Flame Retardant Polyesters. I. Phosphorous Flame Retardants

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ABSTRACT: Commercially available two types of phosphorous flame retardants (FRs) for polyester were compared from the viewpoint of chemical reactivity, reaction mechanism, and byproduct formation. 3-(Hydroxyphenyl phosphinyl) propanoic acid (HPP) and 9,10-dihydro-9-oxa-10-2,3-dicarbonylpropyl)-10-phosphophenanthrene-10-oxide (DI) were used as a main chain type and a pendant type, respectively. HPP and DI showed different behavior with ethylene glycol (EG). More acidic HPP reacted with EG spontaneously and then produced esterified terminal hydroxy end group reacted with EG to form terminal diethylene glycol (DEG) end group. But the composition in the HPP solution was not varied for a long time below the esterification temperature. Contrast to HPP, DI showed normal esterification procedure. DI esterified with EG to form DI ester of EG, and DEG formation is not distinct. The difference of reactivity and DEG formation is caused by the difference of acidity in EG solution. For production of phosphorous containing polyester, it is desirable that HPP is introduced into the reactor in the mere solution state and DI in the esterified state. In addition, for production of polyester having the same phosphorous content in commercial scale, it is more beneficial to apply HPP than DI because of low input of FR due to low molecular weight. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 2870–2874, 2007

Key words: phosphorous flame retardants; main chain type; pendant type; reactivity; DEG

INTRODUCTION

Polyester, especially poly(ethylene terephthalate), is now widely used for textile fiber, technical fiber, film, bottles because of its good mechanical properties, thermal stability, and low production cost. The demand of polyester in 2006 is estimated about 35 million tons and will be grow annually by 9%.[1] Many kinds of flame retardants (FRs) have been tested to improve the flame retardancy of polyester and applied to commercial products.[2] Among these, phosphorous FR and halogenated FR have been usually applied to polymerization or blending. But many kinds of halogenated FR, especially brominated FR, are prohibited in many nations due to the formation of dioxin under combustion.[3] So most of the inherent flame retardant polyesters are now produced using phosphorous FR.[4–7]

In case of commercial phosphorous flame retardant polyester production, two types of FRs are used: main chain type FR[4,6] and pendant (side chain) type FR.[5,7]

Zhao et al.[8] synthesized high phosphorous content polyesters of the two types and compared the decomposition activation energy of them. Sato et al.[9] compared the acidic hydrolytic resistance of the fibers with two comonomer types. They concluded that the flame retardancy is controlled by the phosphorous content and acidic hydrolytic resistance of the polymer and pendant type is better than main chain type. Chang et al.[10] also reported the difference of thermal stability between two types of FRs. They suggested that the thermal degradation activation energy decreases with increase of phosphorous content and the thermal degradation activation energy of pendant type is lower than that of main chain type.

Diethylene glycol (DEG) added as a additive type or formed during the reaction influenced on the polyester properties. It affected the thermal stability,[11] crystallization and melting behavior,[12–14] and fiber properties.[15] DEG formed during the reaction is mainly produced from the etherification between the esterified terminal hydroxy end group and free hydroxy end groups of EG, and high acidity of the reactants generated more DEG.[16–18]

However, there are few reports on comparison of the chemical reactivity between two types of FRs. In this study, we compared the two types of FRs in

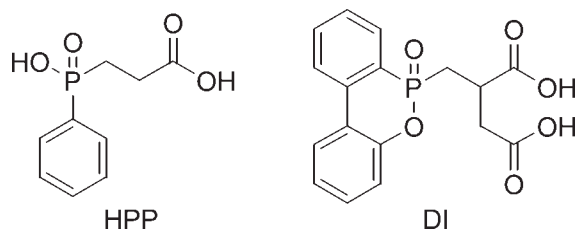*Correspondence to:* S.-C. Yang (imsoo1@snu.ac.kr or imsoo@hyosung.com).

Figure 1 Chemical structures of FRs.

terms of chemical reactivity, reaction mechanism, and byproduct formation. 3-(Hydroxyphenyl phosphinyl) propanoic acid (HPP) was used as a main chain type FR and 9,10-dihydro-9-oxa-10-2,3-dicarbonylpropyl)-10-phosphophenanthrene-10-oxide (DI) as a pendant type FR.

EXPERIMENTAL

Materials

3-(Hydroxyphenyl phosphinyl) propanoic acid (HPP) used as a main chain type flame retardant was supplied by I company and 9,10-dihydro-9-oxa-10-2,3-dicarbonylpropyl)-10-phosphophenanthrene-10-oxide (DI) used as a side chain flame retardant was supplied by S company. They were all used without further purification. Fiber grade EG and OET were also used without further purification as utilized in Hyosung Corp.

The structures of HPP and DI were presented in Figure 1.

Characterization of raw materials

Both FRs were white fine powders having peculiar smell and easily soluble in warm EG. Acid value, melting point, and density have no severe differences as shown Table I. But the molecular weight of DI was higher than that of HPP, so phosphorous content of DI was lower than that of HPP. Therefore, to make products having same phosphorous content with DI, higher feeding quantity is necessary.

The most distinct difference is pH in EG solution. The pH of DI is about 3 times as high as that of HPP, so the acidity of DI is much lower than that of HPP.

And the composition of OET used in this investigation analyzed by high performance liquid chromatography(HPLC) using Jasco LC 2000 in hexafluroisopropanol/dichloro methane (1/3 vol) solution was shown in Figure 2. OET is the mixture of oligomers from monomer to about 11-mer. OET used in this investigation is white flake and basic properties are as follows: acid value 320, DEG content 0.52 wt %, very broad melting temperature about 230°C.

Reaction with EG

HPP and DI were reacted with ethylene glycol (EG) in the reactor equipped with vigreux column and condenser. After 50% FR-EG solution was poured into the reactor, inner temperature was raised to 190°C, and maintained under agitation. The reaction was finished when theoretical amount of water was produced and the top of the vigreux column was dropped from 100 to 70°C. The amount of drained water with time was presented in Figure 3.

The retention time of the products in the reaction solution in the HPLC chromatogram was shown in Figure 4. In Figure 4, the products of FRs with EG were identified with retention time in HPLC chromatogram, respectively. The identification of the materials was carried out by GC/MS method.

In case of HPP, steady DEG formation occurred in the esterification stage. The composition of the HPP solution is analyzed with exposed time at 100°C. HPP was dissolved in EG at room temperature, stored for 8 days at 100°C, and was sampled every day and analyzed using HPLC as shown in Figure 5.

Reaction with OET

In case of normal polyester production, either continuous polymerization process or semibatch polymerization process is used. Polymerization comprises the continuous slurry (TPA and EG paste) introduction to the reactor containing the molten OET, dissolution of terephthalic acid (TPA) in EG-OET mixture, and esterification process. Esterification ratio and content of DEG are important in the polycondensation reaction.[20]

Generally contents of phosphorous in polyester polymer are in the range of 0.5–0.7% by weight.[4–7] So the amount of FR was adjusted to 0.65% of phosphorous atom in the reactant. The FR was intro-

TABLE I
Properties of FRs

Material	HPP	DI	Remark (unit)
Molecular weight	214.15	346.21	g/mol
P-content[a]	14.5	9.0	wt %
Acid value[b]	520	475	mg KOH/g
Melting point[c]	160	188	°C
pH[d]	1.2	3.8	50% EG solution
Density	1.40	1.42	g/cm^3

[a] P-content was analyzed by oxidative degradation-molybdenium blue method[19].
[b] Acid value was analyzed by KOH titration in ethanol solution.
[c] Melting point was determined as endothermic peak by differential scanning calorimetry using DSC 7 of Perkin-Elmer.
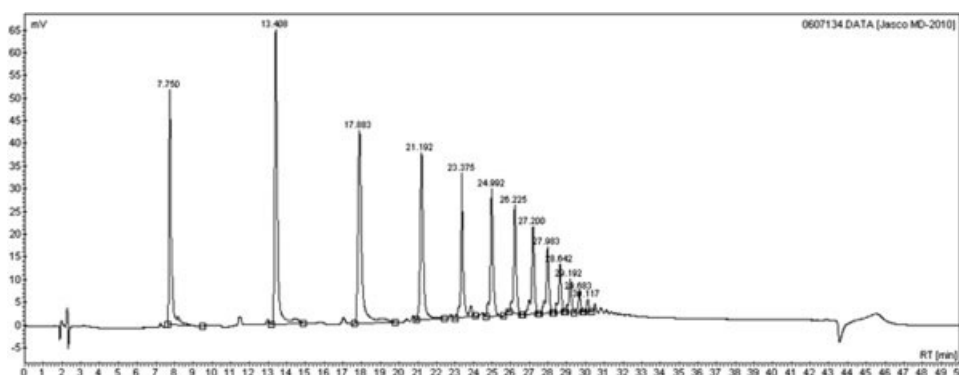[d] pH was determined in 50% EG solution using AB15 of Fischer Scientific.

Figure 2 HPLC chromatogram of OET.

duced to the esterification reactor either as raw powders or 50% EG solution state in the case of HPP and esterified state in the case of DI. Reaction temperature was kept at 250°C for 3 h. The amount of poured FR, the esterification ratio, and DEG content of the resultant oligomers were shown in Table II.

RESULTS AND DISCUSSION

Characterization of FRs

In Figure 1 and Table I, both type FRs contain phosphorous atom in the molecules. But the environments of the phosphorous atom are somewhat different. The phosphorous atom in HPP connected in hydroxy group to form terminal phosphinic acid but the phosphorous atom in DI is substituted into bulky phenanthren structure and cannot show active functionality. So more acidic terminal phosphic acid increase the acidity of EG solution of HPP and decrease pH of the EG solution of HPP. As a result of easier molecular stacking of phospohenanthren and higher molecular weight, the melting point and density of DI are higher than those of HPP.
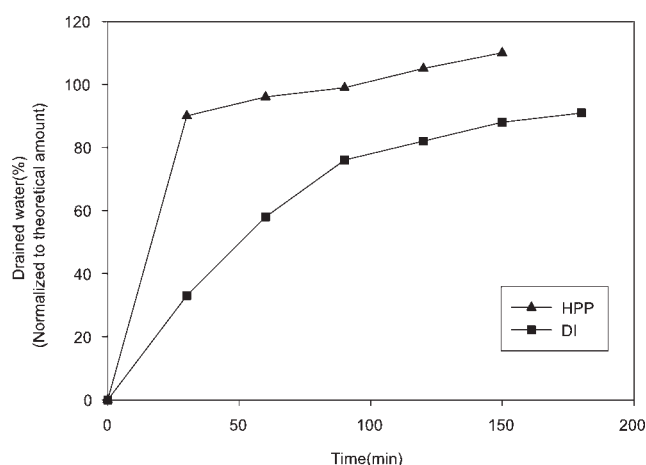
The reactivity of the FRs with EG

The esterification and further etherification of FR and EG are shown in Figures 3 and 6. There is a significant difference between the behaviors of reaction. In the case of HPP, esterification reaction occurs instantly and then etherification reaction is proceeded. However, DI was esterified with EG to monoester, then further esterified with EG remnant carboxylic acid. During this reaction, etherification reaction is not dominant. The composition of the reaction mixture with time is shown in Figure 6.

The esterification reactivity with EG of HPP was much higher than that of DI. In Figure 3, drained water ratio from the reactor of HPP and EG was higher than that of DI and EG in early stage and increases steadily over theoretical amount. In contrast to HPP, drained water ratio from the reactor of DI and EG increases steadily to theoretical amount. From drained water, we can presume that HPP reacts with EG very fast and then another reaction occurred and DI reacts with EG continually. This
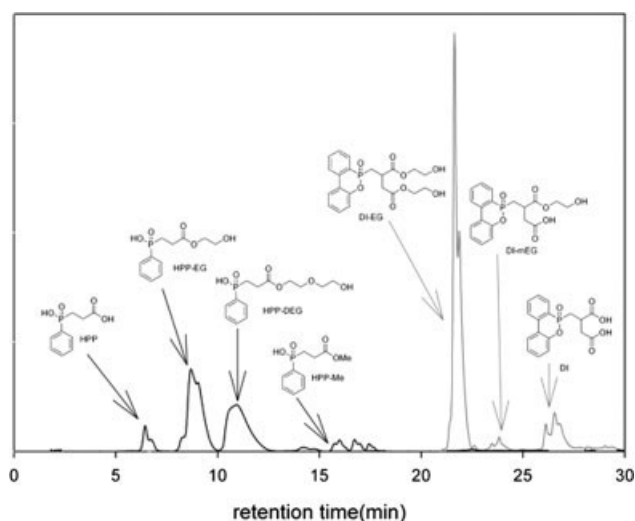

Figure 3 Drained water with reaction time (normalized to theoretical amount).

Figure 4 Peak identification of the materials in the HPLC chromatogram.
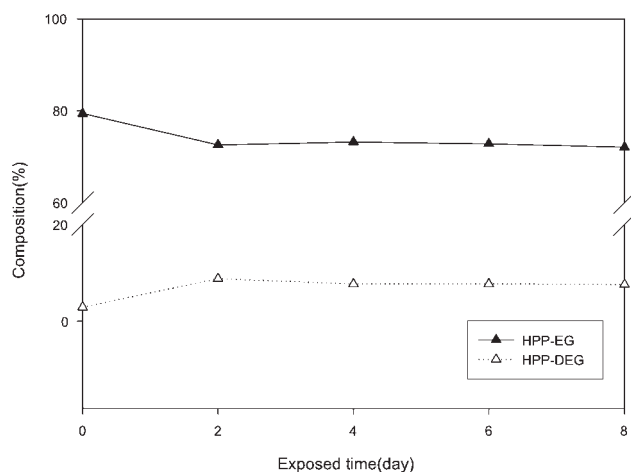
Figure 5 Compositional variation of HPP solution with time at 100°C.

Figure 6 Compositions of reaction mixtures with reaction time.

assumption is clarified with the analysis of the composition in the reactor by HPLC in Figures 4 and 6. So we suggest the reaction mechanisms of FRs with EG as shown in Figure 7.

More acidic HPP reacts with EG spontaneously to form HPP-EG, esterified products of HPP and EG, and HPP-EG further reacts with EG to form HPP-DEG, dehydrated products of HPP-EG and EG. But mild acidic DI reacts with EG to form DI-mEG, esterified products one of two carboxylic acid and EG, and DI-mEG further reacts with EG to form DI-EG, esterified completely esterified products. Difference in terminal DEG group formations is brought about by the difference of the acidity of FRs. And the terminal phosphinic acid of HPP acts as a protic acid, it promote the esterification and further etherification. This phenomenon well coincide with the works of Hovenkamp and Munting[16] and Chen and Chen,[18] which show that the concentration of esterified terminal hydroxy end group is higher because of the small molecular weight and high initial esterification rate.

In case of DI, it shows normal esterification reaction as shown in Figure 3. At 190°C ester formation of DI-EG increased with increasing time. Also unreacted DI and monoester, DI-mEG decreased

with reaction time, and further etherification to DEG was not detected.

As a result of reaction of both FRs, we propose that it is advantageous to use HPP in a solution state at relatively low temperature about 100°C due to the low DEG content in solution, and it is advantageous to use DI in a esterified state due to low DEG formation rate, and relatively low esterification rate.

Reaction with OET

Most of the large-scale commercial polyester production processes using TPA as a raw material include batch process and continuous process. In each process, esterification reaction where the TPA paste reacts in the molten OET at high temperature about 250–260°C occurs first and followed by polycondensation of OET at higher temperature about 280–290°C under high vacuum below 1 Torr, which explains the importance of the reaction between FR and OET.

From the Table II, both FRs introduced into the reactor as a raw powder show lower esterification conversion rate but FRs introduced as a EG solution show higher rate than initial OET.

When both FRs are introduced as a raw powder, free EG in OET (below 1.2% under normal commercial scale polyester production) is not sufficient for the esterification with FRs. So the esterification conversion is lowered. And both FR act as etherification catalysts, especially as a protic acid form, so both FR accelerate the etherification and DEG content is increased. These results in worse polyester polymerization performance.

When both FR are introduced as an liquid state (DI as an esterified solution and HPP as a mere EG solution), the esterificaiton conversion is increased because both FRs is already esterified. However, the

TABLE II
Properties of OETs Before and After Reaction with FRs

FR condition	Initial OET	DI		HPP	
		Powder	Esterified	Powder	Solution
ES%[a]	96.8	95.3	97.4	93.7	97.2
DEG (wt %)[b]	0.52	1.38	1.57	1.78	2.61

[a] ES% is esterification ratio calculated from acid value analyzed by KOH titration in benzyl alcohol solution.
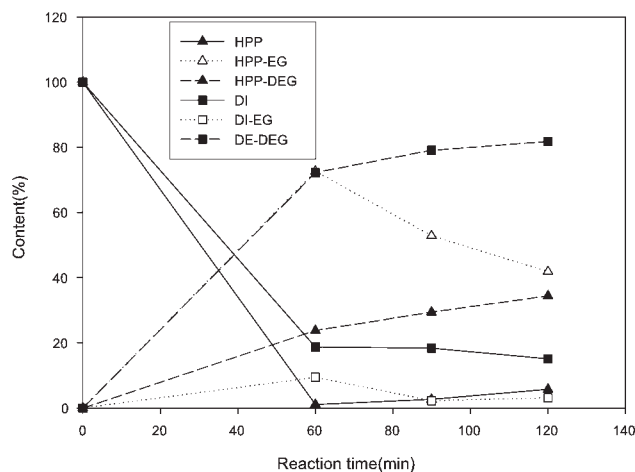[b] DEG was analyzed by monoethanol amine hydrolysis-gas chromatographic method.
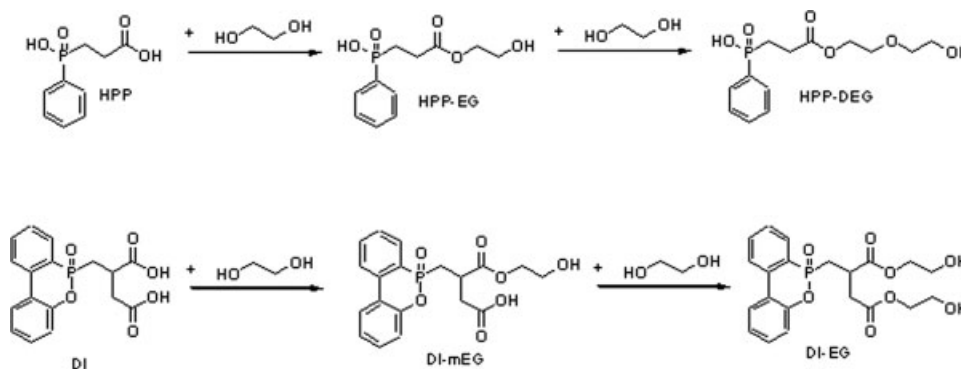
Figure 7 Suggested reaction mechanisms of FRs with EG.

DEG content increased because FRs is added simultaneously with EG. The DEG content is much higher when FR is introduced as a liquid state than as a raw state. Increase of the DEG content were brought from the increase of the concentration of the reactant (EG in the reactor), which was introduced simultaneously with FRs into the reactor.

CONCLUSIONS

Two types of commercial phosphorous FR were compared in terms of the chemical reactivity, reaction mechanism, and byproduct formation. Differences in chemical reactivity, reaction mechanism, and byproduct formation of FRs were found to be brought about by the acidity of FRs. Main chain type FR showed higher chemical reactivity in both esterification and etherification than DI, so DEG formation of main chain type FR was significant. The reaction mechanisms were different. In case of main chain type, spontaneous esterification happened and then steady etherification was dominant. But in case of pendant type, steady esterication proceeded.

Phosphorous atom in main chain type FR forms more acidic phosphinic acid make FR solution more acidic than that of pendant type, the esterifiaction and further etherification rate were promoted. Esterification occurred spontaneously, and then etherification is dominant reaction. So to control the DEG formation, it is profitable to use main chain type FR in solution state at low temperature about 100°C. But phosphorous atom in pendant type FR is more stable than that of main chain type FR, the acidity of pendant type FR solution is mild, and esterification of pendant type FR and EG is continually proceeded and etherification is not severely occurred. It is advantageous to use the pendant type FR in a esterified state due to low esterification rate and insignificant DEG formation.

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