

Synthesis of Phosphorus-, Zinc-, and Chlorine-Containing Poly(ethylene terephthalate)

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SYNOPSIS

Phosphorus-, zinc-, and chlorine-containing oligomer was used as a comonomer including ionic bonds in its molecules in the synthesis of poly(ethylene terephthalate). Phosphorus-, zinc-, and chlorine-containing poly(ethylene terephthalate) including ionic bonds in its main polymer chain was synthesized. With a content of 0.6% P and 1.25% Zn and 0.1% Cl, the resin has the following characteristics: $\eta_{rel} = 1.407$; COOH 39.90 mg equiv KOH/g 10^{-6} ; and mp 255.8°C. The modifier acts as a thermostabilizer. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Introducing phosphorus and metals into poly(ethylene terephthalate) results in increased thermostability¹⁻³, improved antistatic properties⁴⁻⁶, improved flame retardance,^{7,8} increased dyeability,^{7,8} and enhanced resistance against the action of oxygen, light, and UV irradiation.⁹

The present paper reports the synthesis of poly(ethylene terephthalate), including in its molecule ionic bonds, using phosphorus-, zinc-, and chlorine-containing oligomer as a comonomer.

EXPERIMENTAL

Starting Compounds

Dimethyl terephthalate, mp 140–141°C; ethylene glycol, bp 197.5°C, $n_D^{20} = 1.4318$; and phosphorus-, zinc-, and chlorine-containing oligomer.¹⁰

Thermogravimetric Analysis

The thermogravimetric analysis was performed on a Paulik derivatograph (Paulik, Erdey-MOM) at a heating rate of 6°C/min and with Al₂O₃ inert substitution.

Measurements

Flame retardance—determined according to the basket method.¹¹

Hydroxyl value—determined by the acetylation method.

Acid value—a certain amount of the precondensate dissolved in benzyl alcohol was titrated with 0.5N KOH.

Methoxycarbonyl groups—determined gas chromatographically.

Water content of the distillate—determined with Fischer's reagent.

Acetaldehyde content of the distillate—determined gas chromatographically.

Content of 2-methyldioxolane—determined gas chromatographically.

Acetal content—determined gas chromatographically.

Carboxylic groups—a certain amount of the resin dissolved in benzyl alcohol was titrated with 0.02M NaOH in glycol.

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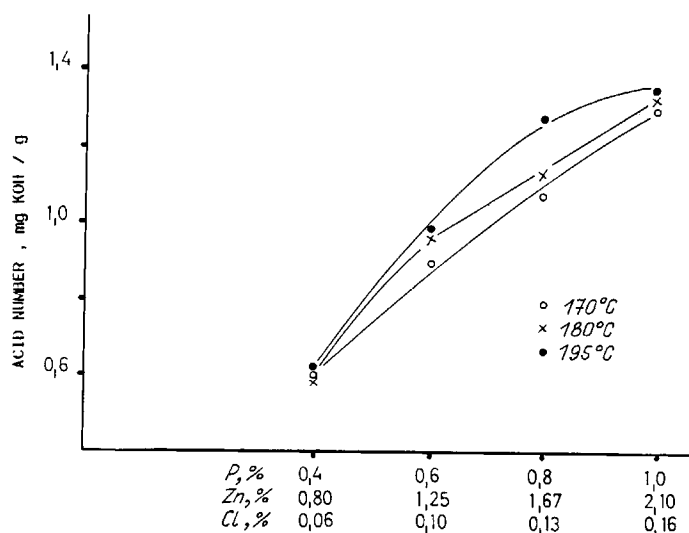


Figure 1 Acid value vs. phosphorus, zinc, and chlorine contents for the system-modifier/ethylene glycol at 170, 180, and 195°C.

Synthesis of Phosphorus-, Zinc-, and Chlorine-containing Poly(ethylene terephthalate)

A. Transesterification Stage

One hundred grams (0.52 mol) of dimethyl terephthalate and 69.3 g (1.12 mol) ethylene glycol, and phosphorus-, zinc-, and chlorine-containing oligomer in solutions of 1.94, 2.91, 3.88, and 4.85 g, respectively, were put in a three-necked (volume 250 mL) flask equipped with a stirrer, Vigreux column, and condenser. The transesterification was carried out at continuous stirring in a nitrogen inlet. $Mn(OAc)_2$, 0.022 g, dissolved in ethylene glycol was added at 150°C.

The transesterification was carried out for 3.5–4 h. The termination of the process was marked by the vapor temperature at the upper end of the col-

umn. Then, the system was heated in vacuum (1 Torr) to separate the excess absorbed ethylene glycol. $Ti(OBu)_4$ (0.1 g) was used as a catalyst for the transesterification run at the same conditions and mol ratios.

B. Polycondensation Stage

The reaction was carried out in a 0.7 L reactor, equipped with a propeller stirrer. Sb_2O_3 (0.1 g) was used as a catalyst for the polycondensation process, and triphenyl phosphite (0.1 g), as a thermostabilizer, which were added at the end of the transesterification.

The polycondensation proceeded *in vacuo* at about 1 Torr and at a maximum temperature of 270–275°C. The duration of the process was followed by

Table I Dependence of Diethylene Glycol and Water Contents in the System Ethylene Glycol (EG)/ Modifier on Modifier Concentration; Heating Temperature 195°C; Duration 90 Min

Introduced Metal (Zn) in 100 mL EG (%)	Introduced Chlorine in 100 mL EG (%)	Introduced Phosphorus in 100 mL EG (%)	Diethylene Glycol Content (%)	Water Content (%)
0.00	0.00	0.0	0.01	0.30
0.80	0.06	0.4	0.13	0.34
1.25	0.10	0.6	0.21	0.87
1.67	0.13	0.8	0.28	1.52
2.10	0.16	1.0	0.37	0.99

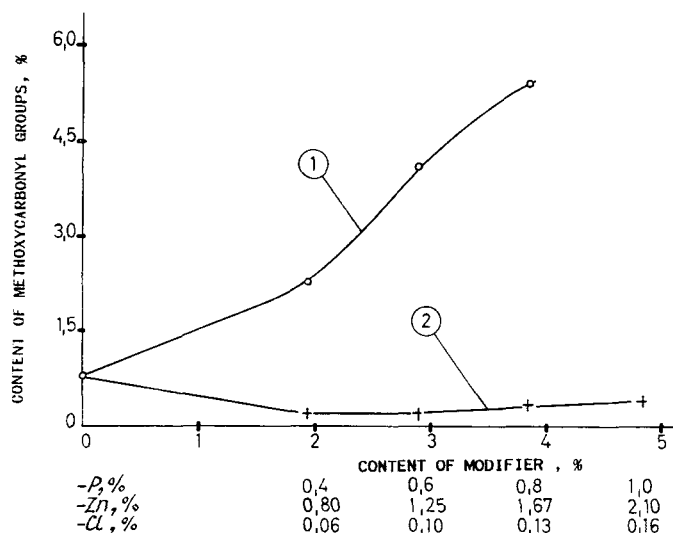
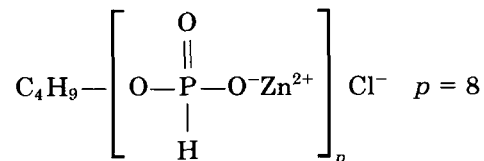


Figure 2 Methoxycarbonyl groups content vs. content of modifier for precondensates. Catalyst: (curve 1) $\text{Mn}(\text{OAc})_2$; (curve 2) $\text{Ti}(\text{OBu})_4$.

power changes in the electric motor of the stirrer (measured in A).

RESULTS AND DISCUSSION

Phosphorus-, zinc-, and chlorine-containing oligomer, synthesized by the interaction between dibutyl phosphonate and ZnCl_2 (Ref. 10), having the following structure:



was suggested as a modifier of the poly(ethylene terephthalate) in the present study.

By studying the dependence of the acid number of the system ethylene glycol/modifier on the mod-

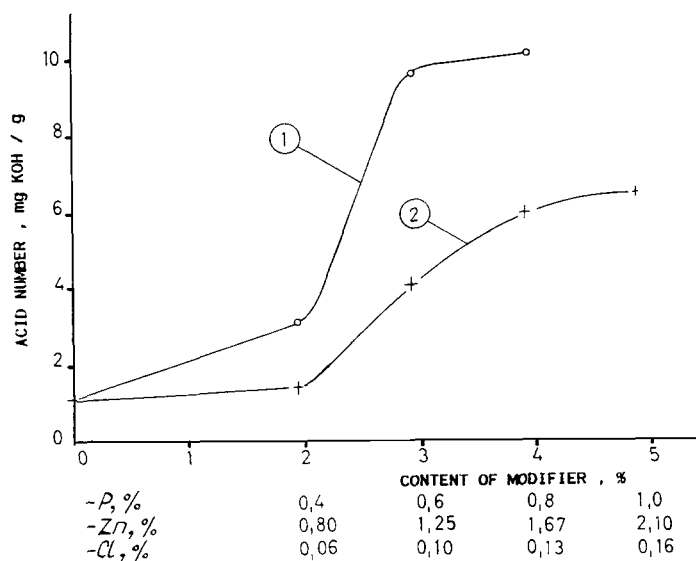


Figure 3 Acid number vs. content of modifier for precondensates. Catalyst: (curve 1) $\text{Ti}(\text{OBu})_4$; (curve 2) $\text{Mn}(\text{OAc})_2$.

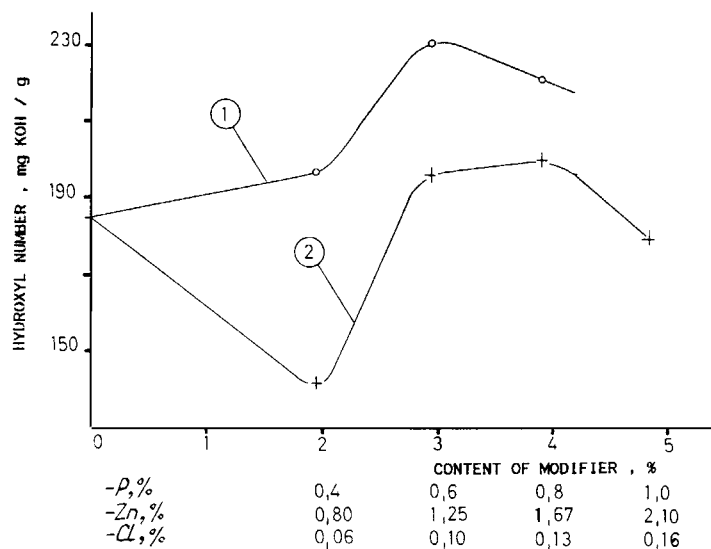


Figure 4 Hydroxyl number vs. content of modifier for precondensates. Catalyst: (curve 1) $\text{Mn}(\text{OAc})_2$; (curve 2) $\text{Ti}(\text{O}i\text{Bu})_4$.

ifier concentration and the temperature, it was found (Fig. 1) that with the increase of phosphorus, zinc, and chlorine content the acid number rises. Its maximum is at the maximum content of the modifier—1.26 mg KOH/g at 195°C. The modifier has a minimal effect upon the acid number. For a certain concentration of the modifier, the acid number changes slightly with increase in temperature, i.e., the phosphorus-, zinc-, and chlorine-containing modifier has good thermostability under the conditions of the investigation. The contents of dieth-

ylene glycol and water (Table I) show that the comonomer does not catalyze the dehydration of ethylene glycol.

Effect of Modifier upon Transesterification Rate

The comonomer was introduced into the reaction system—dimethyl terephthalate/ethylene glycol—at the beginning of the transesterification. Increasing the content of the comonomer, the content of the methoxycarbonyl groups (Fig. 2, curve 1) in-

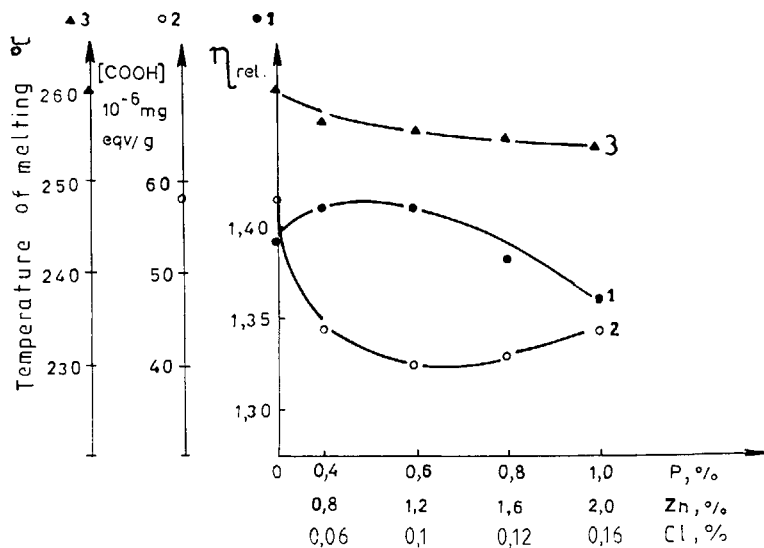


Figure 5 (Curve 1) relative viscosity, (curve 2) carbonyl groups content, and (curve 3) temperature of melting vs. phosphorus, zinc, and chlorine contents.

Table II GC Results of Distillates, Obtained via Transesterification of Dimethyl Terephthalate with Ethylene Glycol in the Presence of the Modifier; Catalyst: $\text{Mn}(\text{OAc})_2$

Introduced Metal (Zn) (%)	Introduced Chlorine (%)	Introduced Phosphorus (%)	Acetaldehyde (%)	Diethylene Glycol (%)	2-Methyldioxolane (%)	Acetal (%)
0.00	0.00	0.0	0.008	1.40	0.132	0.083
0.80	0.06	0.4	trace	0.03	0.05	0.037
1.67	0.13	0.8	trace	0.05	0.05	0.027

creases, reaching 5.4% at a content of Zn, 1.65; P, 0.8%; and Cl, 0.13%. This modifier lessens the catalytic efficiency of manganese acetate—the transesterification catalyst. A considerable increase in the acid number is observed (Fig. 3, curve 1). The oligomerization of bis(2-hydroxyethyl)terephthalate runs at a slow rate. The hydroxy number of the modified precondensates is higher than that of the nonmodified one (Fig. 4, curve 1). The temperature of melting of the modified precondensates also detects the high oligomerization degree.

The side reactions are suppressed in the presence of this comonomer (Table II).^{12,13} The content of acetaldehyde, diethylene glycol, 2-methyldioxolane, acetal, and water in the distillates obtained from the

transesterification conducted with the modifier is quite lower than that in the distillate, obtained from the nonmodified precondensate. Precondensates with the same phosphorus, zinc, and chlorine content were synthesized using $\text{Ti}(\text{O}i\text{Bu})_4$ as the transesterification catalyst.

The presence of this catalyst does not affect the normal run of the transesterification (Fig. 2, curve 2). At the highest concentration of the comonomer, the content of methoxycarbonyl groups is 0.35%. The acid number increases (Fig. 3, curve 2), but less than in the case using manganese acetate as a catalyst. The oligomerization of bis(2-hydroxyethyl)terephthalate proceeds normally (Fig. 4, curve 2). Quite higher are the temperatures of melting of

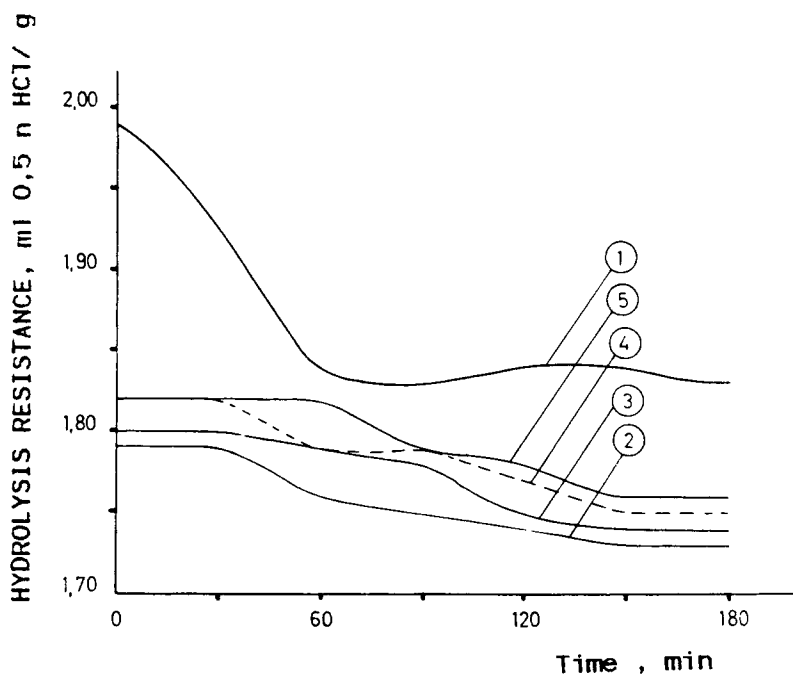


Figure 6 Time dependence of the hydrolysis resistance of modified resins at phosphorus, zinc, and chlorine contents: (curve 1) P, 0.0; Zn, 0.0; Cl, 0.0; (curve 2) P, 1.0; Zn, 2.0; Cl, 0.16; (curve 3) P, 0.8; Zn, 1.6; Cl, 0.12; (curve 4) P, 0.6; Zn, 1.2; Cl, 0.1; (curve 5) P, 0.4; Zn, 0.8; Cl, 0.06.

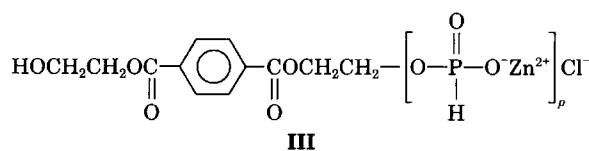
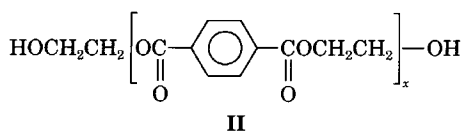
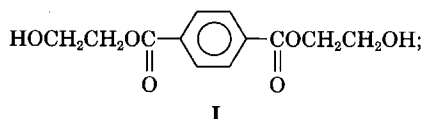
Table III GC Results of Distillates, Obtained via Transesterification of Dimethyl Terephthalate with Ethylene Glycol in the Presence of the Modifier; Catalyst: Ti(OBu)₄

Introduced Metal (Zn) (%)	Introduced Chlorine (%)	Introduced Phosphorus (%)	Acetaldehyde (wt %)	Diethylene Glycol (wt %)	2-Methyldioxolane (wt %)	Acetal (wt %)
0.00	0.00	0.0	0.008	1.40	0.132	0.083
0.80	0.06	0.4	trace	0.06	0.030	0.010
1.67	0.13	0.8	trace	0.02	0.060	0.005
2.10	0.16	1.0	trace	0.08	0.040	0.013

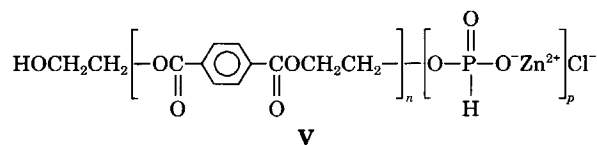
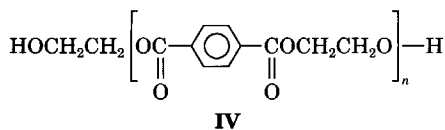
the modified samples when compared to those of the nonmodified samples. The side reactions with this catalyst are suppressed as well (Table III). Acetaldehyde, diethylene glycol, 2-methyldioxolane, and acetal contents are significantly lowered.

Comonomer Effect upon Polycondensation Rate

The modified precondensates have mainly the following structures:



Polycondensation of the modified precondensates will result in polyester resin, composed of two types of macromolecules:



There is a small probability for two molecules of structure V to react and form macromolecules no

longer able to grow due to the low concentration of the modifier.

The characteristics of the synthesized modified (Fig. 5) resins show that the presence of the modifier does not influence the normal running of the polycondensation. At P, 0.4%; Zn, 0.8%; and Cl, 0.1% contents, the relative viscosity of the modified resin is higher than that of the nonmodified resin (Fig. 5, curve 1). For all modified samples, the content of carboxyl groups (Fig. 5, curve 2) is lower, which points to a thermostabilizing effect of the modifier. It is an expected result because the used comonomer is located at the end of the polymer chain and does

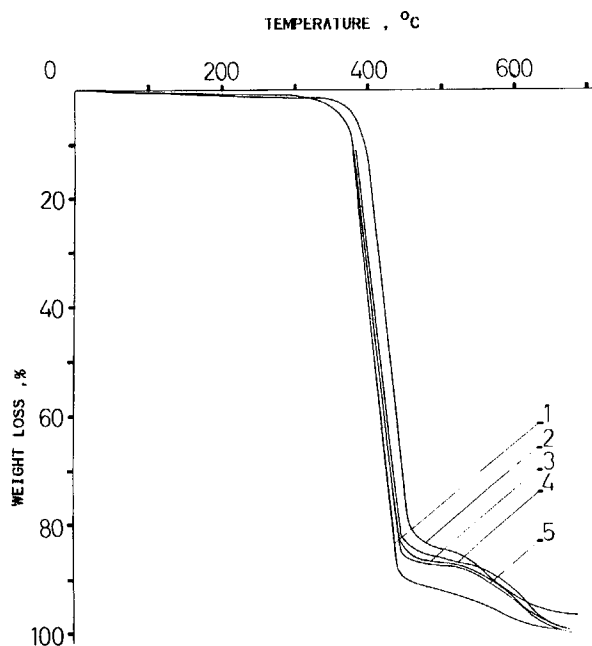


Figure 7 Thermogravimetric curves of modified poly(ethylene terephthalate) at phosphorus, zinc, and chlorine contents: (curve 1) P, 0.0; Zn, 0.0; Cl, 0.0; (curve 2) P, 1.0; Zn, 2.0; Cl, 0.16; (curve 3) P, 0.8; Zn, 1.6; Cl, 0.12; (curve 4) P, 0.6; Zn, 1.2; Cl, 0.1; (curve 5) P, 0.4; Zn, 0.8; Cl, 0.06.

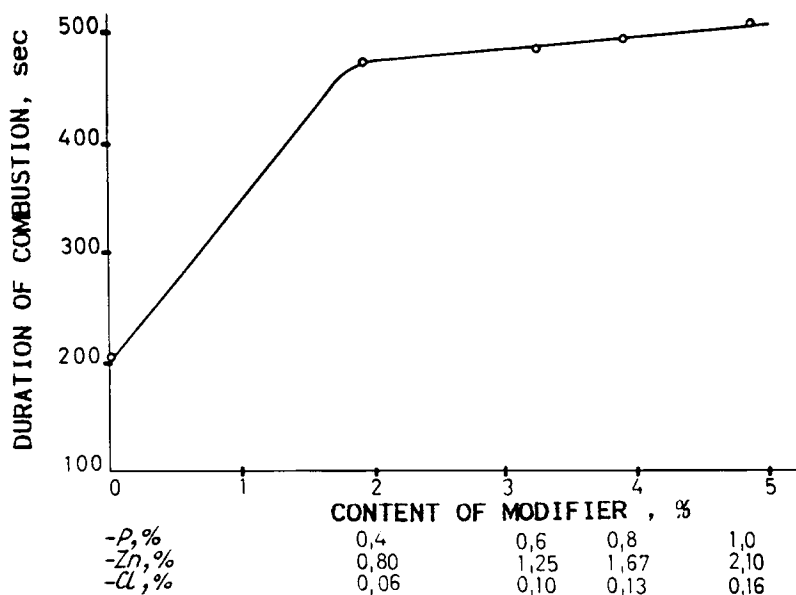


Figure 8 Dependence of duration of combustion vs. content of phosphorus, zinc, and chlorine.

not allow the thermal destruction of hydroxyl groups.

The content of diethylene glycol and oligomers is higher in comparison to that in the nonmodified resin, but not significantly. That is why the determined temperatures of melting (Fig. 5, curve 3) are close to those of the nonmodified samples.

The achieved results show that phosphorus-, zinc-, and chlorine-containing comonomer does not hinder the normal proceeding of the synthesis.

Hydrolysis Resistance

The investigation data show that the modified resin is less hydrolysis resistant than is the nonmodified resin (Fig. 6). The maximum decrease of the hydrolysis resistance is at the highest concentration of the comonomer: 4.4%. Obviously, the presence of the P—O—C bonds is a determining factor for the decreasing of hydrolysis resistance.

Thermal Stability

The study carried on the thermal stability shows that the presence of the modifier does not worsen the thermal stability. At 300°C, the starting destruction temperature, weight losses of the modified samples are 1.0–1.5% (Fig. 7). A lowered destruction rate was observed at higher temperatures for the modified samples. There is a plateau in the TG

curves at the interval 400–500°C, i.e., the structural processes proceed without a weight loss in this interval.

Flame Retardance

Duration of combustion of the modified samples increases in comparison with that of the nonmodified resin (Fig. 8). The data from the combustion test allow the assumption that there is a dependence of flame retardance on polymer structure. The dependence duration of combustion/modifier content shows that the optimum modifier concentration should be 1.94%, since at this concentration, the greatest increase of duration of combustion of the modified sample occurs.

The conclusions drawn from the present study are that phosphorus-, zinc-, and chlorine-containing comonomer does not influence the normal proceeding of poly(ethylene terephthalate) synthesis; the modified resin is of enhanced flame retardance; and the modifier acts as a thermostabilizer as well.

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