

Solid-State Polymerization of Poly(ethylene terephthalate). III. Thermal Stabilities in Terms of the Vinyl Ester End Group and Acetaldehyde

T. Y. Kim, S. A. Jabarin

Polymer Institute and Department of Chemical and Environmental Engineering, University of Toledo, Toledo, Ohio 43606-3390

Received 7 March 2002; accepted 10 August 2002

ABSTRACT: Poly(ethylene terephthalate) (PET), precursors, and solid-stated samples were evaluated in terms of changing vinyl ester (VE) concentrations. The results obtained through the application of reaction kinetics gave VE contents ranging from 0.7 to 5.5 mmol/kg of PET. As the initial intrinsic viscosity (IV) of the precursor increased, the VE content also increased, representing the different thermal histories of the samples during melt-phase polymerization. The VE contents decreased as the solid-state polymerization (SSP) time increased from 0 to 12 h and as the temperature of SSP increased up to 220°C. A series of acetaldehyde (AA) generation experiments were conducted from 270 to 300°C with samples solid-stated from three precursors with different initial IVs. The rate of AA generation decreased as the final IV of the solid-stated PET increased, and this showed

that the SSP process improved the thermal stability of PET. The AA generation rates of samples that had similar final IVs but were solid-stated from different IV precursors were also compared. When the heating temperature was low, the amount and rate of AA generation were higher for samples with higher initial precursor IVs. This tendency, however, became less clear as the generation temperatures increased, probably because interference from the dissociation reactions (occurring between the polymer chains to produce VE) increased with increasing temperature. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 228–237, 2003

Key words: solid-state polymerization; viscosity; polyester; esterification

INTRODUCTION

Degradation of poly(ethylene terephthalate) (PET)

The thermal degradation of PET has been the subject of many publications.^{1–5} The factors that cause degradation reactions can be divided into several categories, including hydrolytic degradation, thermal degradation, and thermooxidative degradation¹ (photodegradation is an additional category but is not considered here because it is beyond the scope of this study). These three forms of degradation are those that occur in PET at temperatures from 270 to 300°C, the usual temperatures for melt-phase polycondensation and molding processes. All three types of degradation require some level of thermal energy for the initiation of the degradation reactions. With enough thermal energy, moisture causes hydrolytic degradation and oxygen causes oxidative degradation. These secondary factors (moisture and oxygen) are known to accelerate the rate of degradation and sometimes allow the deg-

radation to proceed in a different way. For example, even though all the types of degradation cause a decrease in the molecular weight, hydrolytic degradation is known to increase the concentration of carboxylic end groups as a result of the reverse reaction of esterification. Hydrolytic degradation is reported to be affected not only by moisture and temperature but also by acidity and catalysts.^{1,2} Of the three types of degradation mentioned, hydrolytic degradation is the most rapid form in terms of the decrease in the molecular weight.¹

Compared with hydrolytic degradation, thermal degradation includes more complex reaction schemes. Many researchers have proposed possible reaction mechanisms for the thermal degradation of PET; however, there does not seem to exist a unique reaction scheme that is preferred. There are two views on the nature of the degradation mechanism. Marshall and Todd³ believed that thermal degradation is initiated at chain ends, whereas Goodings⁴ and Ritche⁵ agreed that degradation occurs by random chain scission at the ester linkages. The methylene group, which is located at the β position to the carbonyl group, is believed to be the principal point of weakness. Common points in each degradation mechanism include the following: (1) a vinyl ester (VE) group is formed as one of the intermediate substances in the degradation

Correspondence to: S. A. Jabarin (sjabari@utnet.utoledo.edu).

Contract grant sponsor: PET Industrial Consortium.

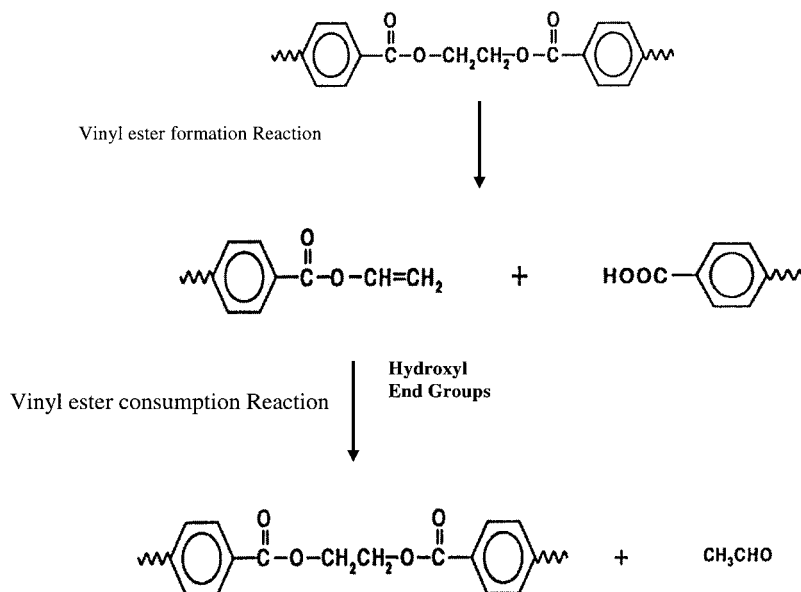


Figure 1 Reaction schemes for the thermal degradation of PET generating AA.⁸

scheme and (2) acetaldehyde (AA) is generated as a result of the degradation reaction. Despite the complicated reaction mechanisms, it seems obvious that at least the thermal degradation of PET entails the generation of VE groups and AA.^{6,7} This gives a brief background explaining why the generation of AA can be used as a way of measuring the degree of degradation for PET. Another reason for the importance of AA generation can be found from the application standpoint of PET as a material for food and beverage packaging. AA should be controlled in PET with food packaging applications because it may affect the flavors of some container contents.⁸ The VE content in PET can be considered an important component in AA generation because it is one of the intermediates in the degradation scheme for the generation of AA, as shown in Figure 1. It is, therefore, important to measure VE contents in PET because these values can be used as indicators for estimating the potential ability of the material to generate AA during processing in the melt phase.

Thermooxidative degradation has been reported to have much higher reaction rates than thermal degradation.^{1,9,10} The effects of oxygen have been studied in various degradation reaction schemes. The presence of oxygen is reported to accelerate degradation reactions; consequently, discoloration and gel formation can be observed much more often than for samples exposed to thermal degradation under an inert atmosphere.

Solid-state polymerization (SSP) and thermal stability of PET

PET was initially developed as a material with fiber and film applications, for which the required intrinsic

viscosity (IV) of the material ranged from 0.5 to 0.6 dL/g. Applications, such as biaxially stretched bottles, tire cord, and crystallized PET sheets for trays, require an IV ranging from 0.7 to 1.2 dL/g. Melt-phase polymerization has been used successfully to prepare PET suitable for the lower IV applications. It is very difficult to polymerize higher IV PET in the melt phase, however, because of the thermal degradation reactions occurring simultaneously and competing with the forward polycondensation reactions. It is generally known that the polycondensation reaction is an exothermic reaction and that the equilibrium constant tends to become greater as the reaction temperature decreases. For this reason, at the lower temperatures at which the material is in the solid state, it is possible to polymerize PET to a very high degree that would be difficult to achieve with melt-phase polymerization, for which the reaction temperatures are usually 50–80°C higher than those of SSP.^{11–13}

In addition to supplying a high degree of polymerization, the SSP process also provides advantages in terms of material properties. Most degradation reactions can be reverse reactions of the main polymerization reactions. For example, hydrolytic degradation can be considered a reverse reaction of the esterification reaction. In the solid state, in which reaction temperatures are low, the rate of reverse reactions can be diminished because of high equilibrium constants. The concentrations of the degradation products, such as AA, can also be decreased by diffusion during the SSP process.¹⁴ The VE end-group concentration is also believed to decrease, as a result of polycondensation reactions, with hydroxyl end groups during the SSP process. Although this reaction between VE end

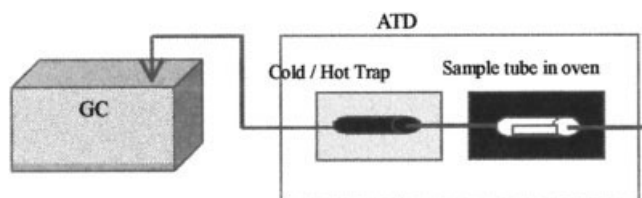


Figure 2 Simplified schematic diagram for the GC-ATD system.

groups and hydroxyl end groups produces additional AA, this AA can be removed from PET pellets by diffusion under SSP conditions.

Some reports have been published regarding the characterization or generation of AA in PET. Halek⁸ reported that AA generation showed a zero-order kinetic behavior, the amount of AA generation being linearly dependent on the generation time. He observed differences in the activation energies (E_a 's) and the entropy changes for AA generation as generation temperatures exceeded the melting temperature of PET while observing the same free energy change, regardless of temperature. Jabarin and Lofgren¹³ reported a change in the residual AA contents during SSP, showing that SSP is a very efficient way of reducing AA contents in PET. They also concluded that SSP is very helpful for increasing the thermal stability of the material, by showing that the solid-stated resin generated less AA than the precursors (from melt-phase polymerization) as functions of SSP conditions such as the temperature and atmosphere. Villain et al.¹⁴ found that the presence of oxygen not only at melting, but also after storage at 100°C for 12 weeks or after drying at 170°C for 5 h, accelerated AA generation. They also found that the AA generation rate decreased as the molecular weight increased; this indicated that the molecular chain ends had some role in the degradation reaction, which was also suggested by Buxbaum.⁷

Many reports have been published regarding the thermal stability of PET, especially in terms of AA generation. Almost no articles, however, have been concerned with the characterization of VE end groups and their relationship to AA generation by solid-stated PET. One purpose of this study was to elucidate the role of SSP with respect to the thermal stability of PET by a characterization of the VE contents of the precursors and solid-stated resins. An additional objective was to relate the results of VE end-group analyses to AA generation behaviors of the various PET precursors. Although there are many factors that influence AA generation, such as the melting (processing) conditions, materials are required to have low contents of residual AA and low potentials for AA generation under melting conditions. The VE content can be used as an indicator for potential AA genera-

tion. This can be an important property, especially for solid-stated materials, because most solid-stated PET is believed to achieve very low contents of residual AA as a result of SSP.

EXPERIMENTAL

A series of SSP reactions were performed in a 50 g/batch bench-scale SSP system, with three precursors of different initial IVs. After SSP, samples were taken for determination of the IV and the contents of carboxyl end groups. The contents of hydroxyl end group were calculated from the results for the contents of the carboxyl end groups and number-average molecular weights of the samples. The details of each procedure are described in the first two articles of this series.^{11,12}

VE group contents

A chemical method was published by Aalbers and Houwelingen¹⁵ for the determination of VE end groups in PET. The method is based on the coulometric bromination of a solution of PET in dichloroacetic acid containing potassium bromide, water, and mercury(II) chloride. This method has not attained popularity because of the chemicals required. Another approach has, therefore, been used to determine VE end-group concentrations with reaction kinetics. In the second article of this series,¹² we show, using simulation results, that the rates of the VE formation reaction are negligible in comparison with those of the VE consumption reaction under the conditions of SSP. Under these conditions, VE end groups can be consumed by a reaction with hydroxyl end groups to form AA. If AA generation rates are measured below melting temperatures and some additional information is known (e.g., the concentration of hydroxyl end groups and the reaction rate constants for the VE consumption reactions), resin VE contents can be calculated. These assumptions are valid because contributions from other pathways to AA generation are

TABLE I
Conditions Used in the GC-ATD for the Calculation of VE Contents

ATD	
Sample amount loaded in each tube	0.09 ± 0.003 g
Desorption temperature range	240°C
Desorption time range	Up to 40 min
Transfer line temperature	160°C
Trap (low/high) temperature	-30°C/300°C
GC	
Oven temperature	60°C
Detector type/temperature	FID/300°C
Carrier gas and flow rate	Helium, 2.7 mL/min

FID, flame ionization detector.

TABLE II
Conditions Used in the GC-ATD for AA Generation

ATD	
Sample amount loaded in each tube	0.083 ± 0.003 g
Desorption temperature range	270–300°C
Desorption time range	Up to 14 min
Transfer line temperature	160°C
Trap (low/high) temperature	–30°C/300°C
GC	
Oven temperature	60°C
Detector type/temperature	FID/300°C
Carrier gas and flow rate	Helium, 2.7 mL/min

FID, flame ionization detector.

minimal in comparison with the contributions resulting from the reaction of VE and hydroxyl end groups.

For these calculations, we assume that all the measured AA is produced through the reaction of VE under the test condition of 240°C. The VE content can be calculated with the following kinetic relation. We also assume that all the chain end groups are located in the amorphous region of PET and that all the reactions take place only in this amorphous region, as developed in earlier publications.^{12,16} As a result of this assumption, the concentrations of the reactants and the reaction rates, based on the entire volume, have been modified by the crystallinity in the following manner:

$$\frac{R_{AA}}{(1-f)} = k_{AA} \frac{[VE]}{(1-f)} \frac{[OH]}{(1-f)}$$

$$[VE] = (1-f) \frac{R_{AA}}{k_{AA} [OH]}$$

$$k_{AA} = A \exp\left(\frac{-E_a}{RT}\right) \quad (1)$$

where R_{AA} is the rate of AA formation based on the entire volume, which was measured from the slope of the line in the AA generation plot, and $[VE]$ is the VE concentration. $[OH]$ is the hydroxyl end-group concentration, and f is the volume fraction crystallinity, which was measured for pellet samples with a density

gradient column. The concentrations of hydroxyl end groups were calculated from number-average molecular weights and carboxyl end-group contents, as described in the first part of this series.¹¹ These calculations used the reaction kinetic constant k_{AA} , which Ravindranath and Mashekar¹⁷ reported, in which the frequency factor (A) is 9.91×10^7 kg/mol/h and E_a is 18.5 kcal/mol (77.4 kJ/mol).

The concentration of AA generated was determined by gas chromatography (GC). A PerkinElmer GC system was used, which consisted of two instrumental parts: an automated thermal desorption (ATD) system and a gas chromatograph, as shown in Figure 2. After PET pellets were ground to particle sizes of less than 40 mesh under an environment of liquid nitrogen, 0.09 ± 0.003 g of PET powder was put into the sample tube. The tube was loaded into the ATD system, in which the sample was held under a constant purge of an inert carrier gas at 240°C for times of up to 40 min for the generation of AA. During the generation and desorption stage, an electrically cooled packed trap concentrated the volatile AA generated from the sample. After the generation stage, the trap was rapidly heated to 300°C to deliver the trapped AA to the capillary column of the gas chromatograph connected to the ATD system. The conditions for ATD and GC are summarized in Table I. The system was calibrated with a standard solution of a known AA concentration that was treated in a manner similar to that of the samples.

AA generation under melting conditions

We conducted a series of AA generation experiments to examine the effects of SSP on the AA generation of PET under melting conditions. Various solid-stated samples and precursors were selected to investigate the best SSP conditions for the generation of minimal levels of AA from 270 to 300°C. Before the evaluation, all the samples were dried overnight in a vacuum oven at 120°C so that interference from hydrolytic degradation would be avoided.

TABLE III
Nine Samples Selected for AA Generation

Sample	Precursor IV (dL/g)	Final IV (dL/g)	SSP temperature (°C)	SSP time (hr)
A0	0.50	—	-	0
B0	0.56	-	-	0
C0	0.64	-	-	0
A1	0.50	0.74	200	12
B1	0.56	0.75	200	8
C1	0.64	0.78	200	4
A2	0.50	0.82	210	12
B2	0.56	0.82	210	8
C2	0.64	0.82	210	4

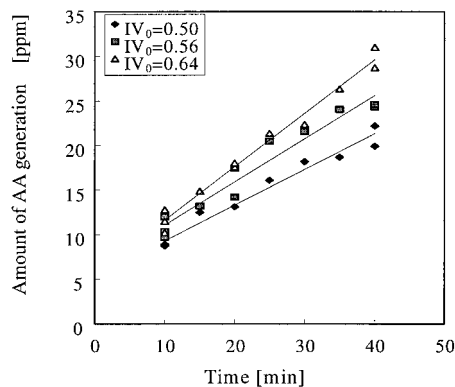


Figure 3 AA generation after various heating times at 240°C for the precursors. The different shapes of the data points refer to the different initial IVs of the precursors.

The amount of AA generated by whole solid-stated PET pellets was determined by GC in a manner similar to that described for VE group measurements. In this case, however, the temperatures ranged from 270 to 300°C, and heating times of up to 14 min were used. Sample amounts loaded into each sample tube were 0.083 ± 0.003 g. The conditions for ATD and GC are summarized in Table II.

The purpose of the AA generation test was to identify the role of SSP from the standpoint of thermal stability in terms of AA generation. Nine samples were selected for this purpose, as described in Table III. The designation A refers to the precursors with an initial IV of 0.50, whereas B and C indicate initial precursor IVs of 0.56 and 0.64, respectively. 0 after each letter indicates no solid-state history for that sample. 1 indicates that these resins have been solid-stated to a final IV value of 0.75, after different times at 200°C. 2 after the letter indicates a final IV value of 0.82 after various solid-stating times at 210°C.

RESULTS AND DISCUSSION

Concentrations of VE end groups

AA generation experiments were conducted at 240°C with powdered samples from three precursors and several PET resins solid-stated under different conditions. Each sample exhibited linear generation behavior with a specific slope, as shown in Figures 3–5. The rates of AA generation were taken from the slopes of the lines. They also showed some amount of intercept as the time approached zero, which could be represented by the residual AA amount and the initial AA generation amount until the temperature reached 240°C. These reaction rates (R'_{AA}), the crystallinity, the reaction rate constant, and the hydroxyl end-group contents were used to obtain the VE contents according to eq. (1) to give the results shown in Table IV.

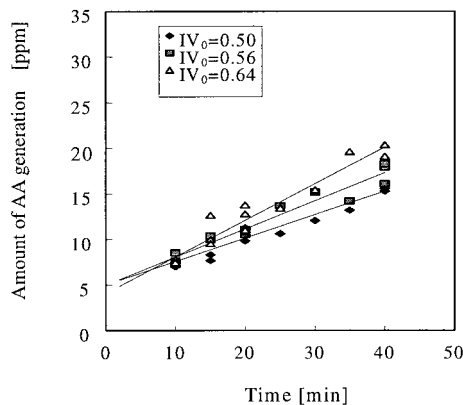


Figure 4 AA generation after various heating times at 240°C for samples solid-stated 4 h at 200°C. The different shapes of the data points refer to the different initial IVs of the precursors.

Figure 6 shows how the VE content changed as SSP proceeded at 200°C for different precursors. The contents of VE end groups in the PET precursors ranged from 1.9 to 5.5 mmol/kg of PET, depending on the precursor IVs. These estimated values of the VE concentration in PET are comparable to the values reported by Aalbers and Houwelingen.¹⁵ They developed a technique with coulometric bromination and reported that PET, polymerized at 280°C, contained VE end groups of 0–5 mmol/kg and that the VE end-group contents could be increased up to 20 mmol/kg as the PET polymerization temperatures increased to 300°C. This shows that the techniques developed by us to estimate VE end-group contents in PET can be used as an alternative method for VE characterizations.

As the precursor IV increased, the content of VE groups increased, representing different thermal histories among the precursors, presumably during the melt-phase polymerization. VE group contents decreased as SSP proceeded. This happened because VE

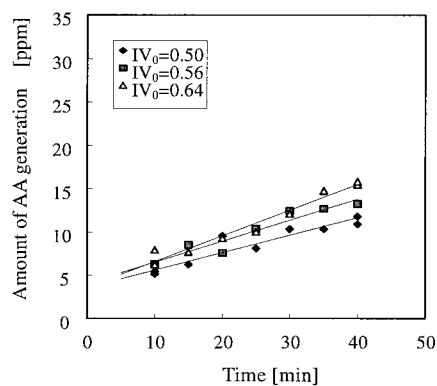


Figure 5 AA generation after various heating times at 240°C for samples solid-stated 12 h at 200°C. The different shapes of the data points refer to the different initial IVs of the precursors.

TABLE IV
Results for the Calculation of VE Group Contents for the Various PET Samples

Sample	SSP temperature (°C)	SSP time (hour)	Precursor	Crystallinity ^a (vol %)	Hydroxyl end-group content ^b (mmol/kg of PET)	AA generation rate ^c (ppm/min)	Vinyl end-group content ^d (mmol/kg of PET)
1	—	—	A0 (IV = 0.50)	52	107	0.40	1.9
2	—	—	B0 (IV = 0.56)	51	78	0.48	3.2
3	—	—	C0 (IV = 0.64)	49	58	0.60	5.5
4	200	4	A0	55	82	0.26	1.5
5	200	4	B0	55	55	0.31	2.6
6	200	4	C0	53	40	0.39	4.7
7	200	12	A0	61	59	0.20	1.4
8	200	12	B0	59	47	0.24	2.2
9	200	12	C0	58	35	0.30	3.7
10	220	12	A0	62	50	0.09	0.7
11	220	12	B0	60	37	0.13	1.5
12	220	12	C0	60	26	0.14	2.2
13	230	12	A0	63	41	0.12	1.1
14	230	12	B0	61	28	0.13	1.9
15	230	12	C0	61	20	0.13	2.6

^a From the measurement of density for the PET pellets crystallized in vacuum oven at 120°C overnight and then processed in the ATD system at 240°C for 20 min.

^b Calculation result from the number-average molecular weight and the carboxyl end-group content.¹¹

^c From the slope of the trend line in Figures 3–5.

^d From the calculation using eq. (1).

groups were consumed by reacting with hydroxyl end groups, as shown in Figure 1, to produce AA. This AA must have diffused out of the PET pellets during SSP. The results show that SSP is an efficient process for the improvement of thermal stability in terms of AA generation, which is possible by reductions in both the VE content and hydroxyl end-group content. These results are supported by those of several other researchers who described the role of chain ends in PET degradation reactions.^{7,14}

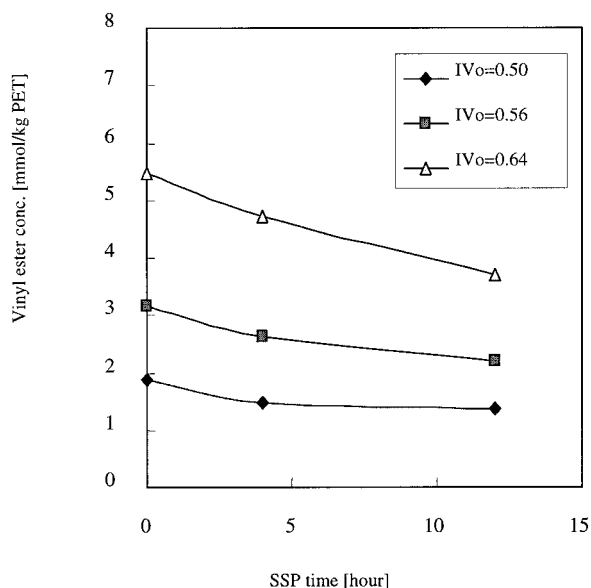


Figure 6 Changes in the VE concentrations during SSP at 200°C for precursors with different IVs.

Figure 7 shows changes in the VE contents for samples solid-stated for 12 h at various SSP temperatures. The VE content decreased as the SSP temperature increased. Figure 8 shows previous modeling results reported for the VE contents.¹² Current experimental values are included in this figure. VE contents were projected to decrease as the SSP time and temperature increased; however, at an SSP temperature of 230°C, the measured VE content in PET after 12 h of SSP was almost the same as, or slightly higher than, that obtained at an SSP temperature of 220°C. The reason for the stabilization or the slight reincrease in the VE

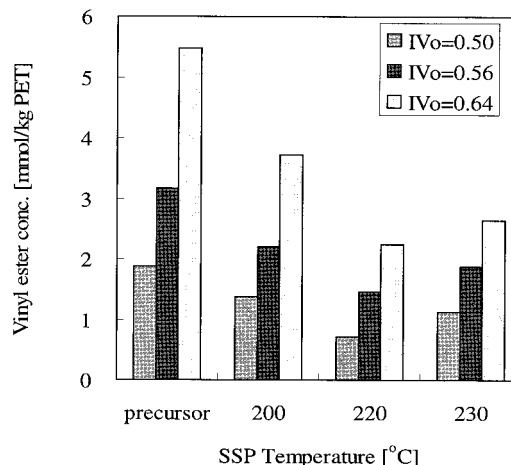


Figure 7 Effects of the SSP temperatures on the VE contents for the samples solid-stated for 12 h from precursors with different IVs.

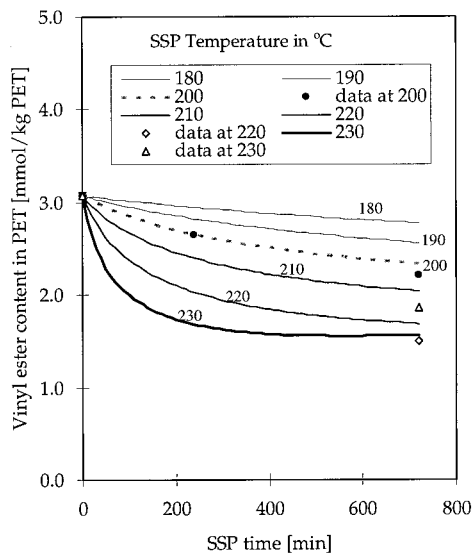


Figure 8 Modeling results and experimental data indicating the changes in the VE contents as functions of the SSP times with respect to the SSP temperatures for the precursor with $IV = 0.56$ dL/g. The experimental data were obtained at 200, 220, and 230°C.

content at the SSP temperature of 230°C can be found in the reaction kinetics. The VE concentration is determined by the relative magnitude of the rates of two reactions, the VE formation reaction and the AA formation reaction (or the VE consumption reaction). These reactions have been reported to have E_a 's of 37.8 kcal/mol (158 kJ/mol) for VE formation and 18.5 kcal/mol (77 kJ/mol) for VE consumption.^{16,17} Because of the higher E_a value of the VE formation reaction, as the temperature increases, a situation occurs in which the rate of the VE formation exceeds that of the VE consumption.

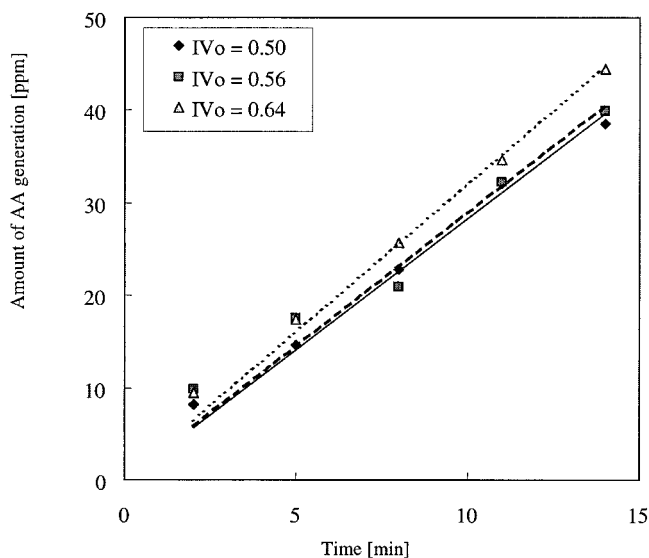


Figure 9 AA generation after various heating times at 270°C for the three precursors A0, B0, and C0.

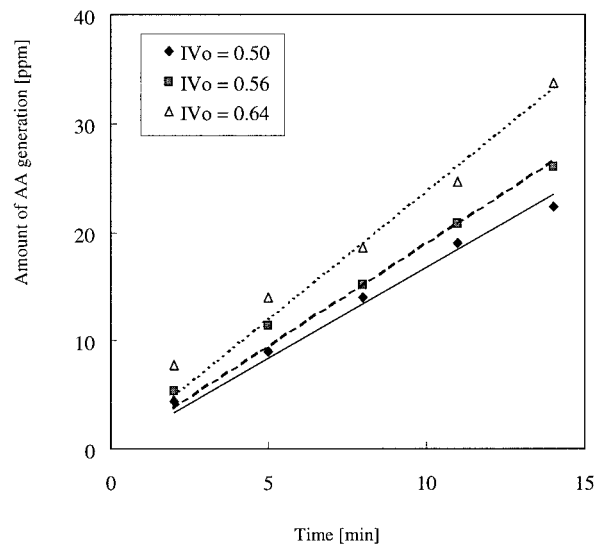


Figure 10 AA generation after various heating times at 270°C for the solid-stated samples A1, B1, and C1.

Figures 6 and 7 contain important information in terms of AA generation regarding the polymerization of thermally stable PET. It is noteworthy that the precursor with $IV = 0.50$ had a similar or lower VE content than the solid-stated samples from precursors of $IV = 0.56$ or $IV = 0.64$. This indicates that most vinyl end groups must have been produced during the last stages of melt-phase polymerization. It is important from the standpoint of the vinyl end-group concentration to stop the melt-phase polymerization earlier before increased amounts of VE are formed.

AA generation under melting conditions

The AA generation tests were performed from 270 to 300°C for the nine samples described in Table III.

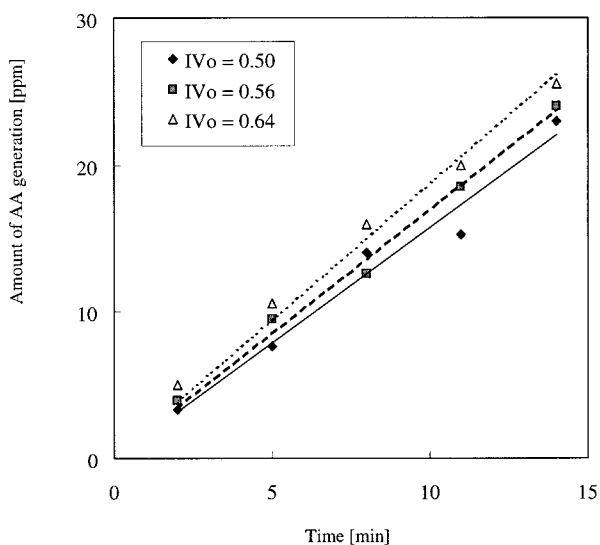


Figure 11 AA generation after various heating times at 270°C for the solid-stated samples A2, B2, and C2.

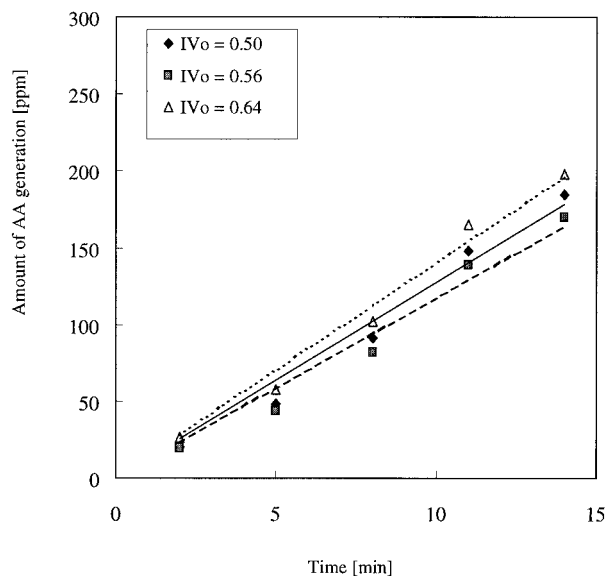


Figure 12 AA generation after various heating times at 300°C for the solid-stated samples A1, B1, and C1.

Figures 9–12 show amounts of AA generated as functions of the residence time for selected cases heated at 270 and 300°C only.

If zero-order kinetics are assumed, the rate constant for AA generation can be obtained from the slope of the line after data are fit to the relation of $[AA] = kt$. $[AA]$ is the amount of AA measured, and t is the time of AA generation (min). The rate constant k is the rate of AA generation for zero-order kinetics, as summarized in Table V. Comparing k values of the samples, we can see that the rate of AA generation decreased as the final IV of the samples increased [precursor IV (0) \rightarrow 0.75 (1) \rightarrow 0.82 (2)]. This agrees with the previous observations for the concentrations of VE groups.

When we see the dependency of the k values on the initial precursor IV, relationships among samples (A–C) are not clear. We can, however, observe that the samples from precursor C0 (IV = 0.64) generated the most AA under any conditions in comparison with other samples from lower IV precursors. The samples from precursor A0 (IV = 0.50) generated the least AA when the temperature was as low as 270°C. These trends agree well with previous observations concerning VE group concentrations. The VE group is an intermediate in the reaction path to AA generation.

We could expect that the samples solid-stated from precursor A0 (IV = 0.50) would generate less AA than the other samples because of their lower VE contents. This expectation was observed in the results obtained when the generation temperature was comparatively low (270°C). As the temperature of AA generation was increased, more instances occurred for which the trend did not agree with the results expected on the basis of the concentration of VE groups. The VE end group is an intermediate to AA formation, not an initial reactant. Its content can, therefore, change during AA generation because of the VE formation reaction and the AA formation reaction (or the VE consumption reaction) shown in Figure 1. When the temperature is low, fewer chain dissociation reactions may occur, and the AA formation reaction is relatively important for determining the amount of AA generation. This is why A series samples generated less AA at relatively low temperatures than B and C series samples. As the temperature increased, the dissociation reactions from polymer chains became more dominant, so the benefit of A series samples, having lower initial concentrations of VE groups, was not as important.

The slope of the trend line in an Arrhenius plot can be related to E_a :

$$k = Ae^{(-E_a/RT)}$$

$$\ln k = \ln A - \frac{E_a}{R} \left(\frac{1}{T} \right) \quad (2)$$

where R is the gas constant (1.987 cal/mol K), k is a specific rate constant, and T is the absolute temperature. E_a 's of all the samples tested can be obtained from the slopes in the Arrhenius plot shown in Figure 13, with values for k summarized in Table V. E_a 's (Fig. 14) were slightly different [ranging from 35 to 43 kcal/mol (from 146 to 180 kJ/mol)] according to the sample history. This range agrees with E_a values previously reported for PET degradation by several authors. Halek⁸ reported $E_a = 37.5$ kcal/mol (146 kJ/mol) for the degradation measured by AA generation, whereas Goodings⁴ reported $E_a = 35.7$ kcal/mol from the measurement for the viscosity change during PET degradation. The plot given in Figure 14 helps us to compare E_a 's of the samples. We can see clearly that E_a

TABLE V
Apparent Rate Constants (k , ppm/min) for AA Generation with Nine Samples

AA generation temperature (°C)	A0	B0	C0	A1	B1	C1	A2	B2	C2
270	2.8	2.9	3.2	1.7	1.9	2.4	1.6	1.7	1.9
280	4.6	4.7	4.8	3.3	3.2	4.1	2.7	2.7	3.3
290	8.0	8.4	8.7	6.6	6.4	7.5	5.7	5.3	5.8
300	15.7	15.2	16.5	12.7	11.8	14.0	12.8	12.0	12.6

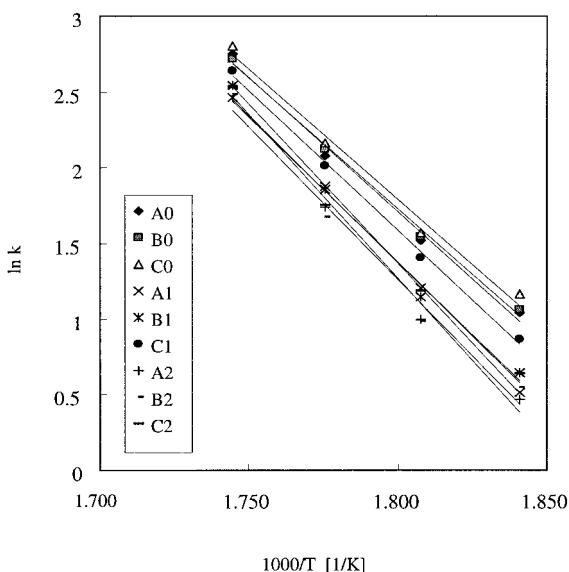


Figure 13 Arrhenius plot of the rate constants for the AA generation of various selected samples.

for AA generation increased as SSP proceeded (as the final IV increased; i.e., $0 \rightarrow 1 \rightarrow 2$) and as precursors had lower initial IV values (as more of the molecular weight increases were made by SSP rather than by melt polymerization; i.e., $C \rightarrow B \rightarrow A$). E_a can be understood in reaction kinetics as an energy barrier to be overcome for a reaction to take place. We find that this energy barrier increases with SSP instead of melt-phase polymerization for the attainment of higher molecular weight resins.

The following thermodynamic relationship can be used to estimate an entropy change (ΔS) and a free energy change (ΔG). We assume that the enthalpy change (ΔH) is equal to E_a :

$$\Delta S = 2.303R \left[\log k - 10.753 - \log T + \frac{E_a}{2.303RT} \right] \quad (3)$$

$$\Delta G = \Delta H - T\Delta S \quad (4)$$

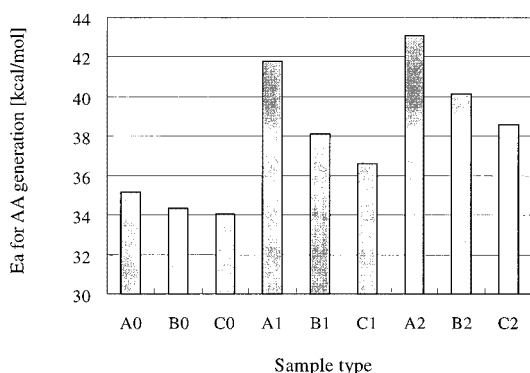


Figure 14 Comparison of E_a values for the AA generation of various selected samples.

TABLE VI
Changes of Entropy (cal/mol/K) of the AA Generation for Each Sample

AA generation temperature (°C)	A0	B0	C0	A1	B1	C1	A2	B2	C2
270	5	4	4	16	10	8	19	14	11
280	5	4	3	16	10	7	18	13	11
290	5	4	3	16	10	7	18	13	11
300	5	4	3	16	10	8	19	13	11

Entropy changes were calculated for the samples, as given in Table VI. According to SSP conditions, the entropy was observed to vary from 3 to 20 cal/mol/K (13–84 J/mol/K), as shown in Table VI. It is noticeable that, as SSP proceeded (as the final IV increased; i.e., $0 \rightarrow 1 \rightarrow 2$) and as more of the molecular weight increase was made by SSP rather than by melt-phase polymerization (i.e., $C \rightarrow B \rightarrow A$), ΔS increased. Entropy changes can be related to the degree of order in the configurations of the transition state in the degradation reaction path. It is interesting that the degree of order in the transition state depends on the initial and final IVs of the sample in SSP.

The entropy values obtained in this way can be compared with the values obtained by others. Halek⁸ reported the entropy to be 1.5 cal/mol K (6 J/mol K) for the AA generation of PET with IV = 0.62, which was very close to the case of sample C0, for which the IV was 0.64. The entropy value for C0 was 3 cal/mol K (13 J/mol K), which was very comparable to Halek's entropy value. The difference can be better explained if we consider the effect of the material IV. We observe that the entropy increased with increasing IV. Despite the differences in ΔS , all the samples showed about the same Gibbs free energy changes (Table VII). This indicates that the initial and final states of the degradation reaction taking place were identical, regardless of the sample type.

CONCLUSIONS

A method was developed to calculate VE end-group concentrations through the measurement of the AA generation rates at 240°C and the subsequent application of reaction kinetics. The concentrations of VE end-groups in PET precursors and solid-stated PET samples were found to range from 0.7 to 5.5 mmol/kg of PET. The VE end-group concentrations decreased as SSP proceeded and as PET was solid-stated from lower IV precursors. Under most conditions, the VE end-group concentrations decreased as the SSP temperature and time increased.

In the AA generation reaction, the amount of AA generated under a melting condition decreased as the final resin IV increased as a result of SSP. This was in

TABLE VII
Gibbs Free Energies (kcal/mol) of AA
Generation for Each Sample

AA generation temperature (°C)	A0	B0	C0	A1	B1	C1	A2	B2	C2
270	32	32	32	33	33	32	33	33	33
280	32	32	32	33	33	32	33	33	33
290	32	32	32	33	33	32	33	33	33
300	32	32	32	32	32	32	32	32	32

good agreement with results obtained from VE end-group concentrations because the VE contents decreased with increasing final resin IV.

When the effect of the precursor IV on AA generation was considered, samples solid-stated from lower IV precursors generated less AA than those from higher IV precursors, especially when the generation temperatures were as low as 270 or 280°C. As the generation temperatures increased, the trend of increasing AA with increasing precursor IV became less clear; this implied that more interference occurred from the dissociation reactions of the original polymer chains. This also indicates that, as the generation temperature increased, the benefits of low initial contents of VE groups became negligible in comparison with other factors that influenced the thermal degradation

of PET. As SSP proceeded and as precursors had lower initial IV values, the E_a values and the entropy for AA generation were observed to increase.

The authors thank the members of the PET Industrial Consortium who supported our research at the Polymer Institute of the University of Toledo.

References

1. Yuki, K. Saturated Polyester Resin Handbook; Nikkan Kougyo-sha: Tokyo, 1989; Chapter 4.
2. Zimmerman, H.; Kim, N. *Polym Eng Sci* 1980, 20, 680.
3. Marshall, J.; Todd, A. *Trans Faraday Soc* 1953, 49, 67.
4. Goodings, E. *Soc Chem Ind (London) Monogr* 1961, 13, 211.
5. Ritchie, P. *Soc Chem Ind (London) Monogr* 1961, 13, 107.
6. Ravindranath, K.; Mashelkar, R. *Chem Eng Sci* 1986, 41, 2197.
7. Buxbaum, L. *Angew Chem Int Ed* 1968, 71, 182.
8. Halek, G. *J Polym Symp* 1986, 74, 83.
9. Jabarin, S.; Lofgren, E. *Polym Eng Sci* 1984, 24, 1056.
10. Yoda, K.; Tsuboi, A.; Wada, M.; Yamadera, R. *J Appl Polym Sci* 1970, 14, 2357.
11. Kim, T.; Lofgren, E. A.; Jabarin, S. *J Appl Polym Sci* 2003, 89, 197.
12. Kim, T.; Jabarin, S. *J Appl Polym Sci* 2003, 89, 213.
13. Jabarin, S.; Lofgren, E. *J Appl Polym Sci* 1986, 32, 5315.
14. Villain, F.; Coudane, J.; Vert, M. *Polym Degrad Stab* 1994, 43, 431.
15. Aalbers, J. G. M.; Houwelingens, G. *Fresenius Z Anal Chem* 1983, 314, 472.
16. Mallon, F.; Ray, W. *J Appl Polym Sci* 1998, 69, 1233.
17. Ravindranath, K.; Mashelkar, R. *AIChE J* 1983, 30, 415.