordinate metal ions according to the following pattern:
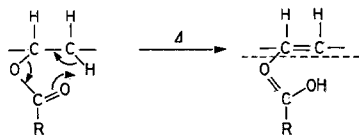
A quite simple method for attainment of the interaction between polyester molecules and metal ions is to react a polyester with base anhydride-type metal oxides (such as MgO, ZnO, CaO) in the presence of a trace amount of water [5]. As a first step, metal carboxylates are produced; an association of the further ligand groups in the polyester molecule may then occur according to the pattern in Fig. 1.
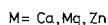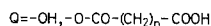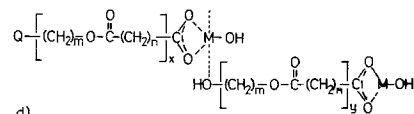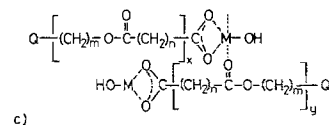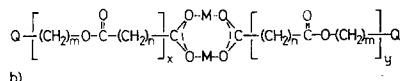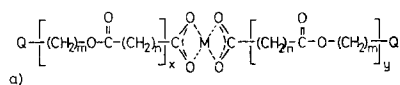

Fig. 1a, b. Possible structure of carboxylate complexes formed by different metal ions. c. Coordination of mixed hydroxo-carboxylate complexes of divalent metal ions to the ester-carbonyl groups of a polyester chain. d. Coordination of mixed hydroxo-carboxylate complexes of divalent metal ions to the chain-end hydroxy group of a polyester

Such a reaction leads to considerable changes in the physical and chemical properties of the original polyester.

"Ionization" of polyesters is an important procedure in the industry of unsaturated polyesters.

In the present paper, thermal investigations were selected as one of the test methods of ionized polyester systems, providing well-interpretable diverse information.

Experimental

Materials

Polyesters were synthetized in the molten state by polycondensation of a dicarboxylic acid with the equivalent amount of a diol as described previously [7]. The following polyesters were prepared:

— semicrystalline polyester of adipic acid with butane-diol-1,4 (ABu), with an average molecular weight of about 1000;
— syrup-like amorphous polyester of succinic acid with diethyleneglycol (SuDig), with an average molecular weight of about 700.

"Ionized" compounds of these polyesters were prepared by their reactions with different amounts of MgO or ZnO (analytical grade) in benzene solution, followed by thorough removal of the solvent [8]. Metal contents of all preparates were checked analytically.

Methods

Thermal investigations were carried out with a derivatograph (Paulik–Paulik–Erdey system [9], Hungary) recording the differential thermoanalytical (DTA), thermogravimetric (TG) and derivative thermogravimetric (DTG) curves simultaneously as a function of temperature. A heating rate of 5°/min was used, under a N_2 atmosphere.

Results and discussion

From the thermal curves of the adipic acid–butanediol (ABu) polyesters (Fig. 2), considerable differences were found between the "ion-free" and "ionized" polyester systems. The DTA trace of the former (with zero metal ion content) shows a single sharp endothermic peak at 375°, corresponding to the decomposition of the polyester. The DTA peak of the main decomposition of Mg^{2+}-containing polyesters, however, is at a considerably lower temperature (about 330°); in fact, at a Mg^{2+} content of 1.0 equivalent, the peak is split into several bands, the first of them at 300°. Another peak for the ion-containing samples, observed at about 360°, is assigned as the decomposition of $MgCO_3$ into MgO and CO_2.

The temperature of the initial weight loss, as indicated by the DTG traces, is 300 and $235-240°$ for the ion-free and ionized samples, respectively. This difference in thermal stability between ion-free and Mg-containing polyesters can be observed in the TG traces as well. No essential influence of the Mg concentration was found in the range studied.

The first DTA peak, at $57 \pm 2°$, corresponds to the melting heat of crystalline samples.

Figures 3 to 5 present the individual thermal curves for the above samples.

The same polyester resin (ABu) was reacted with different amounts of ZnO. Results obtained on the products are shown in Fig. 6. It can be seen that the presence of Zn ions alters the thermal behaviour of the resin, to an extent depending
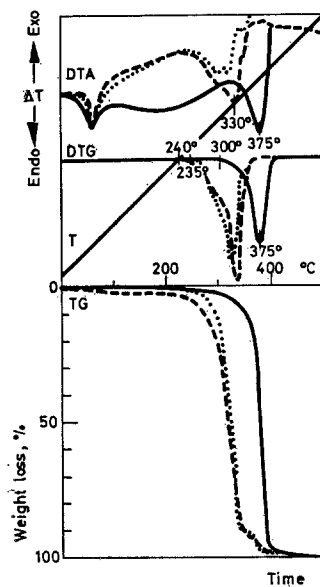
Fig. 2. Thermal curves of poly-(butanediol-1,4-adipate) polyester ($M_n = 1000$ g · mol^{-1}) and its metal complexes containing 1.0 and 1.5 equiv. Mg^{2+}/chain-end COOH groups, respectively.
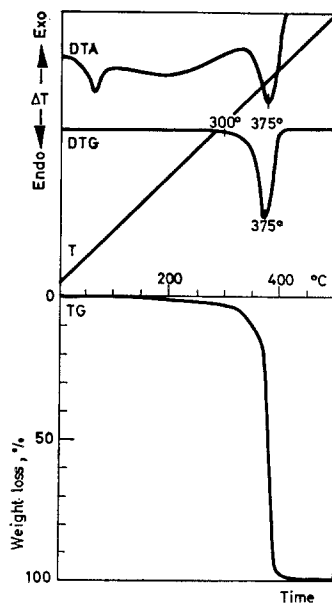0 ——————, 1.0 Mg ....., 1.5 Mg ------

Fig. 3. Thermal curves of poly-(butanediol-1,4-adipate) polyester ($M_n = 1000$ g · mol^{-1}).
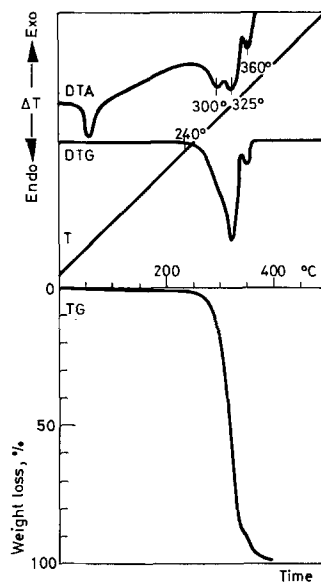
Fig. 4. Thermal curves of poly-(butanediol-1,4-adipate) polyester ($M_n = 1000$ g · mol^{-1}) containing 1.0 equivalent Mg^{2+}/chain-end COOH group
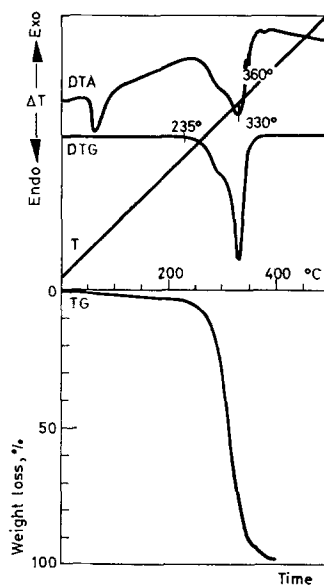

Fig. 5. Thermal curves of poly-(butanediol-1,4-adipate) polyester ($M_n = 1000$ g · mol^{-1}) containing 1.5 equivalents Mg^{2+}/chain-end COOH group

on its amount. The most striking effect is that the originally one-step thermal decomposition becomes bimodal. The initial temperature of its first step (as estimated from the DTG curve) is lower by about 50° than that for the ion-free polyester. The sample containing 0.4 equivalents of Zn^{2+} exhibits only a vague indication of the two decomposition steps but, at higher ion concentrations, a complete separa-
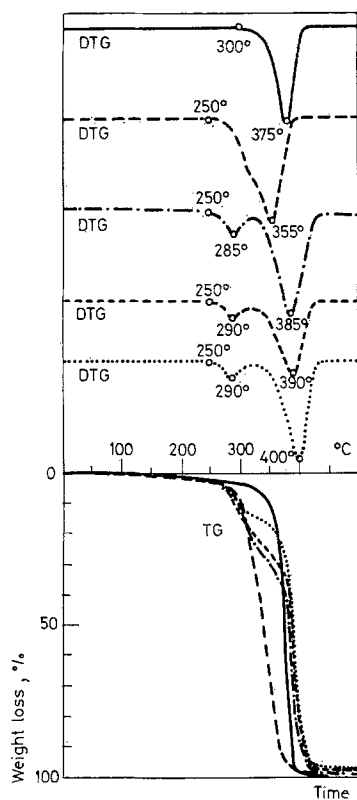

Fig. 6. TG and DTG curves of the Zn complexes of poly-/butanediol-1,4-adipate) polyester $M_n = 1000$ g · mol^{-1}) containing 0 (————), 0.4 (----), 0.97 (—.—.—), 1.09 (----) and 1.32 (.....) equiv. Zn^{2+}/chain-end COOH group, respectively

tion takes place. The TG curves, in accordance with the DTG traces, show the two decomposition steps, permitting their quantitative estimation. The ratio between the first and the second steps is influenced by the concentration of Zn.

In Fig. 7, DTA and TG traces are shown. Similarly to the DTG curves, the DTA curves indicate the splitting of the originally unimodal decomposition, accompanied by a successive increase in the temperature of the second step as a function of the ion content.

In Fig. 8, thermal curves of the ion-free ABu polyester and its ionized derivatives containing a nearly equivalent amount of Mg^{2+} or Zn^{2+} are compared. The difference between the two ions is striking. For both ions, the first decomposition step (I) in the DTG curves starts at a temperature lower by 50° than that for the ion-free polyester. The larger second step (II) for Zn^{2+} is shifted toward somewhat higher

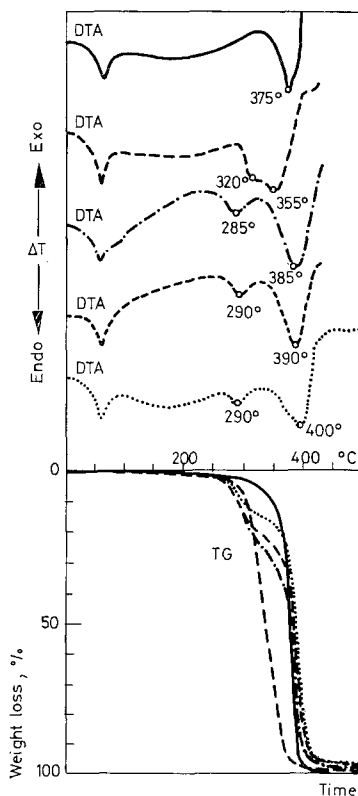Fig. 7. TG and DTA curves of the Zn complexes of poly-(butanediol-1,4-adipate) polyester ($M_n = 1000$ g · mol^{-1}) containing 0 (———), 0.4 (----), 0.97 (—.—.—), 1.09 (----) and 1.32 (.....) equiv. Zn^{2+}/chain-end COOH group, respectively

temperatures (as mentioned before), while that for Mg^{2+} is rather overlapped by step I (appearing only as a shoulder). In this case, the temperature of the last stage of the decomposition (325° at the DTG peak) is much lower than that for the ion-free sample (375°).

Results for polyesters from succinic acid and diethyleneglycol (SuDig) and their Mg^{2+}-modified samples are presented in Fig. 9. It can be seen in the composite curve that the shapes of the TG traces are practically the same. The differences in
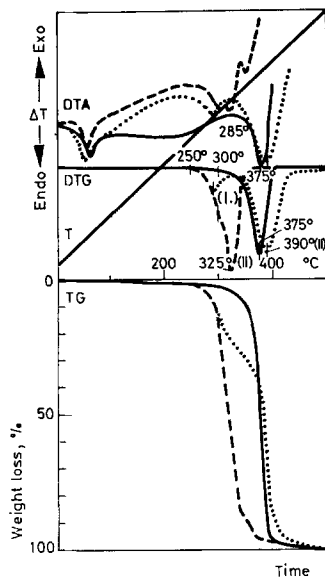
Fig. 8. Thermal curves of poly-(butanediol-1,4-adipate) polyester ($M_n = 1000$ g · mol^{-1}) (————) and its complexes containing 0.97 equiv. Zn^{2+}/chain-end COOH group (.....) and 1.0 equiv. Mg^{2+}/chain-end COOH group (---), respectively

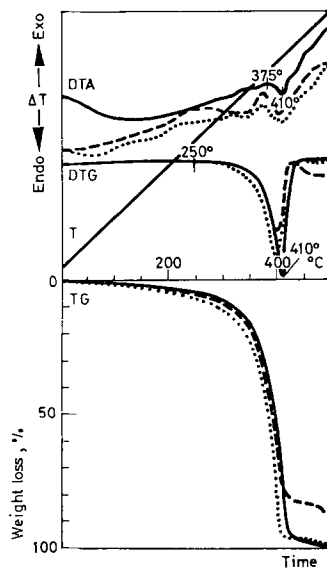Fig. 9. Thermal curves of poly-(diethyleneglycol-succinate) polyester ($M_n = 700$ g · mol^{-1}) (————) and its complexes containing 0.75 (.....) and 1.5 (-----) equiv. Mg^{2+}/chain-end COOH group, respectively

the DTA curves before the decomposition stage are presumably caused by some chemical reactions such as condensation or hydrolysis due to the thermal effect. Their extent depends on the ion content. Exothermic and endothermic reactions follow each other in this stage, some of them (condensations) resulting in a weight loss, too. This is the reason for the slight deviations in the TG curves before the thermal decomposition stage. After the decomposition has started (at about 300°), the thermal curves are essentially independent of the Mg content.

Before the interpretation of the present experimental results, let us recall the knowledge relating to the mechanism of thermal decomposition of polyesters.

In the literature, the thermal decomposition of polyesters is treated on the basis of the mechanism of decomposition of simple esters. It was established long ago that the main thermal decomposition step for simple aliphatic esters, in the presence of β-H atoms, is a *cis*-elimination resulting in olefins and carbonyl compounds, preceded by formation of a six-membered chelate ring through H-bonding [10, 11]:

This result was adapted to the decomposition of polyesters by several authors [12, 13], presenting the following basic mechanism:
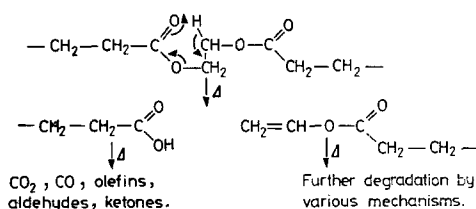
In the first step, therefore, a carboxyl compound and a vinyl ester are formed. Later, the carboxyl compounds are decarboxylized and the vinyl ester decomposes. The latter process may take place by various kinetic patterns (such as simultaneous or concurrent reactions) [14, 15].

The final products of the complete decomposition are mainly CO_2, CO, olefins, aldehydes, etc. During the process, decomposition products can react with each other: unsaturated compounds can polymerize; vinyl groups can react with COOH compounds; etc.

In the presence of metal ions, the thermal decomposition of polyesters is modified. Zimmermann *et al.* [16] conducted extensive studies on the catalytic effects of metal ions on the decomposition of the industrially important poly(ethylene terephthalate) and its related model polyesters. They intended to obtain information about the effects of polyesterification catalysts and of polyesters on the thermal stability of the product. They followed the decomposition by quantitative measurements of COOH groups under isothermal conditions. From the kinetics of decomposition, they concluded that the rate constant of decomposition was markedly increased by the presence of metal ions, introduced generally in acetate form. The order of catalytic efficiency of the individual ions towards the thermal decomposition is as follows:

$$Ca < Mn < Co < Zn$$
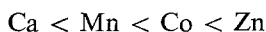
This order is in agreement with the complex stability order presented by Irving and Williams [17].

Zimmermann and his co-workers gave an explanation for the mechanism of ionic catalysis, starting from the mentioned transient cyclic structure between the ester carbonyl and the other H atoms in β position, followed by a disproportionation. If an electron acceptor (metal ion) was present in the system, it coordinated the adjacent ester carbonyl; then an inductive effect appeared, due to the deformation of the electron distribution, which promoted splitting-off of that particular proton and formation of a COOH compound (the latter was measured as a function of time):
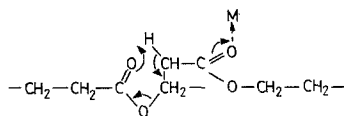
This obvious interpretation was related to their experimental result that diol-based polyesters containing ether bonds exhibited practically no metal ion catalysis since, in this case, polarization could not act to the hydrogen through the $-O-CH_2-CH_2-$ group in the chain:
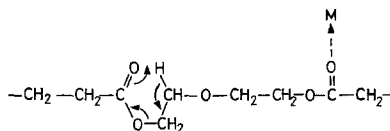
These mechanisms boldly outlined in the literature were based generally on iso-thermal decompositions, chemical analyses of decomposition products, pyrolysis gas chromatography, and mass spectrometry. The latter contemporary method was successful in the elucidation of several details related principally to non-catalytic decompositions and to the determination of the decomposition products [18, 19].

As far as the present results are concerned, it can be established that Mg^{2+} ions cause considerable quantitative changes in the thermal behaviour of polyesters based on adipic acid and butanediol (ABu). In the presence of the ion, the decomposition temperature is markedly lower and the originally uniform decomposition splits into two overlapping steps.

Zn^{2+} ions have a greater, but essentially qualitative effect on the decomposition as a function of their concentration. Ion-containing samples decompose in two distinct steps. The first starts at a temperature lower by 50°, while the temperature of the second is higher than that of the single step of the ion-free polyester.

According to literature data, in the first step of the decomposition of polyesters, the formation of carboxyl compounds and vinyl esters is independent of the catalytic effect.

The decomposition temperatures of these compounds into volatile products are obviously affected by the mechanisms of the consecutive reactions. Decarboxylation of the carboxylic acid formed in the first step inevitably dominates the first TG step of polyesters containing Zn^{2+}. Its lower temperature is evident, since the carboxyl compound as initial product from the decomposition of the ion-containing polyester appears at a low temperature, due to the ion-catalyzed decomposition. The other initial decomposition product from the ion-free polyester, a vinyl ester, decomposes in the same temperature range as decarboxylation, and thus a single decomposition step is observed. In the presence of Mg^{2+}, a slight splitting of the decomposition takes place, as the majority of the vinyl ester decomposition precedes decarboxylation. With Zn^{2+}, on the contrary, the quite complete separation of the two steps is attributed to a shift in the vinyl ester decomposition toward higher temperatures as compared with that for the ion-free polyester. This can only be interpreted by a change in the mechanism of the vinyl ester decomposition by virtue of the presence of Mg or Zn ions. This assumption is supported by some literature data [14, 15] emphasizing the diversity of the decomposition mechanism of vinyl esters. It is worthwhile to take into account that metal ions have a specific effect on the thermal stability of organic materials; they can either stabilize the system or even catalyze the thermal decomposition.

Obviously, the concurrent reactions taking place during the decomposition are also dependent on the temperature. At alternative heating rates, therefore, the thermal curves showed different courses as compared to those obtained at 5°/min. The presentation of these curves has been omitted.

Results for succinic acid–diethyleneglycol-based (SuDig) polyesters are in good agreement with the mechanism of decomposition of polyesters synthetized from etheric glycols [16], as the presence of Mg ions is practically ineffective towards the thermal decomposition.

Application of the decomposition mechanisms described in the literature led only to an outlined interpretation of the present experimental results. A detailed quantitative analysis of such a complicated reaction system would have been beyond the scope of the first part of the present work, which intended to give a general picture of the thermal decomposition of ionized polyesters.

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ZUSAMMENFASSUNG — Poly-(butandiol-1,4-adipat) und Poly-(diethylenglycolsuccinat) poly-ester und ihre «ionisierten» Derivate — mit Mg^{2+} — und Zn^{2+}-Ionengehalt in verschiedenen stöchiometrischen Verhältnissen zu den endständigen COOH-Gruppen der Polyester — wur-den im Derivatographen untersucht.

Die thermische Zersetzung der metallhaltigen Polyester unterscheidet sich wesentlich von nicht-ionisierten Polyestern. Diese Unterschiede sind mit den sich wiederholenden chemischen Einheiten der Polyester und der chemischen Beschaffenheit der Metallionen verbunden, und proportional dem Anteil derselben.

Es wird eine Erklärung des katalytischen Effekts der Metallionen auf den Zersetzungsvor-gang der Polyester gegeben.

Резюме — С помощью дериватографа была исследованы полиэфиры полибутандиол-1,4-адипиновой кислоты и полидиэтиленгликоль янтарной кислоты и их «ионные»производные, содержащие ионы Mg^{2+} и Zn^{2+} различного стехиометрического состава относительно концевых СООН групп полиэфиров. Установлено, что термическое разложение металло-содержащих полиэфиров значительно отличается от разложения «неионных» полиэфи-ров. Эти различия обусловлены химически повторяющейся цепью полиэфиров и химичес-кой пррпдой ионов металла и зависит от количества последних. Представлено объяснение каталитического действия ионов металла на процесс разложения полиэфиров.