

Kinetic and Thermogravimetric Analysis of the Thermal Oxidative Degradation of Flame-Retardant Polyesters*

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Synopsis

Untreated and flame-retarded poly(ethylene terephthalate) fabrics have been subjected to thermogravimetric analysis in air at several heating rates between 0.1°C/min and 100°C/min. The data have been analyzed using a variety of methods to obtain kinetic parameters for the sequential stages in the thermal degradation process. The data obtained reveal that the phosphorus-only flame retardants do not significantly effect the degradation kinetics. The two bromine-containing flame retardants, however, are capable of modifying the degradation kinetics, with the Dacron 900F material being responsible for a beneficial condensed-phase effect while the TRIS-treated sample is responsible for reduced activation energies and more rapid weight loss.

INTRODUCTION

The thermal degradation of poly(ethylene terephthalate) (PET) has been studied extensively over the years,¹⁻⁵ and it is now generally accepted that the primary degradation process is a random chain scission of the ester bonds to give vinyl ester and carboxylic acid end groups. These primary fragmentation products are then capable of undergoing further ester scission reactions to give low molecular weight volatile fragments and resultant weight loss of the material. Detailed kinetic analyses of these processes have been performed using thermogravimetric techniques⁶⁻¹⁵ however, information in the literature concerning the role of flame retardants, both as additives and comonomers, is slight. Granzow et al.⁸ studied phosphorus-containing samples of PET and observed reduced weight loss rates and zero reaction orders suggesting that phosphorus was capable of inhibiting the secondary reactions leading to volatile product formation. Bechev^{11,12} meanwhile reported that certain phosphorus compounds were responsible for reduced activation energies.

Kinetic analysis of thermogravimetric data from untreated PET fabrics in our laboratories¹⁵ has shown that the degradation is a complex multistage process, with at least three decomposition stages and a possible preliminary stage discernible at low conversions. This paper describes the effects of various flame-retardant systems upon the kinetics of the thermal degradation as measured using three mathematical methods found satisfactory for untreated PET samples.

EXPERIMENTAL

The four commercial flame retardant fabric samples¹⁶⁻¹⁹ and two control samples studied in this investigation are given in Table I along with their limiting

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TABLE I
Polyester Fabrics Investigated

Commercial name	Dacron T54	Unknown	Antiblaze I9	Trevira T271	Tris-treated PET	Dacron 900F
Fabric designation	T54	MICH	AB19	T271	TRIS	900F
Source	Testfabrics	Velsicol Chemical ^a	Mobil Chemical	Hoechst Fibres Ind.	Velsicol Chemical ^a	E. I. DuPont
Nature of flame retardant	none	none	cyclic phosphonate esters additive	Phosphinic acid comonomer	Tris(2,3-dibromopropyl) phosphate additive	Ethoxylated tetrabromo bisphenol A comonomer
Reference	—	—	16	17	18	19
Weight (g/m ²)	126	124	79	169	148	144
Chemical analysis w/w % on fabric						
Br	—	—	—	—	6.6	4.3
P	—	—	0.28	0.20	0.33	—
LOI	18.9	18.9	21.8	20.5	23.9	21.8

^a Formerly Michigan Chemical Co. now part of Great Lakes Chemical Co.

oxygen indices (LOI) as determined previously.²⁰ Table II lists the results of trace elemental analysis obtained by dc-arc spectroscopy on samples ashed for 1 h at 600°C. These semiquantitative data are good to within a factor of 3 of the actual value. The TRIS and MICH fabrics were identical with the exception of the flame-retardant treatment and therefore only one set of analytical data is presented in Table II.

The thermogravimetric (TG) analyses were performed in a flowing air atmosphere with a DuPont 951 Instrument coupled to a 1090 Thermal Analyzer according to the technique described previously.¹⁵ Ten heating rates from 0.1°C/min to 100°C/min were employed and appropriate temperature corrections performed. In all cases the sample weight, first derivative, and temperature were recorded as a function of time enabling kinetic calculations to be performed on the acquired data.

RESULTS AND DISCUSSION

The results obtained for the two untreated control samples T54 and MICH were almost identical and, therefore, for the sake of clarity, only the T54 data has been presented in the Figures 1–4. The complexity of the degradation process can be seen by examination of Figures 1 and 2, which are thermograms obtained at heating rates of 0.1°C/min and 100°C/min, respectively, the two extreme conditions employed in this study. Clearly, more detail is evident at the lower heating rate than at the higher rate; however, in both cases the derivative curves enable the different degradation stages to be observed. Examination of the 0.1°C/min data (see Fig. 1), for example, enables the three stages to be seen at about 250–315°C, 315°–370°C, and 370–420°C, respectively. The samples

TABLE II
Elemental Analysis of the Residual Ash

Fabric	T54	MICH	AB19	T271	900F
% ash	0.4	0.3	0.3	0.4	0.3
Composition (% of ash)					
Ti	major	major	major	major	major
Sb	3	6	0.06	6	0.3
Mn	3	3	2	0.03	3
Ca	1	3	1	0.6	1
Na	1	0.3	1	0.3	0.3
Fe	0.3	0.6	0.3	0.3	0.3
Cu	0.3	0.3	0.3	0.3	0.3
Sn	0.2	0.1	0.03	—	0.01
Al	0.2	0.3	1	0.6	1
Pb	0.1	0.1	0.1	0.03	0.1
Mg	0.1	0.3	0.1	0.06	0.06
Si	0.06	1	2	1	1
B	0.03	0.03	0.1	0.03	0.03
Au	0.01	0.03	0.01	3	0.03
Cr	0.01	0.06	0.01	0.01	0.03
Ag	0.01	0.06	0.1	0.003	0.01
Zr	—	0.03	—	—	0.03
Zn	—	0.3	—	1	—
Co	—	—	1	—	1

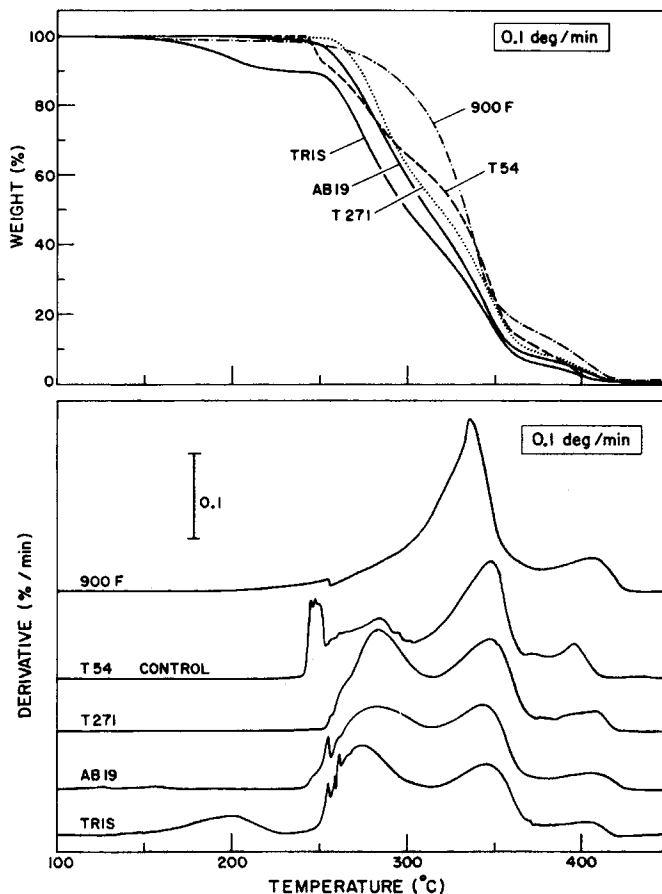


Fig. 1. Thermogravimetric curves and rates of decomposition for the PET samples at a heating rate of $0.1^{\circ}\text{C}/\text{min}$.

also show small peaks at about 240°C associated with the melting of the PET, although in the case of the T271 it is only present as a small shoulder. The remaining peaks are very similar with the exception of the TRIS and 900F samples. The TRIS-treated fabric has a characteristic low temperature preliminary peak not found in any of the other systems. The 900F sample, meanwhile, does not have a very distinct first stage.

The results obtained at the higher heating rates (see Fig. 2), although similar to those obtained at the lower heating rates, are not quite as clear. The peaks associated with the melting of PET are no longer evident whereas the low temperature preliminary stage peak observed with the TRIS sample is still present. The resolution of the first and second stages at the higher heating rates is no longer as clear as it was at the lower heating rates. Consequently, the calculation of kinetic data for the individual stages in the degradation is more difficult. The fact that some differences are observed, however, suggests that the flame retardants being studied are capable of influencing, to some extent, the nature of the thermal degradation process occurring with PET. The overall appearance of the weight loss curves with the exception of the TRIS system are, however, quite similar suggesting that the changes being induced are not very large.

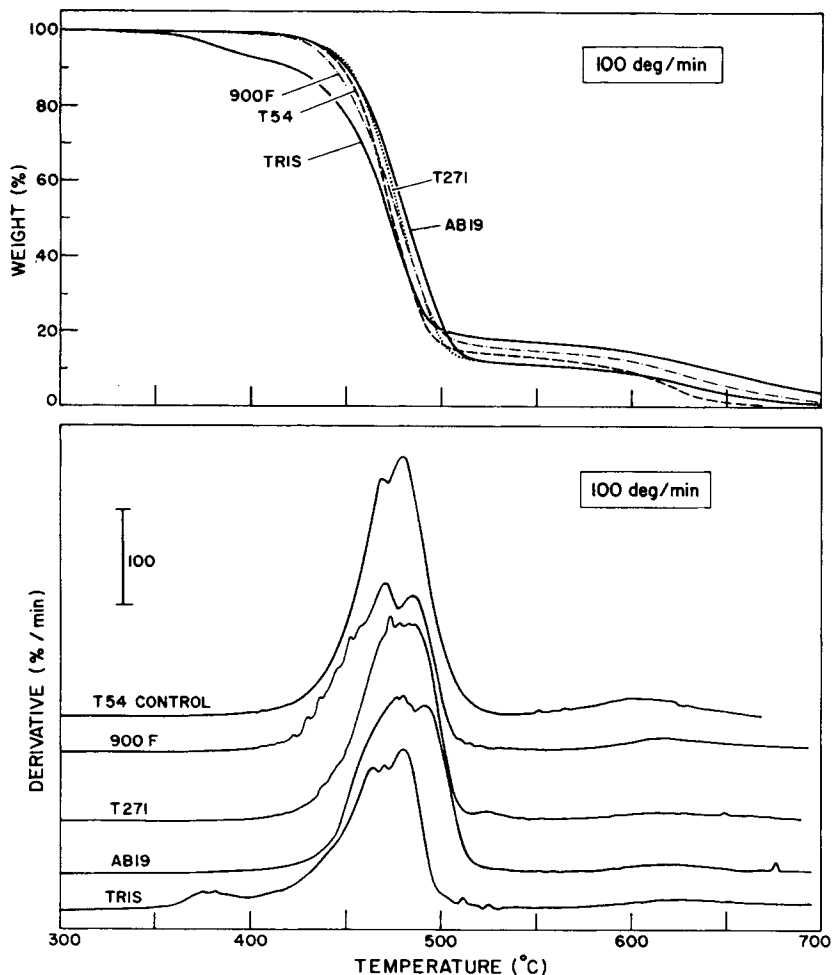


Fig. 2. Thermogravimetric curves and rates of decomposition for the PET samples at a heating rate of 100°C/min.

Since Figures 1 and 2 are only representative of the extreme heating rates employed in this study, the peak temperatures (temperatures of maximum degradation rates) are summarized in Table III for each heating rate. These temperatures have been corrected using ICTA Curie point standards as previously described.¹⁵ Examination of these data reveals some interesting observations, e.g., the peak temperatures for each degradation stage of the flame-retarded samples are very similar to those of the untreated samples, especially the data obtained for the major (second) stage of decomposition. Meanwhile, all the flame-retardant samples tend to have slightly higher peak temperatures for the third stage process. Data obtained for the first stage show the largest amount of scatter due to the peak being mainly a leading shoulder on the second stage peak. The only clear indication of a significant difference between the treated and untreated samples is observed with the TRIS sample which shows a heating-rate-dependent low temperature preliminary stage peak. In the case of the untreated samples and the AB19 sample the low temperature peak appears to be independent of heating rate and characteristic of the melting process of

TABLE III
Temperatures (°C) of Maximum Rates of Weight Loss

Sample	Stage	Heating rate (°C/min)													
		0.1	0.3	1.0	2.0	5.0	10.0	20.0	30.0	50.0	100.0				
T54	Prelim	248.2	249.9	254.9	255.9	261.2	—	—	—	—	—	—	—	—	—
	1st	283.5	292.8	331.5	339.5	355.2	363.7	374.7	388.5	392.7	399.2	399.2	399.2	399.2	399.2
	2nd	346.8	365.8	386.5	394.4	412.8	419.5	433.6	440.5	462.3	474.7	474.7	474.7	474.7	474.7
MICH	3rd	394.3	423.6	454.7	481.9	507.5	532.8	546.7	566.1	576.5	603.9	603.9	603.9	603.9	603.9
	Prelim	247.3	251.3	254.4	—	—	—	—	—	—	—	—	—	—	—
	1st	278.9	298.1	330.2	339.4	354.8	368.6	382.1	386.2	391.8	—	—	—	—	—
AB19	2nd	349.0	364.0	389.1	399.3	415.7	427.2	437.4	443.7	461.4	478.4	478.4	478.4	478.4	478.4
	3rd	398.9	424.9	458.3	476.4	506.5	530.1	550.5	569.3	584.8	615.8	615.8	615.8	615.8	615.8
	Prelim	255.6	254.5	249.4	253.7	254.3	—	—	—	—	—	—	—	—	—
T271	1st	285.0	306.8	334.3	345.2	357.7	360.7	361.2	376.8	405.5	—	—	—	—	—
	2nd	343.3	365.1	388.9	396.2	411.6	426.1	437.3	451.5	465.4	480.5	480.5	480.5	480.5	480.5
	3rd	403.9	432.9	470.5	484.0	511.6	535.4	554.4	573.6	596.0	619.9	619.9	619.9	619.9	619.9
Tris	1st	283.3	297.7	322.0	347.5	369.4	369.5	387.6	391.0	396.4	413.3	413.3	413.3	413.3	413.3
	2nd	346.7	368.0	382.4	399.4	413.2	428.4	445.2	456.0	463.4	479.1	479.1	479.1	479.1	479.1
	3rd	402.1	434.9	460.6	487.4	513.8	534.3	561.1	572.3	593.8	615.7	615.7	615.7	615.7	615.7
900F	Prelim	197.2	221.9	250.8	253.7	297.6	318.9	327.0	333.6	356.4	—	—	—	—	—
	1st	274.3	294.5	315.3	330.1	365.0	386.6	383.8	399.0	408.3	—	—	—	—	—
	2nd	345.2	364.5	386.1	399.1	414.2	425.2	438.0	444.8	462.7	479.2	479.2	479.2	479.2	479.2
900F	3rd	400.7	433.6	461.5	483.2	507.7	535.0	561.0	572.8	597.1	625.7	625.7	625.7	625.7	625.7
	2nd	336.2	358.0	381.1	397.3	418.4	424.8	439.6	445.8	456.9	472.9	472.9	472.9	472.9	472.9
	3rd	407.1	435.1	464.9	489.8	523.1	539.4	553.4	573.8	591.1	616.6	616.6	616.6	616.6	616.6

PET. With the exception therefore of this difference observed with the TRIS sample, the TG data presented in Figures 1 and 2 and Table III indicate that the flame-retardant systems are not having major influences on the degradation mechanisms, confirming our observations based on pyrolysis-gas chromatography studies.⁵

In the kinetic analysis of solid state thermal decomposition reactions of polymeric materials, it has been common practice to assume that the rate expression can be represented by the equation

$$d\alpha/dt = kf(\alpha) = k(1 - \alpha)^n \quad (1)$$

where α is the degree of conversion, k the rate constant, and n the apparent order of reaction. The combination of the above expression with the Arrhenius expression

$$k = A \exp(-E/RT) \quad (2)$$

gives rise to the following relationship which is the basis of numerous analytical approaches to the calculation of kinetic parameters from TG data:

$$d\alpha/dt = A(1 - \alpha)^n \exp(-E/RT) \quad (3)$$

Kissinger²¹ has shown that the peak temperatures given by the maxima of the first derivative weight loss curve can be used to calculate apparent Arrhenius activation energies (E) by the use of the following expression:

$$\frac{d(\ln \beta/T_m^2)}{d(1/T_m)} = \frac{-E}{R} \quad (4)$$

where β is the heating rate, T_m the peak absolute temperature, and R the gas constant. Application of this analytical technique to the data presented in Table III gives the activation energies summarized in Table IV. The values in Table IV represent the mean activation energies calculated from all 10 heating rates. The data presented in this table and subsequent tables listing kinetic parameters have been assigned error limits based on 95% confidence limits.

Examination of these data allows some general observations to be made. It should be noted that the values obtained for the first stage are subject to larger errors than stages 2 and 3. This arises since in most cases these values are based upon interpretation of peak maxima from shoulders on the main peak (second stage). From an examination of the first stage data, it can be seen that, with the exception of an apparent reduction in the activation energy for the TRIS- and T271-treated samples, the value obtained for the AB19 system is similar to those obtained for the untreated samples. Meanwhile, in all cases, the activation

TABLE IV
Calculated First-Order Activation Energies (kJ/mol) According to Kissinger's Method²¹

System	Preliminary	Stage 1	Stage 2	Stage 3
T54	—	162.9 ± 10.0	202.1 ± 6.7	147.3 ± 3.5
MICH	—	156.5 ± 10.2	200.6 ± 5.0	145.5 ± 1.0
AB19	—	169.4 ± 16.6	188.4 ± 4.8	149.3 ± 2.3
T271	—	138.0 ± 9.9	193.9 ± 6.0	148.3 ± 2.3
TRIS	86.7 ± 3.7	125.8 ± 7.0	194.2 ± 4.2	143.6 ± 1.9
900F	—	—	182.2 ± 5.7	152.9 ± 3.3

energies for the second stage are all slightly less for the treated samples than the untreated ones. The third stage data, however, reveal no significant dependence of the activation energy upon the treatment with all samples having values between 144 and 153 (kJ/mol).

While the above technique of Kissinger has some merit in providing kinetic data, it, unfortunately, uses only one data point for each stage, namely, the temperature maximum, and can therefore be regarded as being restrictive in its interpretation. In our previous in depth study¹⁵ of various analytical methods applicable to the calculation of kinetic parameters, the best approaches were found to be those of Friedman²² and Ozawa.²³ The Friedman technique employs the differential form of the rate eq. (3),

$$\ln(d\alpha/dt) = \ln[\beta(d\alpha/dT)] = \ln A + n \ln(1 - \alpha) - E/RT \quad (5)$$

while the Ozawa method uses an integral solution,

$$\log \beta = \log(AE/R) - \log F(\alpha) - 2.315 - 0.4567E/RT \quad (6)$$

Both the above equations can be applied to fixed α values, when the function " $n \ln(1 - \alpha)$ " and its integral form " $F(\alpha)$ " can be considered constant, enabling kinetic parameters to be calculated from appropriate isoconversional plots. The apparent activation energies calculated using these two approaches are presented in Figures 3 and 4 as a function of α . The graphs presented in both these figures clearly indicate that for all the systems studied in this investigation, there is not a single value for the apparent activation energy but a range of values dependent upon the degree of conversion, α . The general appearance of the two figures also indicates that both the differential method of Friedman and the integral method of Ozawa are capable of providing very similar information, although the values do not appear to fluctuate as widely with the latter method. In ad-

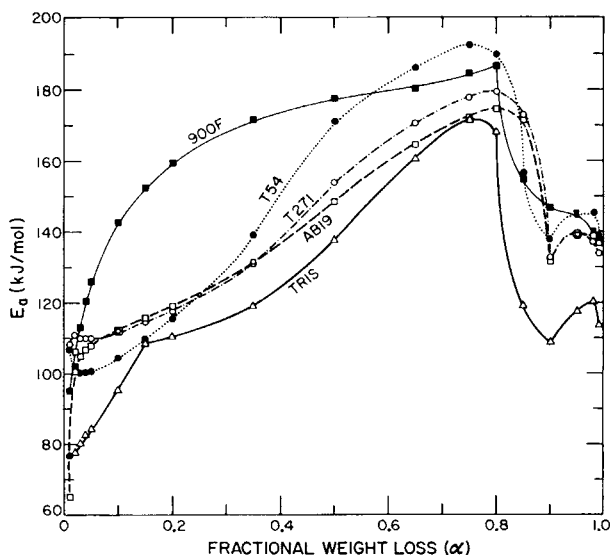


Fig. 3. Activation energies calculated using Ozawa's method as a function of fractional weight loss: (●) T54; (○) T271; (□) AB19; (△) TRIS; (■) 900F.

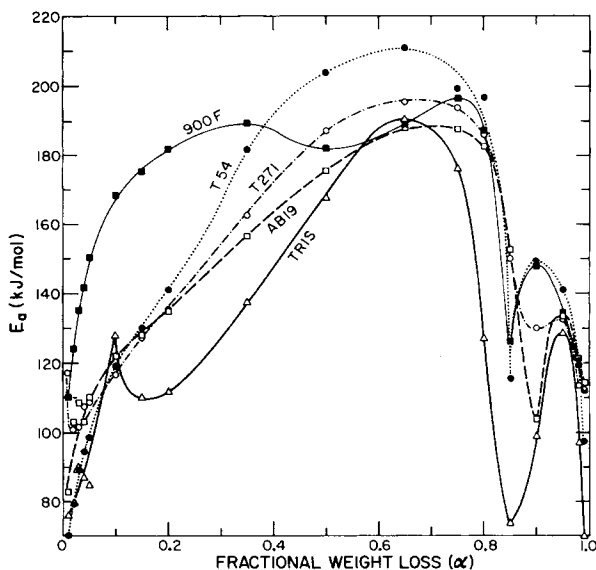


Fig. 4. Activation energies calculated using Friedman's method as a function of fractional weight loss: (●) T54; (○) T271; (□) AB19; (△) TRIS; (■) 900F.

dition, the errors in the calculated apparent activation energies were higher for Friedman's method than those obtained with Ozawa's method.

According to our previous study, it is possible to identify three major stages in the thermal decomposition of untreated PET from the apparent activation energies derived from Ozawa's isoconversional plots. For the untreated sample, examination of Figure 3 reveals these three stages at α values of 0–0.2, 0.5–0.8, and 0.9–1.0. The T271 and AB19 samples can also be identified by the presence of these three stages, although the second stage appears to be displaced to slightly higher conversions (0.65–0.85). In addition, the AB19 sample appears to have a lower apparent activation energy in the very early stages of the reaction. Meanwhile, the 900F and TRIS samples show unique behaviors. The 900F shows no indication of a first stage zone between 0 and 0.2. Instead, the apparent activation energy increases steadily with increasing fractional conversion from 0 to about 0.35 whereupon it appears to take up an approximately constant value between 0.35 and 0.8 during the second stage process. The third stage process, however, occurs at α values 0.9–1.0 and with similar values to those obtained with the untreated sample. The TRIS sample, like the 900F sample, also fails to show a uniform first stage, in that the apparent activation energies are increasing with increasing alpha values. However, unlike the 900F sample which shows signs of leveling off at 0.35 as it enters the second stage, the TRIS sample exhibits an apparent two-step increase in activation energy from 0 to 0.15 and 0.15 to 0.75, making it difficult to associate an actual zone of degradation as the first and second stages, respectively. There is, however, a clearly defined zone for the third stage process with TRIS, as was obtained with the other samples.

Having utilized the Ozawa data to identify the three stages in the thermal degradation of the untreated PET and the corresponding stages for the flame-retardant systems, it is now possible to obtain "global" kinetic parameters.

TABLE V
Calculated "Global" Kinetic Parameters According to Ozawa's²³ Method^a

Region		Stage 1	Stage 2	Stage 3
Fractional weight loss α		0.01-0.20	0.5-0.8	0.90-0.99
T54	<i>E</i>	101.8 ± 2.5	182.6 ± 7.5	142.4 ± 3.8
	log <i>A</i>	9.6 ± 0.2	15.9 ± 0.6	12.0 ± 0.2
MICH	<i>E</i>	101.9 ± 2.9	176.0 ± 6.5	136.8 ± 3.4
	log <i>A</i>	9.4 ± 0.3	15.4 ± 0.5	11.6 ± 0.2
AB19	<i>E</i>	110.6 ± 3.5 ^b	170.8 ± 4.3 ^c	137.7 ± 2.5
	log <i>A</i>	10.1 ± 0.4 ^b	15.0 ± 0.3 ^c	11.5 ± 0.2
T271	<i>E</i>	111.2 ± 1.7	175.8 ± 4.1 ^c	137.6 ± 2.5
	log <i>A</i>	10.0 ± 0.2	15.3 ± 0.3 ^c	11.6 ± 0.2
TRIS	<i>E</i>	76.6 - 110.6 ^d	167.7 ± 4.9 ^e	112.9 ± 5.2
	log <i>A</i>	7.9 - 10.7 ^d	14.8 ± 0.4 ^e	10.0 ± 0.2
900F	<i>E</i>	94.8 - 159.4 ^d	177.3 ± 4.9 ^f	144.1 ± 3.5
	log <i>A</i>	8.4 - 14.0 ^d	15.4 ± 0.4 ^f	12.0 ± 0.3

^a *E* in kJ/mol and *A* in min⁻¹.

^b Calculated for $\alpha = 0.03-0.20$.

^c Calculated for $\alpha = 0.65-0.85$.

^d Range for $\alpha = 0.01-0.20$.

^e Calculated for $\alpha = 0.65-0.8$.

^f Calculated for $\alpha = 0.35-0.8$.

These parameters determined using a weighed mean statistical procedure are presented in Table V for comparative purposes.

Examination of the Friedman data presented in Figure 4 reveals that the apparent activation energies once again vary with the degree of conversion, α , with the distinct stages once again being identifiable. For example, it is possible to identify the second stage in the 0.35-0.85 α region and the third stage in the 0.85-0.99 α region. At the low conversions, however, the apparent activation energies do not appear to have constant values; instead, they show a gradual increase in value as α is increased. The calculated "global" kinetic parameters obtained at the higher conversions using the weighed mean procedure are summarized in Table VI.

From the kinetic data presented in Figures 3 and 4 and summarized in Tables V and VI, it would appear that the two phosphorus only systems (i.e., AB19 and T271) are having only slight effects on the calculated apparent activation energies for the several decomposition stages of PET. For example, the activation energy

TABLE VI
Calculated "Global" Kinetic Parameters According to Friedman's²² Method^a

	Stage 2 ($\alpha = 0.35-0.80$)			Stage 3 ($\alpha = 0.85-0.99$)		
	<i>E</i>	log <i>A</i>	<i>n</i>	<i>E</i>	log <i>A</i>	<i>n</i>
T54	201.0 ± 8.5	13.1 ± 0.3	2.0 ± 0.2	141.9 ± 12.7	8.6 ± 0.2	1.3 ± 0.3
MICH	191.6 ± 6.7	12.3 ± 0.3	1.9 ± 0.2	130.8 ± 11.6	8.1 ± 0.1	1.0 ± 0.2
AB19	183.5 ± 8.4	11.8 ± 0.2	1.9 ± 0.1	120.2 ± 9.0	7.1 ± 0.2	1.3 ± 0.3
T271	187.8 ± 10.4	12.0 ± 0.3	2.0 ± 0.2	126.9 ± 8.3	7.5 ± 0.2	1.4 ± 0.2
TRIS	177.0 ± 9.9	10.9 ± 0.3	2.2 ± 0.2	89.2 ± 16.3	4.9 ± 0.1	1.3 ± 0.2
900F	187.0 ± 4.3	10.1 ± 0.9	3.0 ± 0.6	126.2 ± 5.8	7.8 ± 0.1	0.8 ± 0.2

^a *E* in kJ/mol and *A* in min⁻¹.

for the first stage of the decomposition is marginally higher than that for the control indicating a small increased thermal stability at the onset of thermal degradation.

In terms of obvious beneficial effects with respect to the combustion process, the only system to demonstrate this to any great extent is the 900F. This system has greater activation energies for the degradation process during the initial decomposition such that the primary chain scission processes are being retarded, delaying the release of volatile flammable gaseous species.

Interestingly, the TRIS system appears to be responsible for reduced apparent activation energies for all stages in the decomposition process. This suggests that the chemical TRIS has an adverse effect as a condensed-phase flame-retarding material. This observation is in line with pyrolysis-GC data and combustion studies performed in our laboratories,²⁴ which indicated that TRIS has a detrimental condensed-phase effect while having a strong beneficial effect as a gas-phase inhibitor.

One of the characteristics of the kinetic data generated by the Ozawa and Friedman methods was that an increase in E , the activation energy, was always accompanied by an increase in $\log A$, the preexponential factor. These variations in the Arrhenius parameters obtained from nonisothermal thermogravimetric results are known as the "kinetic compensation effect."²⁵ From a plot of these two parameters it is possible to determine the regression coefficients a_0 and a_1 from the slope and intercept since

$$\log A = a_0E + a_1 \quad (7)$$

These coefficients have been utilized by Mincheva et al.²⁶ to study the effect of bromine flame retardants on the degradation of PET. From the changes observed in the slopes of the compensation effect plots, they were able to deduce that changes were taking place in the degradation kinetics due to the presence of the flame retardant. Table VII shows the computed regression coefficients of the compensation effect plots of the kinetic parameters derived by Ozawa's method in this study. The data presented in this table encompasses the overall thermal degradation process, without due consideration for the individual stages. It is obvious from these calculated regression coefficients that the untreated samples and the AB19 are very similar, and, therefore, it can be assumed that these systems degrade by similar kinetic processes. The T271 system and 900F meanwhile are responsible for changes in a_1 and a_0 which have been interpreted

TABLE VII
Regression Coefficients of the Compensation Effect plots of the Kinetic Data Obtained from Ozawa's Method²³

	a_0	a_1	r^a
T54	0.079 ± 0.002	1.24 ± 0.31	0.994
MICH	0.080 ± 0.002	1.13 ± 0.32	0.993
AB19	0.078 ± 0.003	1.39 ± 0.39	0.989
T271	0.082 ± 0.003	0.75 ± 0.04	0.990
TRIS	0.074 ± 0.003	2.22 ± 0.39	0.984
900F	0.084 ± 0.003	0.35 ± 0.42	0.991

^a Correlation coefficient.

as beneficial. On the other hand, an opposite change is noted in the regression coefficients of the TRIS system suggesting a nonbeneficial kinetic effect.

CONCLUSION

Thermogravimetric analysis of flame retardant PET using a nonisothermal technique is capable of providing valuable information on the kinetics of the thermal degradation processes. First derivative thermograms and Arrhenius type plots have revealed the thermal degradation process to be a complex one involving several stages. From a comparison of the thermograms and the derived kinetic parameters, it can be concluded that the presence of phosphorus-only flame retardants (AB19 and T271) caused no large differences in the measured kinetic parameters. This suggests that the phosphorus species studied in this investigation do not greatly influence the degradation kinetics.

In the case of the bromine-containing polyesters (i.e., 900F and TRIS) some changes are noted. With the 900F compound the change appears beneficial as the degradation is retarded and larger apparent activation energies have to be overcome to produce the volatile species. Meanwhile, the TRIS polyester system appears to have a nonbeneficial effect on the condensed-phase degradation. With this system volatilization of gaseous fuel appears to be proceeding at an earlier stage than is encountered with the untreated PET samples and the energy barrier (apparent activation energy) to be surmounted to produce volatile products is reduced. Thus the TRIS system would appear to facilitate the degradation and, consequently, acts in a detrimental fashion as a condensed-phase flame retardant.

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