A THERMOANALYTICAL STUDY OF POLYESTERIFICATION REACTIONS IN SOLID MIXTURES OF PENTAERYTHRITOL AND DICARBOXYLIC ACIDS, OXALIC ACID AND SUCCINIC ACID

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ABSTRACT

DSC and TG, supported by IR spectrophotometry, evolved gas anaysis and pyrolysis–gas chromatography, were applied to the study of reactions in solid mixtures of pentaerythritol, 2,2-bis(hydroxymethyl)-1,3-propanediol, with succinic acid and with oxalic acid. In all cases the pentaerythritol reacted with the acid in 1:2 mole ratio to form polyesters. However, the nature of the polymeric product depended on the amounts of reactants taken.

INTRODUCTION

Condensation and polycondensation reactions of solids at elevated temperatures have been observed. Polycondensation reactions which involve only a single material include the formation of Nylon-6 (polycapramine) from ϵ-aminocaproic acid [1–3], the thermal conversion of N-carboxy-α-amino acid anhydrides to the corresponding polypeptides [4], and the preparation of poly(phenylene sulfide) from *para*-halogen substituted thiophenol salts [4]. The occurrence of polycondensation reactions between two solid reactants at elevated temperatures is also known [5]. On the basis of differential scanning calorimetry curves of solid mixtures of polyhydric alcohols and dicarboxylic acids, the possibility of polycondensation reactions was proposed [6,7]. In this investigation reactions in solid samples of pentaerythritol (PE), 2,2-bis(hydroxymethyl)-1,3-propanediol, mixed with succinic acid (SA) and PE mixed with oxalic acid (OA) were studied. Using differential scanning calorimetry (DSC) and thermogravimetry (TG), along with evolved gas analysis, infrared spectrophotometry, and pyrolysis–gas chromatography, the stoichiometries of these reactions were established and evidence of the natures of the products was obtained.

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EXPERIMENTAL

The chemicals used were reagent grade pentaerythritol (Eastman Organic Chemicals), reagent grade succinic acid (Matheson, Coleman and Bell), and Certified A.C.S. oxalic acid dihydrate (Fisher Scientific). Finely powdered mixtures of $5:1$, $2:1$, and $0.5:1$ mole ratios of acid to alcohol were prepared. These mixtures, identified simply as $5:1$, $2:1$, and $0.5:1$ mixtures, were used throughout the investigation. DSC and TG studies were carried out using both powdered samples and samples pressed into disk form at 2000 psi. For DSC and TG studies, each sample was run in a sealed aluminum pan with a pin hole to allow the escape of evolved gases. Dynamic nitrogen and air atmospheres were employed in order to study effects of inert and reactive atmospheres. The results reported here were obtained at a heating rate of $20°C$ min^{-1} using 10–20-mg samples. Solids taken for infrared analysis were formed directly on a KBr pellet inserted in the thermobalance on a specially made aluminum boat.

All DSC runs were carried out on a Perkin-Elmer DSC 1 with a Leeds and Northrup Speedomax W Recorder. TG curves were obtained from the DuPont 950 TGA.

IR spectra of intermediate and final solid products were obtained using a Perkin-Elmer 137 sodium chloride spectrophotometer. The boat used to form the intermediate and final solid products consisted of a piece of aluminum foil shaped to hold the KBr pellet. It was suspended from the quartz balance beam by a nichrome wire attached to opposite sides of the boat. For hot-stage microscopy, a Nagle Co. hot stage microscope was used.

Samples for evolved gas analysis (EGA) were formed under helium atmosphere in the DuPont 950 TGA and collected in a 1/8 in. stainless-steel liquid-nitrogen trap, packed with Waters Associates 80/100 mesh Porapak Q. After the evolved gases were collected, the liquid nitrogen was removed, and the trap was heated in a paraffin oil bath at $110°C$. The gases were flushed into a Gow Mac Instrument Co. gas chromatograph equipped with a thermal conductivity detector (TCD). The carrier gas was helium, and the flow rate was approximately 40 ml min^{-1}. Separation was carried out on a 1/4 in. 2-ft. stainless-steel column packed with 80/100 mesh Porapak Q. The TCD response was recorded on a Leeds and Northrup Speedomax W Recorder.

Pyrolysis equipment included a Chemical Data Systems Pyroprobe 100, a Varian 3700 gas chromatograph equipped with a TCD, and a Houston Instruments Omniscribe model number B 5117-5 chart recorder. The column used for the separation was a 1/8 in. stainless-steel column packed with Chromasorb 103.

RESULTS AND DISCUSSION

The nature of the atmosphere (i.e., air vs. nitrogen) had no effect on the TG curves and little effect on the DSC curves. Further, in terms of the information provided, the TG and DSC curves of samples pressed into disk form were the same as those of unpressed powdered mixtures. Reported here are TG and DSC curves of unpressed powdered mixtures obtained in air.

The TG and DSC curves of SA and PE mixtures are given in Fig. 1. The TG curves show a gradual weight loss which started at temperatures slightly greater than 200°C. From the 2:1 mixture a relatively stable product was obtained in the 325–410°C temperature range. The TG curve of the 5:1 mixture indicates a relatively stable product at 410°C and the TG curve of the 0.5:1 mixture provides at least a hint of such a product, also at 410°C. The materials which existed at 410°C underwent decomposition at temperatures greater than 410°C. Under the conditions of this study, the decomposition of pure SA was complete at 300°C and that of pure PE was complete at 400°C. Clearly, the products at 410°C were more stable than either of the starting materials.

A comparison of the materials which existed at 410°C is of interest. From the 0.5:1 mixture a white powder was obtained. Both the 2:1 and the 5:1
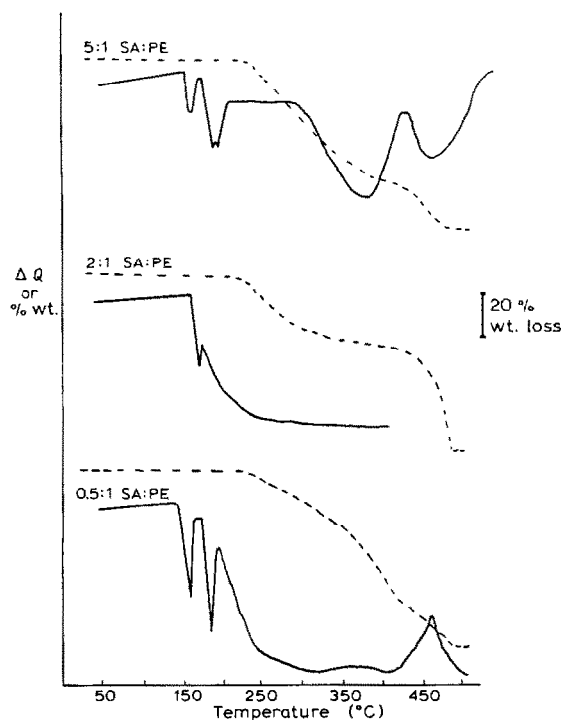

Fig. 1. TG (- - - - - -) and DSC (————) curves of succinic acid–pentaerythritol mixtures.
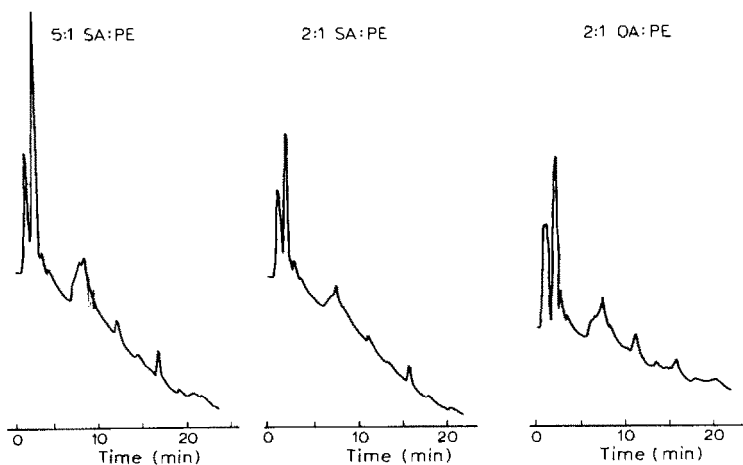
Fig. 2. Pyrograms of polymeric products.

mixtures produced a transparent, plastic-like film. However, the pyrograms for the 5 : 1 and the 2 : 1 mixtures, given in Fig. 2, show rather different decomposition patterns, indicating that the nature of the plastic-like material depends on the relative amounts of the reactants. Such a dependence is consistent with theory [8]. While none of the peaks was identified, the complete repeatability of the pyrograms was established.

All three DSC curves of Fig. 1 contain an endothermic peak, the onset temperature of which was about 150°C. This peak arose from the melting of an SA–PE eutectic mixture. A melting-point plot obtained as part of this work indicates the existence of two eutectic mixtures, at approximately 15 and 80 mol% SA, both of which melt at about 150°C. The presence of both solid and liquid materials at the latter temperature was observed by hot-stage microscopy. This melting endotherm was followed by a general endothermic trend.

Both the 5 : 1 and the 0.5 : 1 mixtures produced a second endothermic peak, the onset temperatures of which were in the range 185–190°C. This temperature range includes both the melting temperature of SA and the temperature at which PE undergoes a phase change from tetragonal to plastic cubic [9]. It appears that, at 185–190°C, excess unreacted SA existed in the 5 : 1 mixture and excess unreacted PE existed in the 0.5 : 1 mixture. The absence of a peak indicates that neither unreacted SA nor unreacted PE was present at 185–190°C in the 2 : 1 mixture.

Infrared spectra of the solid residues produced by the 2 : 1 mixture in the 250–350°C temperature range are given in Fig. 3. At 250°C, the broad peak at 2.8–3.0 μm suggests both the alcohol and the carboxylic acid OH groups stretch. At 300 and 350°C a sharp peak at 2.8 μm indicates that only alcohol groups were present. Further, as the temperature increased from 250 to 350°C the carbonyl stretch peak in the range 5.7–5.9 μm became much
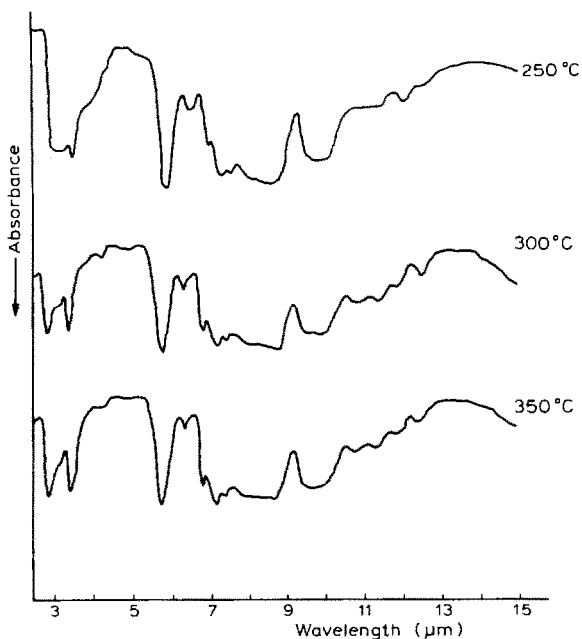
Fig. 3. Infrared spectra of the residues obtained from the 2:1 mixture of succinic acid and pentaerythritol.

sharper and of the lower wavelength, characteristic of esters. A similar sequence of infrared spectra was obtained using the 5:1 mixture; the infrared spectra of the white powder produced by the 0.5:1 mixture were too poorly resolved to be useful.

Chromatograms of the gases evolved during the heating of SA–PE mixtures from room temperature to 400°C are shown in Fig. 4. The gas chromatogram of the 5:1 mixture includes, in order of increasing retention time, peaks due to carbon monoxide, carbon dioxide, and water. The small size of the carbon dioxide peak is due, largely, to the low sensitivity to carbon dioxide of the thermal conductivity detector. The chromatogram of the 2:1 mixture contains only carbon monoxide and water peaks. Gas chromatograms obtained under the same conditions using pure SA and pure PE included water, carbon dioxide, and carbon monoxide peaks. However, the carbon monoxide peaks of the latter were much smaller than those of the mixtures.

The occurrence of esterification reactions in all three mixtures is clearly indicated. Moreover, the stability of the products at relatively high temperatures as well as the physical nature of the products gives evidence of polyesterification. If the equation

$$n \text{ PE} + 2n \text{ SA} \rightarrow \text{Polymeric product} + 4n \text{ H}_2\text{O} \tag{1}$$
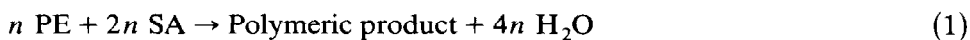
is taken as the model, the calculated weight losses (including the decomposi-
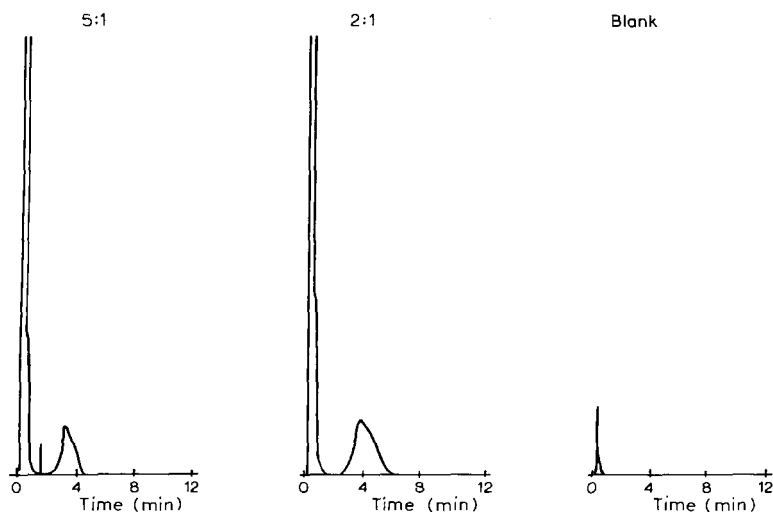
Fig. 4. Gas chromatograms of succinic acid–pentaerythritol mixtures.

tion of excess reactant in the 5 : 1 and 0.5 : 1 mixtures) are 58.7, 19.4, and 61.5% for the 5 : 1, 2 : 1, and 0.5 : 1 mixtures, respectively. As shown in Table 1, only the value calculated for the 0.5 : 1 mixture agrees with the experimentally observed weight loss. However, using the equation

$$n \text{ PE} + 2n \text{ SA} \rightarrow \text{Polymeric product} + 4n \text{ H}_2\text{O} + n \text{ CO} \qquad (2)$$
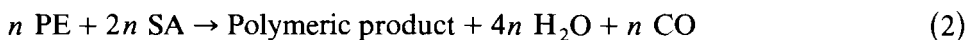
as the model, the calculated weight losses for the 5 : 1 and 2 : 1 mixtures become those given in Table 1.

It appears that unless PE is present in excess the end groups of the polymeric product are acid groups and that these undergo decarbonylation. This is consistent with the presence of alcohol groups in the product even when the initial mixture contained excess SA, as indicated by the infrared spectra. Further, it is consistent with the fact that the amounts of carbon monoxide produced by the 5 : 1 and 2 : 1 mixtures were much greater than the amounts produced by the decomposition of the pure starting materials. It is believed that the carbon dioxide peak of the 5 : 1 mixture (Fig. 4) arose from the decomposition of excess SA. The absence of a carbon dioxide peak

TABLE 1

Weight losses of SA–PE mixtures

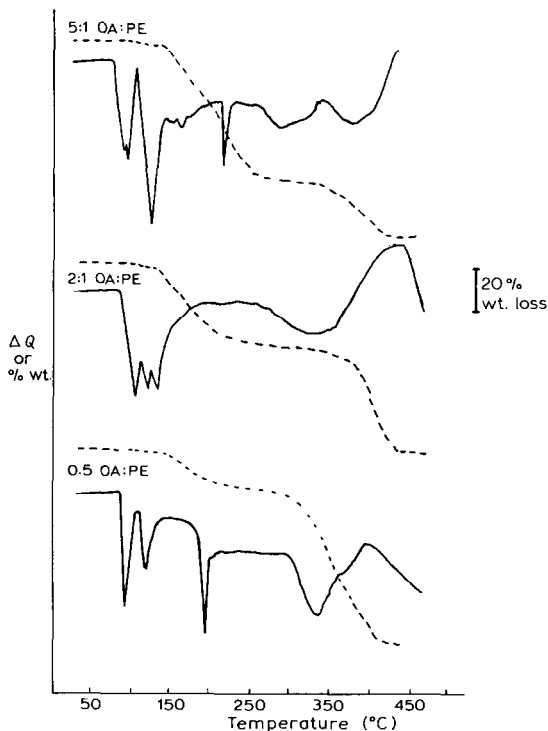| Mole ratio SA : PE	Temp. (°C)	Weight loss (%)		
		Observed	Calculated	(model eqn.)
5 : 1	410	62	62.5	(2)
2 : 1	360	28	26.9	(2)
0.5 : 1	410	62	61.5	(1)

Fig. 5. TG (- - - - - -) and DSC (————) curves of oxalic–pentaerythritol mixtures.

of the 2 : 1 mixture is taken as additional evidence for the 2 : 1 stoichiometry. Why the number of moles of carbon monoxide evolved should be equal to the number of moles of PE taken is not clear. However, in all cases where the PE was not present in excess the weight losses agree with this model.

The TG and DSC curves of OA and PE mixtures are given in Fig. 5. The TG curves of the 5 : 1 and 2 : 1 mixtures show the formation of a product which decomposed at temperatures greater than 320°C. The TG record of the decomposition of the comparable product of the 0.5 : 1 mixture is obscured by the concurrent decomposition of excess PE.

The DSC curves of Fig. 5 contain several endothermic peaks in the 75–150°C temperature range. These peaks arose from melting and reaction as well as from the dehydration of the oxalic acid. The PE phase change at 185°C and the decomposition of the excess PE are clearly evident in the 0.5 : 1 mixture but not in the other mixtures. The source of the endothermic peak at about 210°C of the 5 : 1 mixture has not been established. Possibly, melting of the mixture of product and excess OA occurred.

The materials formed between room temperature and 320°C in all three mixtures were white powders. Only poorly resolved infrared spectra of these materials were obtained but, as in the SA–PE mixtures, the spectra indicate ester formation. Further, the pyrogram of the product of the 2 : 1 mixture,
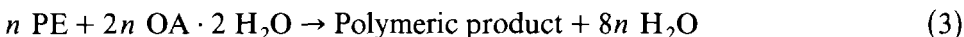
TABLE 2

Weight losses of OA–PE mixtures

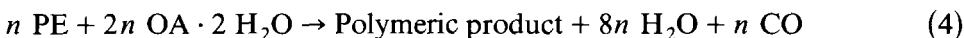| Mole ratio OA : PE	Temp. (°C)	Weight loss (%)		
		Observed	Calculated	(model eqn.)
5 : 1	300	71	72.0	(4)
2 : 1	300	44	44.3	(4)
0.5 : 1	240	19	18.1	(3)

given in Fig. 2, is essentially the same as that of the 2 : 1 mixture of SA and PE. This suggests the same chemical structure for both, even though the former was a white powder and the latter a plastic film.

Chromatograms of the gases evolved from the 5 : 1 and 2 : 1 mixtures between room temperature and 320°C were the same as those of their SA–PE counterparts except that a small carbon dioxide peak was obtained when the 2 : 1 mixture was used. The decomposition of pure OA, under the conditions of this investigation, occurred in the temperature range 150–230°C, some 70°C lower than the decomposition temperature of SA. It was accompanied by the evolution of carbon dioxide. Therefore, it is believed that a small amount of OA underwent decomposition prior or concurrent with the polyesterification reaction.

Using as models the equations

$$n \text{ PE} + 2n \text{ OA} \cdot 2 \text{ H}_2\text{O} \rightarrow \text{Polymeric product} + 8n \text{ H}_2\text{O} \qquad (3)$$

for samples in which PE is present in excess and

$$n \text{ PE} + 2n \text{ OA} \cdot 2 \text{ H}_2\text{O} \rightarrow \text{Polymeric product} + 8n \text{ H}_2\text{O} + n \text{ CO} \qquad (4)$$

for samples in which PE is not present in excess, the calculated values of weight loss agree well with the experimentally determined values, as shown in Table 2. The calculated value for the 5 : 1 mixture includes the decomposition of excess OA but that of the 0.5 : 1 mixture presumes no decomposition of excess PE at 240°C.

REFERENCES

1 E. Macchi, N. Morosoff and H. Morawetz, J. Polym. Sci., Part A-1, 6 (1968) 2033.
2 E. Macchi, J. Polym. Sci., Part A-1, 10 (1972) 45.
3 H. Morawetz, in J. Wood, O. Lindqvist, C. Helgesson and N. Vannerberg (Eds.), Reactivity of Solids, Plenum Press, New York, 1976, p. 457.
4 H. Morawetz, J. Polym. Sci., Part C, 12 (1966) 79.
5 H. Morawetz, in D. Fox, M. Labes and A. Weissberger (Eds.), Physics and Chemistry of the Organic Solid State, Interscience, New York, 1963, p. 287.
6 P. Brasseur and G. Champetier, Bull. Soc. Chim. Fr., 13 (1946) 265.
7 P. Brasseur and G. Champetier, Bull. Soc. Chim. Fr., 14 (1947) 117.
8 G. Odian, Principles of Polymerization, 2nd edn., Wiley Interscience, New York, 1981.
9 E. Murrell and L. Breed, Thermochim. Acta, 1 (1970) 239.