Flame-Retardant Polyesters. II. Polyester Polymers

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ABSTRACT: Two flame-retardant polyesters were polymerized with two types of phosphorous flame retardants. 3-(Hydroxyphenyl phosphinyl)propanoic acid (HPP) was used as a main-chain type, and 9,10-dihydro-9-oxa-10-2,3-dicarbonylpropyl-10-phosphophenanthrene-10-oxide (DI) was used as a pendant type. Polymerization was accomplished on a commercial scale with a three-reactor system to exclude the compositional variation of oligomeric ethylene terephthalate. A longer polycondensation time and a higher dosage of the catalyst were necessary for DI with respect to HPP because of the high content and relatively low reactivity of the flame retardant. However, the content of diethylene glycol (DEG) in the polyester, which formed during the polymerization, was much higher in the case of HPP. The produced polyesters had almost the same molecular weight, but the DEG contents in the polyesters were quite different. The higher DEG content in the HPP polyester reduced the thermal stability. The greater flexibility of the HPP polyester chain resulted in easier crystallization and a lower crystalline temperature. The HPP polyester had higher susceptibility to thermal degradation because of low resistance to thermal chain scission, degraded at a lower temperature, and was more easily degraded because of a weak P—O bond linkage in the main chain. The DI polyester, whose phosphorous atom was highly sterically hindered, showed better alkaline resistance than the HPP polyester because of the lower acidity and lower hydrophilic DEG content. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 1274–1280, 2007

Key words: esterification; flame retardance; polycondensation; polyesters

INTRODUCTION

Polyesters [mainly poly(ethylene terephthalate) (PET)] are now widely used for textile fibers, technical fibers, films, and bottles because of their good mechanical properties, thermal stability, and low production cost. Their demand has been estimated to be about 35 million tons in 2006 and is expected to grow annually by 9%.[1] In connection with the danger of a fire, there have been many studies to improve the flame retardancy of polyesters. In particular, flame-retardant (FR) polyester yarns have been produced by blending or copolymerization with an FR master batch or FR additives.[2,3] Nowadays, polyesters that are almost inherently FRs are produced with copolymerizable phosphorous FRs.[4–7]

FR polyesters with mainly two types of FRs have been widely investigated. Zhao et al.[8] synthesized high-phosphorous-content polyesters of the two types and compared the decomposition activation energies. They concluded that the decomposition energy in air was lowered when the phosphorous

linkage was on the side chain versus the main chain. They did not examine the diethylene glycol (DEG) content in the polyesters and did not consider the thermal degradation caused by DEG. Sato et al.[9] compared the acidic hydrolytic resistance of the fibers according to the monomer types. They concluded that the flame retardancy was controlled by the phosphorous content and acidic hydrolytic resistance of the polymers and that a pendant type was better than a main-chain type. Chang et al.[10] also reported the difference in the thermal stability between the two types of FRs. They suggested that the thermal degradation activation energy decreased with an increase in the phosphorous content and that the thermal degradation activation energy was lower for the pendant type. However, they did not consider the effect of DEG on the thermal stability.

DEG, which is an additive itself that is formed during the reaction, has an influence on the crystallization and thermal degradation of polyesters. Hergenrother[11] reported that the mechanism of degradation of DEG in polyesters was different from that of PET and that thermal degradation occurred very rapidly at lower temperatures. Fakirov et al.[12] reported that the incorporation of DEG into polyester chains lowered the melting temperature, density, and lamellar thickness.

The formation of DEG in polymerizations has been widely reported. Hovenkamp and Munting[13] reported that DEG is formed mainly by unusual reactions (e.g., ester + alcohol → ether + acid), not by dehydration reactions between the alcohols. Chen and Chen[14,15] reported that the esterification stage is the most critical stage for DEG formation and that an esterified terminal hydroxyl end group has higher reactivity than pure ethylene glycol (EG) in the formation of DEG. The protons in the reactant lower the activation energy in the formation of DEG. Polyesters are mainly produced with terephthalic acid (TPA) as a raw material, which needs oligomeric ethylene terephthalate (OET) to increase the esterification rate, so DEG is formed by side reactions; the concentration can be about 0.5–1.5 wt % according to the process and polymerization conditions.

We previously reported the differences in phosphorous FRs according to the types: a main-chain type and a pendant type.[16] We concluded that the acidity of FRs exerts an influence on the reactivity and that the reaction mechanisms are different. 3-(Hydroxyphenyl phosphinyl)propanoic acid (HPP), a main-chain-type FR, is very acidic and reacts with EG spontaneously to produce an esterified product of HPP and EG, and the product further reacts with EG into an etherified product (an esterified form of HPP with DEG) at high temperatures, but it is stable in an EG solution at a relatively low temperature. However, mildly acidic 9,10-dihydro-9-oxa-10-2,3-dicarbonylpropyl-10-phosphophenanthrene-10-oxide (DI) reacts with EG to produce a monoester of DI with EG, and the remaining carboxylic acid further esterifies with EG. In the case of DI, the formation of DEG is not distinct. Therefore, it is advantageous to use HPP in a solution state at a relatively low temperature and to use DI in an esterified state.

In this study, we produced polyesters with two types of phosphorous FRs on a commercial scale and compared the polymerization behaviors, thermal stabilities, and chemical resistance.

EXPERIMENTAL

Raw materials

All materials for this study were used without further purification. TPA was supplied by Hyosung Corp. (Ulsan, Korea), EG was purchased from Honam Petrochemical Corp. (Yeocheon, Korea), and antimony trioxide as a polycondensation catalyst was purchased from Golden Sea Chemicals (Yiyang, China); they were used without purification. 3-HPP powder as a main-chain-type FR was purchased from I Co. (Ulsan, Korea), and 65 wt % DI–EG in an EG solution came from S Co. (Boeblingen, Germany).

Polymerization equipment

Polymerizations with both types of phosphorous FRs were accomplished in a three-reactor system, as briefly shown in Figure 1. The volume and capacity of the reactors were 4.5 m^3 and 1.5 ton/batch, respectively.

The polymerization equipment consisted of a slurry preparation tank, a slurry storage tank, a first esterification reactor, a second esterification reactor, and a polycondensation reactor. TPA and EG were mixed in the slurry preparation tank and stored in the slurry storage tank. OET (1.3 tons) was kept in the first esterification reactor, and the slurry was
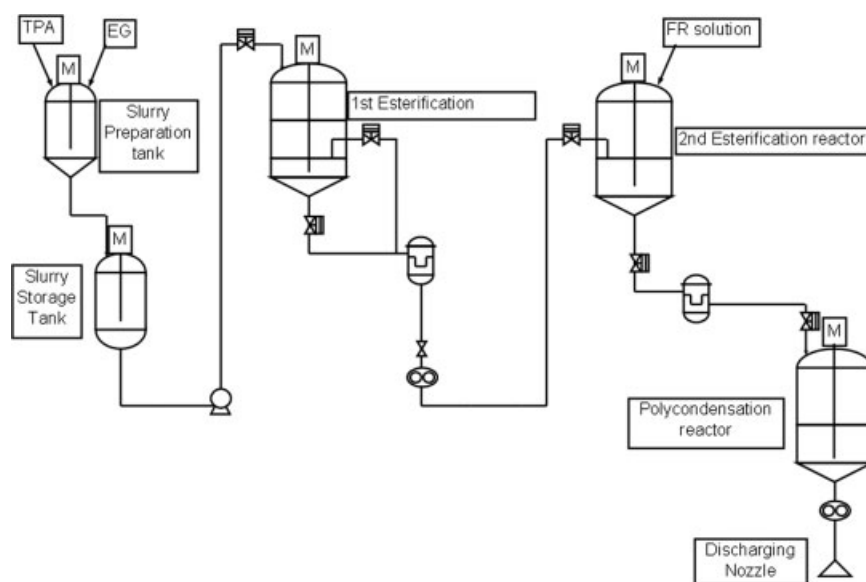
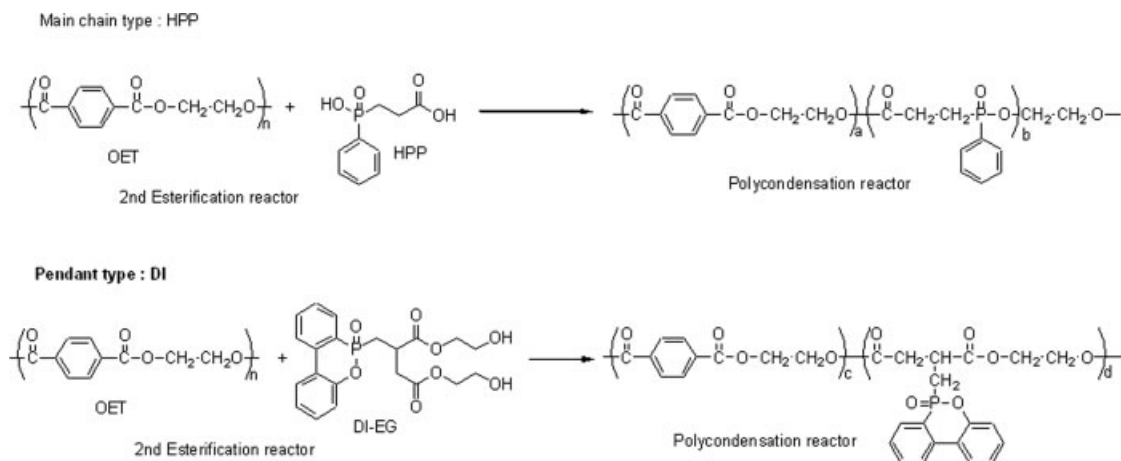**Figure 1** Schematic diagram of the polymerization equipment.

Figure 2 Reaction scheme for the second esterification and polycondensation reactor.

introduced into the first esterification reactor continually, the inner temperature kept constant. This was called a semibatch process. OET acted as a solvent of TPA. In the first esterification reactor, TPA and EG reacted to produce OET. The initial OET and reacted OET kept almost the same compositions if there were no additional additives and they were operated under the constant conditions discussed in a previous article.[16] OET (1.5 tons), which reacted in the first esterification reactor, remained in the first esterification reactor, and the other OET was transferred into the second esterification reactor. FRs were introduced into the second esterification reactor. The oligomers produced in the second esterification reactor were fully transferred into the polycondensation reactor. Into the polycondensation reactor, the polycondensation catalyst and antimony trioxide were introduced, and the polycondensation proceeded at a higher temperature and in a high vacuum to produce the polyester polymer.

Esterification and polymerization

As mentioned previously, both types of FRs were introduced into the second esterification reactor to maintain the composition of OET in the first esterifi-

cation reactor; a brief reaction scheme for the second esterification and polycondensation reactors is shown in Figure 2.

HPP was introduced into the reactor as a solution at 100°C, and DI–EG was introduced in an esterified state containing EG to reduce the solution viscosity, as previously published.[16]

Polymerizations of both types were accomplished in the same method with an antimony trioxide solution as a catalyst at 285°C. The brief esterification and polycondensation condition and the properties of the resultant oligomer and polymer are shown in Tables I and II, respectively. The figures in Tables I and II were collected and averaged from over 100 batches in the plant.

To compare the reactivity of both FRs and test the possibility of a high-phosphorous-content polymer, polymers containing about 1 wt % phosphorous atoms were polymerized with the same equipment and method. The polymerization conditions and chemical properties are shown in Table III.

Polyester characterization

The produced polyesters were characterized with a conventional analysis method, just as the normal

TABLE I
Esterification Conditions and Results

| | Feeding content | | | | |
| | mol %[a] | wt %[b] | ES (%)[c] | Acid value (mequiv/kg)[c] | DEG (wt %)[d] |
FR type					
Initial OET[e]	—	—	96.8	320	0.52
HPP oligomer[f]	4.03	4.47	98.2	180	1.50
DI oligomer[f]	4.11	8.85	97.8	280	1.02

[a] Ratio calculated from the moles of FR to the moles of the total diacid (TPA and FR).
[b] Ratio calculated from the weights.
[c] Esterification ratio calculated from the acid value analyzed by KOH titration in a benzyl alcohol solution.
[d] Analyzed by the monoethanol amine hydrolysis/gas chromatography method.
[e] Before the introduction of the FRs.
[f] Reacted with the second esterification reactor of the FRs.

TABLE II
Polycondensation Condensation and Polymer Properties

Polyester	Sb_2O_3 (ppm)	Reaction time (min)	IV (dL/g)[a]	DEG (wt %)	CEG (mequiv/kg)[b]	P (wt %)[c]
Normal PET[d]	290	167	0.630	0.65	29	—
HPP–PET-1	330	180	0.644	2.15	40	0.65
DI–PET-1	390	242	0.642	1.38	28	0.64

[a] Intrinsic viscosity measured at 30°C in *ortho*-chlorophenol with an Ubbelohde viscometer.
[b] Carboxylic end group calculated from the acid value analyzed by KOH titration in a benzyl alcohol solution.
[c] In the polymer as analyzed by the oxidative degradation/molybdenium blue method.[17]
[d] Polymerized with OET and produced in the first esterification reactor in the polymerization reactor without the use of the second esterification reactor.

polyester was. Chemical analyses were performed as described in Tables I and II.

The molecular weight and polydispersity index were analyzed in a hexafluoroisopropanol solution by gel permeation chromatography (GPC) with a Waters 515 pump, 2487 UV detector, and Styragel 4E+5E column.

Thermal analyses were carried out with a Perki-nElmer DSC 7 and a DuPont Pyris 1 thermogravimetric analyzer.

The chemical resistance was tested in a frozen milled powder state, and the powder was treated in a 0.05M NaOH water solution at 95°C and was dried and weighed.

RESULTS AND DISCUSSION

Esterification behavior

The esterifications of both FRs shown in Table I are in good agreement with small-scale experiments previously reported.[16] Increasing the esterification ratio with respect to the initial OET was brought about by the additional EG contained in the FR solution. Longer retention times and the introduction of FR solutions increased the DEG formation. The HPP oligomer had a higher DEG content than the DI oligomer because of the high acidity.

Polycondensation behavior

In Table II, there is a distinct difference between the reaction time and catalyst content. Despite the higher catalyst content, DI–PET-1 needed a longer polycondensation time than HPP–PET-1. It was assumed that the higher quantity of FR in the reactant to be

introduced for the same phosphorous content in the polymer made it hard to polymerize, and DI–PET-1 needed more catalyst and a longer polycondensation time. High-phosphorous-content polyesters were in agreement with this. Table III shows that the phosphorous contents of HPP–PET-2 and DI–PET-2 were 1.12 and 0.92 wt %, which corresponded to 6.95 (7.7 wt %) and 6.02 mol (12.7 wt %), respectively. The polycondensation times were longer than those shown in Table I, but the intrinsic viscosities were much lower. Comparing Tables II and III, we found that the DEG content and carboxylic end group increased as the phosphorous content increased.

Molecular weights

Chromatograms of the molecular weight distributions analyzed by GPC are shown in Figure 3. The two polyesters showed similar molecular weights and similar intrinsic viscosities, but HPP–PET-1 showed a slightly broader molecular weight distribution than DI–PET-1. This may have been due to the rapid polycondensation of HPP–PET-1 versus that of DI–PET-1.

Thermal properties

The thermal properties of the polyesters are briefly listed in Table IV. The low glass-transition temperature of HPP–PET-1 showed the increased flexibility of the polymer chains, and the high glass-transition temperature of DI–PET-1 was caused by the high aromaticity of DI. The crystallization was hard in the order of normal PET, HPP–PET-1, and DI–PET-1. This resulted from the bulkiness of the FR and had an effect on the heat of fusion. The lowest crystalline

TABLE III
Polycondensation Conditions and Polymer Properties of High-Phosphorous-Content Polyesters

Polymer	Sb_2O_3 (ppm)	Reaction time (min)	IV (dL/g)[a]	DEG (wt %)	CEG (mequiv/kg)[b]	P (wt %)
HPP–PET-2	330	186	0.623	3.30	65	1.12
DI–PET-2	390	250	0.617	1.42	38	0.92

[a] Intrinsic viscosity.
[b] Carboxylic end group calculated from the acid value analyzed by KOH titration in a benzyl alcohol solution.
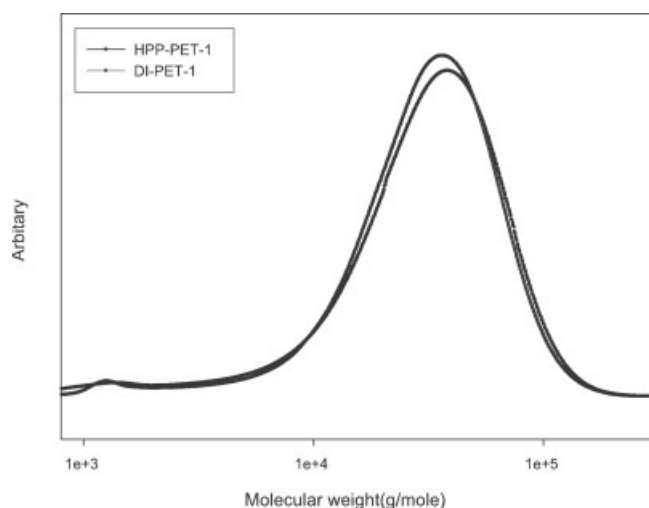
Figure 3 Molecular weight distribution analyzed with GPC.

melting temperature of DI–PET-1 was brought about by the higher DEG content incorporated into the polyester chain.

The intrinsic viscosity at 280°C, changing with time, showed differences, as displayed in Table V. It corresponded well to the results of Zhao et al.,[8] Chang et al.,[10] and Hergenrother.[11] The intrinsic viscosities of the HPP polyester decreased more rapidly than those of the normal polyester and DI polyester. The intrinsic viscosities decreased more rapidly for the polyesters having higher phosphorous contents and higher DEG contents in common. The retention ratios of the intrinsic viscosity to the phosphorous content and DEG content are plotted in Figure 4. The correlation coefficients were 0.6602 and 0.9598, respectively. Therefore, the retention of the intrinsic viscosity was more related to the DEG content than the phosphorous content. It can be concluded that the DEG content played the main role in the thermal degradation of the polyesters with the synergistic effect of FRs. The synergistic effect on the intrinsic

TABLE IV
Thermal Properties of the Polyesters

Polyester	T_g (°C)[a]	T_c (°C)[b]	T_m (°C)[c]	ΔH_f (J/g)[d]
Normal PET	78.1	146.2	253.9	43.1
HPP–PET-1	74.4	154.2	241.7	39.3
DI–PET-1	78.2	162.2	244.3	35.5

[a] Glass-transition temperature determined as the temperature of the extrapolated half-heat capacity.
[b] Crystallization temperature determined as the exothermic peak.
[c] Crystal melting temperature determined as the endothermic peak.
[d] Heat of fusion.

TABLE V
Intrinsic Viscosities with the Treatment Time

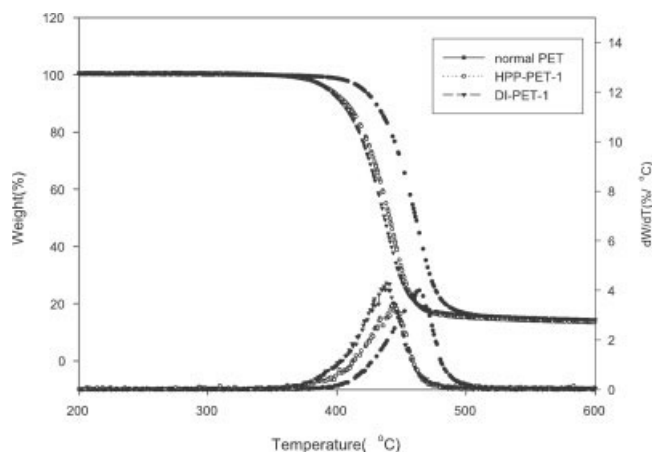| Polyester	0 min	10 min	20 min
Normal PET	0.630	0.628	0.626
HPP–PET-1	0.644	0.637	0.631
HPP–PET-2	0.623	0.618	0.599
DI–PET-1	0.642	0.640	0.635
DI–PET-2	0.617	0.611	0.602

viscosity decrease of the main-chain FR was much higher than that of the pendant-type FR. It meant easy breakage of the weak ether bonds in DEG and the P—O bond in FR into the formation of active radicals, and the formed radicals easily propagated in the more flexible chain of the main-chain-type FR.

The thermogravimetric analysis in Figure 5 shows a tendency similar to the intrinsic viscosity drop shown in Figure 4.

Thermal degradation in a nitrogen flow showed similar trends for the two types of FRs: the FR polyesters degraded at lower temperatures than the normal polyesters. Sato et al.[9] proposed that a phosphorous-containing polymer changes into a metaphosphoric acid and then into a polyphosphoric acid, and they assumed that the degradation of a pendant-type polyester would be slower than that of a main-chain type, but both polymers have the same flame retardancy. However, in this research, we observed a difference in the thermal degradation under heating and at a constant high temperature. We propose that the thermal degradation of an HPP polyester occurs at a lower temperature than that of a DI polyester and that an HPP polyester more easily degrades into polyphosphoric acid.
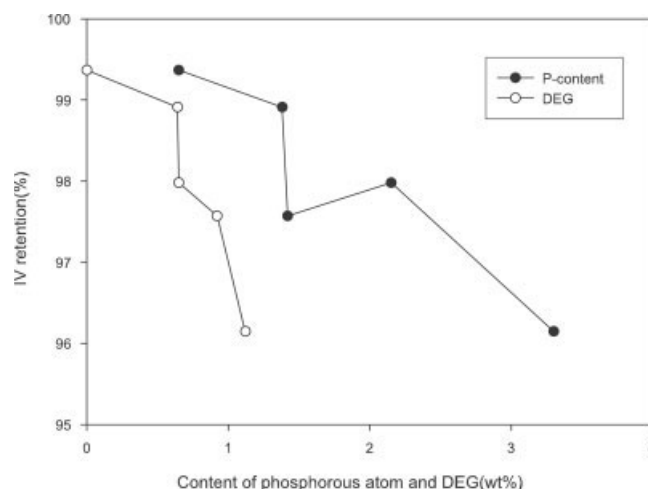
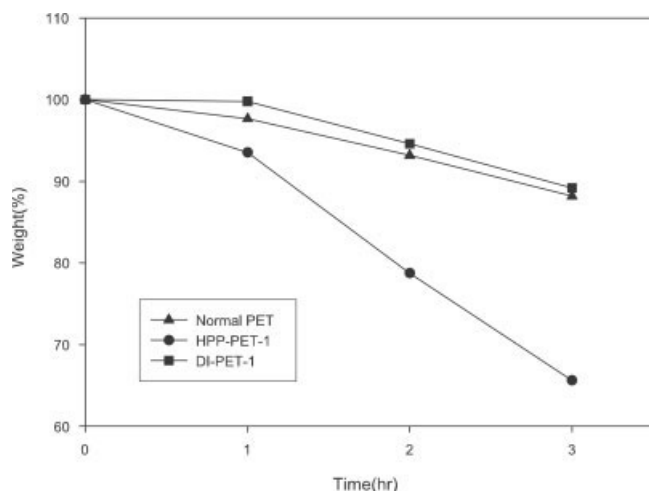**Figure 4** Intrinsic viscosity (IV) retention versus the phosphorous content and DEG content.

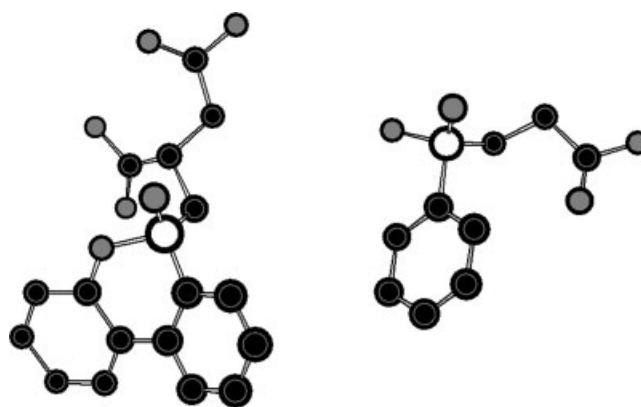**Figure 5** Thermogravimetric diagram of the polyesters.

Figure 7 Molecular structures of both FRs with the MOPAC program. On the left, DI is shown, and on the right, HPP is shown. The black, white, and gray circles represent carbon, phosphorous, and oxygen atoms, respectively.

Chemical resistance

The alkaline treatment of the polyesters showed distinct behaviors. The weight retention of the polyesters is shown in Figure 6.

The normal polyester and DI polyester showed similar weight reductions, but the HPP polyester showed more rapid weight reduction than the others. This meant that alkaline hydrolysis happened in the polymer backbone, especially for the more acidic HPP polyester. If the linkage between the pendant group and polymer backbone were vulnerable to hydrolysis, the phosphorous content of the treated polyester would need to be reduced, but the phenomenon was not observed. The phosphorous atom in a pendant type is more sterically hindered than that in a main-chain type, as shown in Figure 7. Figure 7 shows the molecular structures of both energy-minimized FRs from CS Chem 3D Pro 5.0 MOPAC (CambridgeSoft Corp.). The phosphorous atom of DI, shown as a bold circle, must be highly

sterically hindered, so the reactivity with an alkali metal is reduced versus that of HPP.

On the basis of the thermal stability and alkaline resistance, the DI polyester was more stable against thermal degradation and alkaline attack than the HPP polyester. Therefore, the HPP polyester was more labile and degraded easily into polyphosphoric acid, which contributed to the flame retardancy of the polyester.

CONCLUSIONS

Two types of FR polyesters containing the same phosphorous content were polymerized and characterized according to the phosphorous FRs. There were differences in the polymerization behaviors according to the FR type and FR content.

The feeding molar ratios were similar, but the feeding quantity was almost doubled in the case of DI–EG. For the same molecular weight, or the same intrinsic viscosity, DI–EG needed much more polymerization catalyst and time.

The produced polymers had almost the same molecular weight, but the DEG contents were quite different. The HPP polyester had a DEG content approximately twice that of the DI polymer. The higher DEG content reduced the thermal stability.

The HPP polyester had more flexible chains, which resulted in easier crystallization than that of the DI polyester. The HPP polyester had a lower crystalline melting temperature than the DI polyester because of the high DEG content in the polyester.

As the HPP polyester had higher susceptibility to thermal degradation due to the higher activity because of the low resistance to thermal chain scission, the HPP polyester degraded at a lower temperature and more easily degraded into polyphosphoric

Figure 6 Weight retention of polyesters in NaOH solutions.

acid. The weight reduction under an alkaline treatment was higher for the HPP polyester, and this may have been brought about by the difference in the acidity of the polymer and the ease of migration of the small molecules into the polymer chain.

Highly sterically hindered DI was more stable against thermal degradation and alkaline attack, and the DI polyester showed stability similar to that of the normal polyester.

For higher phosphorous content polymer production, it is profitable to adopt main-chain-type phosphorous FRs rather than pendant types because of the lower molecular weight and higher reactivity.

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