Phosphorus-Containing Epoxy Resins for Flame Retardancy V: Synergistic Effect of Phosphorus–Silicon on Flame Retardancy

GING-HO HSIUE, YING-LING LIU, JUN TSIAO

Department of Chemical Engineering, National Tsing Hua University, Hsinchu, Taiwan, 30043, Republic of China

ABSTRACT: Epoxy resins containing phosphorus and/or silicon are prepared from phosphorus/silicon-containing epoxides and diamine curing agents. The flame-retardant properties of the phosphorus/silicon-containing epoxy were studied. Furthermore, the phosphorus–silicon synergistic effect on LOI enhancement and increasing flame retardancy of the epoxy materials were demonstrated. While under flame, phosphorus provides the tendency of char formation, and silicon provides the enhancement on thermal stability of the char, to show their individual benefit on flame retardancy. Introducing both phosphorus and silicon together in the epoxy resin composition brings the success of combining these two factors in a flame retardation mechanism. An LOI enhancement from 26 to 36 is observed for epoxy resins containing both phosphorus and silicon. Moreover, the synergistic effect of phosphorus–silicon on fire resistance can be further leveled up by using siloxane reagents to replace silanes. Epoxy resins with a composition of phosphorus epoxides and siloxane diamines exhibit a high LOI value of 41, to demonstrate the high synergistic efficiency of phosphorus and silicon on flame retardation. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 1–7, 2000

Key words: epoxy resins; flame retardancy; phosphorus; silicon

INTRODUCTION

Phosphorylation, in recent years, is considered to be one of the most efficient means of conferring flame retardancy on polymeric systems.[1–10] Several advantages of phosphorus being utilized as a flame-retardant element are demonstrated. High flame-retardant efficiency, less production of corrosive and toxic gases in flames, and less destruction to the earth's environment are the noteworthy benefits of replacing halogens with phosphorus in flame retardants. Therefore, flame retardation on polymeric systems via phosphorylation is being widely studied. Most of the "green"

flame-retardant polymeric products also come from phosphorous systems.

The phosphorus moiety confers fire resistance mainly by modifying the thermal decomposition mode of the polymers.[7,10,11] Generally, the phosphorus moiety decomposes at low temperatures relative to the polymer matrix. Thus, a phosphorus-rich char is formed to act as an insulation layer of heat transfer and to reduce the production of combustible gases during fire.[3–11] This action provides a solid-phase mechanism of flame retardation. However, by the literature, oxidation of the phosphorous char is observed at temperatures higher than 600°C.[3–8] Because the efficiency of flame retardation of phosphorus highly depends upon the amount of char formation, the flame-retardant efficiency could also further level up by improving the thermal stability of phospho-

rous char at high temperatures. On the other hand, polymers with phosphorus functions as an integral part of the chain (reactive-type flame retardant) exhibit better flame retardancy and overcome several drawbacks associated with the physical blend of the polymer and flame retardants.[9–13] Furthermore, due to the limit from chemical structures in molecular design, the phosphorus content of the reactive-type flame retardant could not be raised as high as expected. This limit in phosphorus content brings some drawbacks in application of reactive-type phosphorus flame retardants, especially while being used for the product requiring critical flame-retardant properties.

Based on the above, further leveling up the flame retardancy of the phosphorus element is highly attractive. For this purpose the synergistic effects on flame retardancy of phosphorus with other elements like halogens and nitrogen have been investigated.[14–16] However, the phosphorus–halogen system still brings about the drawbacks of the production of toxic and corrosive gases associated with the existence of halogens. In addition, the improvement of flame-retardant efficiency is observed for the phosphorus–nitrogen system. However, this phosphorus–nitrogen synergistic effect on flame retardancy is not as dominate for all polymeric systems. Therefore, another combination for phosphorus synergistic effect on flame retardancy is highly interesting.

In addition to halogens, metal oxides, phosphorus, nitrogen, etc., silicon is demonstrated to be another one of the choices for use as a flame-retardant element.[17–24] The silicon dependence of the limiting oxygen index (LOI) has been investigated in several families of silicon-containing polymers. Auxiliary investigation suggested that the enhancement in LOI brought about by incorporating silicon into the polymers resulted from the production of continuous layers of silica that retarded oxidation of the char.[19] Moreover, as mentioned above, the flame retardancy of phosphorus could be leveled up if providing an environment to eliminate/reduce the thermal oxidation of phosphorus char at the high temperature region. Based on this concept, silicon would be the one of choices for enhancing the flame retardancy of the phosphorus systems. The aim of the present study is to introduce the phosphorus–silicon synergistic effect on flame retardancy.

EXPERIMENTAL

Materials

Phosphorus-Containing Epoxide

Bis(3-glycidyloxy)phenylphosphine oxide (BGPPO) was synthesized in our laboratory according to our previous work.[4] Glycidol (12.5 g) (0.169 mol) (from the Aldrich Co.) was stirred with 60 mL of tetrahydrofuran (THF) in a 250-mL round-bottom flask. Distilled dry triethylamine (17.1 g) was added into the solution, and then the solution was cooled to 0°C with ice bathing. After adding Cu_2Cl_2 (0.3 g), a solution of phenylphosphonic dichloride (15 g, from the Aldrich Co.) in 40 mL THF was added to the solution dropwise over a period of 30 min. After maintaining it at 0°C for 2 h, the solution was kept at room temperature for another 48 h. The precipitant was filtered and washed with an 2 wt % ice aqueous solution of NaOH and then with water, and finally extracted with ethyl acetate (EA) three times. The extract was dried over $MgSO_4$ and then concentrated. The obtained product was purified by passing it through column chromatography (using EA/n-hexane 1/1 as the eluent). The final product was obtained with 54% yield (^{31}P NMR: $\delta = 20.6$ ppm).

Silicon-Containing Epoxide

Triglycidyloxy phenyl siliane (TGPS) was synthesized in the laboratory according to our previous work.[17] Phenyltrimethoxysilane (20 g) (0.1 mol) (from TCI, Japan), 5.4 g water, and 0.1 g of p-toluenesulfonic acid monohydrate (from TCI, Japan) were added in a 1000-mL four-necked flask equipped with a stirrer, a thermometer, a condensor, and a droppping funnel. The reaction mixture was stirred at 20°C for 30 min. Epichlorohydrin (82.8 g, 0.9 mol, from Merck) and 0.1 g benzyltrimethylammonium chloride (from Merck) were then added to the reaction mixture. The reaction mixture thus was heated to 60°C. NaOH (0.3 mol) was then added, and the reaction mixture was stirred at 60°C for 1.5 h. The excess of epichlorohydrin was distilled off at 60°C under vacuum. The residule was cooled to room temperature and then disolved in 100 mL dichloromethane. The undisolved salt was removed by vacuum filtration. After distilling off the solvent, a viscous liquid silicon containing epoxy resin TGPS was obtained with a yiled of 85% (epoxy equivalent weight = 108).

Phosphorus-Containing Curing Agent

A phosphorus-containing diamine curing agent, bis(3-aminophenyl)phenyl phosphine oxide (BAPPO), was synthesized accoring to our previous work.[25] Bis(3-nitrophenyl)phenyl phosphine oxide (BN-PPO) was first obtained from DCPP and *p*-nitrophenol (from the TCI Co.) through the above-mentioned process for synthesis of BGPPO. After that, BNPPO (25 g) was placed in a 1000-mL round-buttom flask with 180 g of powder tin (II) chloride dihydrate (from the Aldrich Co.). A solution of 200 mL fuming hydrochloride acid in 400 mL ethanol was introduced into the flask. The reaction mixture was stirred at room temperature for 5 h. The solution was concentrated and then was neutralized by 25% NaOH aqueous solution. The obtained solution was extracted with chloroform. The organic layer was collected and concentrated. The obtained solid was recrystallized from dichloromethane to give a pure product in a 95% yield. (^{31}P NMR: δ = 12.97 ppm).

Silicon-Containing Curing Agent

Aminopropyl-terminated poly(dimethyl siloxane (M_n = 1600, M_w = 2060, from the Dow Corning Co.) was used as received.

Others

4,4′-Diaminodiphenylmethane (DDM) from the Aldrich Co. and Epon 828 from the Shell Chemical Co. were used as received.

Instrument Analysis

Differential scanning calorimetry (DSC) thermograms were recorded with a Seiko DSC 5200 at a heating rate of 10°C/min under a nitrogen atmosphere. Thermogravimetric analysis (TGA) was performed by a DuPont 951 thermogravimetric analyzer at a heating rate of 10°C/min under a nitrogen or air atmosphere. Limiting oxygen index (LOI) values were measured on a Stanton Redcraft flame meter by a modified method:[2] power samples (500 mg) were placed in a glass cup (diameter 25.6 m; height 4.5 mm) situated in the middle of the chimney. The flame was applied from the top of the chimney for 10 s. The flow rate (N_2 + O_2) was maintained at 17 L/min. The percentage of oxygen in the O_2 and N_2 mixture just sufficient to sustain the flame was taken as the LOI.

Preparation of Epoxy Resins

A certain amount of epoxy monomer and curing agents basing on the predicted phosphorus and silicon contents were dissolved in acetone. The solution was stirred for about 10 min, and then acetone was removed out under vacuum. The residuals were then thermally cured. The conditions for curing reactions are listed in Table I.

RESULTS AND DISCUSSION

By using phosphorus- or silicon-containing epoxide compounds and dimaine compounds (as curing agents), epoxy resins containing phosphorus and/or silicon are thus obtained. Based on the above, a silicon-containing epoxide, triglycidyloxy phenyl siliane (TGPS), and a phosphorus-containing diamine, bis(3-aminophenyl)phenyl phosphine oxide (BAPPO) (Fig. 1), used as a curing agent, are first utilized. For compensating the phosphorus and silicon contents of the resulting epoxy resins, commercially epoxy Epon 828 and diamine curing agent diaminodiphenyl methane (DDM) are also used. The compositions, phosphorus and silicon contents, thermal properties, and flame retardancy of the resulting epoxy resins are collected and shown as Table II. The effect of the phosphorus contents on the flame retardancy is noteworthy. The phosphorus-free epoxy resin, which is based on Epon 828 and DDM, shows a LOI value of 26. While 0.8 wt % phosphorus is introduced into the epoxy resin, the LOI values are raised from 26 to 30.5 (sample P-1 in Table II), to demonstrate that phosphorus plays an important role in flame retardation.[3] On the other hand, the silicon-containing epoxy resins raise LOI values from 26 to 31 with a silicon contents of 1.1 wt %. However, despite the fact that the LOI values increase with the phosphorus or silicon contents increase, the increase is not as significant. On the other hand, based on the same weight percent, it is noteworthy that phosphorus exhibits a relatively higher flame retardant efficiency than silicon. According to the literature,[1–8,18–20] both the phosphorus and silicon play their enhancement on flame retardation by formation stable char and through a solid phase mechanism. Figure 2 shows TGA thermograms of phosphorus-containing (P-4) and silicon-containing (Si-4) epoxy resins. Both of the phosphorus- and silicon-containing epoxy resins show a higher char formation tendency than the P and Si free sample (Table II). Furthermore, not only the amount of the formed but also the thermal stability of char play an important role on the flame retardancy. It can be seen that the char of phos-

Table I   Compositions and Curing Conditions of Epoxy Resins Based on Silicon Epoxy and Phosphorous Curing Agent

Sample	P Compound (wt %)	Si Compound (wt %)	Cure Cycle	Postcure Cycle
N	—	—	100°C, 2 h	180°C, 2 h
P-1	BGPPO (7.4)	—	120°C, 2 h	180°C, 2 h
P-2	BGPPO (13.8)	—	120°C, 2 h	180°C, 2 h
P-3	BGPPO (20.3)	—	120°C, 2 h	180°C, 2 h
P-4	BGPPO (25.8)	—	120°C, 2 h	180°C, 2 h
Si-1	—	TPSO (12.3)	100°C, 2 h	140°C, 2 h
Si-2	—	TPSO (26.9)	100°C, 2 h	140°C, 2 h
Si-3	—	TPSO (43.7)	100°C, 2 h	140°C, 2 h
Si-4	—	TPSO (66.1)	100°C, 2 h	140°C, 2 h
P-Si-1	BAPPO (28.6)	TPSO (10.1)	120°C, 2 h	180°C, 2 h
P-Si-2	BAPPO (30.4)	TPSO (22.4)	120°C, 2 h	180°C, 2 h
P-Si-3	BAPPO (33.2)	TPSO (37.0)	120°C, 2 h	180°C, 2 h
P-Si-4	BAPPO (36.9)	TPSO (53.8)	100°C, 2 h	140°C, 2 h
Si-P-1	BAPPO (11.1)	TPSO (62.8)	100°C, 2 h	140°C, 2 h
Si-P-2	BAPPO (20.3)	TPSO (59.4)	100°C, 2 h	140°C, 2 h
Si-P-3	BAPPO (29.5)	TPSO (57.1)	100°C, 2 h	140°C, 2 h
Si-P-4	BAPPO (36.9)	TPSO (53.8)	100°C, 2 h	140°C, 2 h

phorus epoxy still shows weight loss at the high temperature region ($>700°C$) under air. On the other hand, this weight loss is not observed for

Figure 1 The chemical structures of the phosphorus or silicon containing epoxides and curing agents.

the char of silicon epoxy. This result shows that the silicon char is observed to be more thermally stable than the phosphorus char, to imply that silicon epoxies should be more flame retardant than phosphorus epoxies. However, this prediction is contrary to the experimental results discussed above. This disagreement between the LOI measurement and TGA prediction on flame retardancy of phosphorus and silicon might come from the fact that the char formation of silicon is not as great as that of the phosphorus. From the above preliminary results and discussion, it can be concluded that in a flame-retardation system, silicon favorably provides thermal stability of char, and phosphorus provides a tendency of char formation. Because both of the above effects are essential factors for flame retardation, the concept of the combination of these two factors in a flame-retardation system is highly attractive and interesting. In addition, as mentioned above, because a very high flame retardancy could not be obtained by increasing the P or Si contents of the epoxy resins, the technique of combining P and Si in an epoxy system might provide a convenient and cheap way to gain a very high flame-retardant system.

For maintaining both the tendency of char formation and char thermal stability in our flame-retardant system, epoxy resins containing both phosphorus and silicon are prepared from the sil-
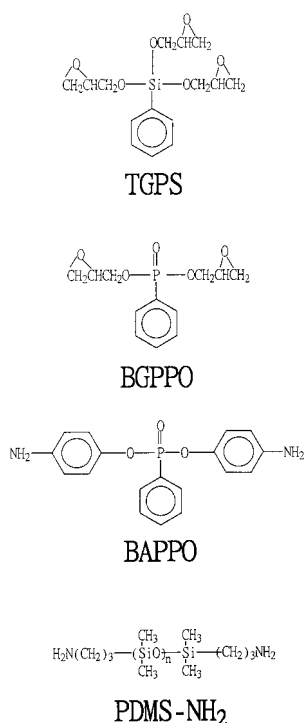
Table II   Compositions and Properties of Epoxy Resins Based on Silicon Epoxy and Phosphorous Curing Agent

| Sample | Phosphorus Content (wt %) | Silicon Content (wt %) | 700°C Char (%) | | LOI |
			N_2	Air	
N	0	0	16.3	0	26
P-1	0.8	0	25.1	0.2	30.5
P-2	1.5	0	27.5	6.1	32
P-3	2.2	0	27.6	8.2	32.5
P-4	2.8	0	27.8	20.3	33
Si-1	0	1.1	23.7	0.7	31
Si-2	0	2.4	30.9	3.8	32
Si-3	0	3.9	36.9	7.6	32.5
Si-4	0	5.9	36.8	12.5	33
P-Si-1	3.1	0.9	28.4	22.2	34
P-Si-2	3.3	2.0	32.4	24.7	34.5
P-Si-3	3.6	3.3	41.5	26.	35.5
P-Si-4	4.0	4.8	42.8	31.9	36
Si-P-1	1.2	5.6	42.6	15.4	33.5
Si-P-2	2.2	5.3	428	26.5	34
Si-P-3	3.2	5.1	42.5	29.5	35
Si-P-4	4.0	4.8	43.3	31.9	36

icon-containing epoxide TGPS and the phosphorus-containing diamine BAPPO as a curing agent. Figure 3 shows the TGA thermograms of the epoxy resins containing both phosphorus and silicon (series P-Si and Si-P in Table II). It can clearly be seen that the weight loss of the char at temperatures above 500°C is retarded by incorporating silicon into the phosphorus-containing epoxy resins. Furthermore, the weight loss from oxidation of the char is not observed at temperatures above 700°C. This result implies that the introduction of silicon has efficiently improved the thermal stability of the formed char, to result in high char yields for the phosphorus–silicon-containing epoxy resins (Table II). Based on the above, an LOI enhancement coming from the phosphorus–silicon synergistic effect is expected, and has been examined. LOI values leveling from 33 up to 36 is observed (Table II). Therefore, the synergistic effect of phosphorus and silicon on LOI enhance-
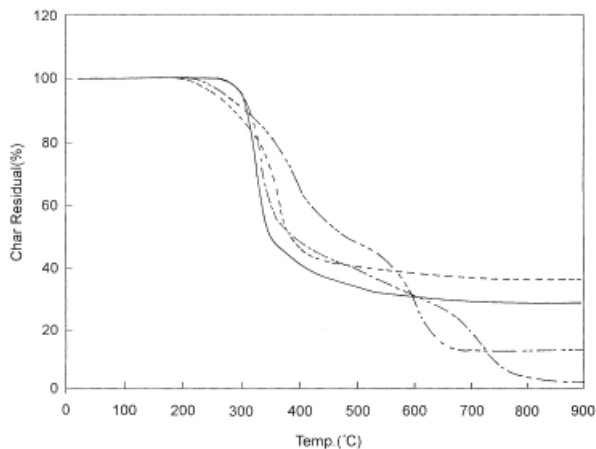

Figure 2   The TGA thermograms of phosphorus and silicon containing epoxy resins: (—) P-4 in N_2, (_ . _) P-4 in air, (. . .) Si-4 in N_2, (_ . . _) Si-4 in air.
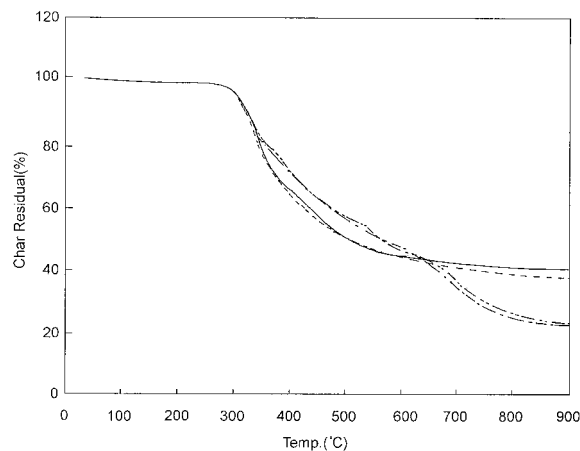

Figure 3   The TGA thermograms of epoxy resins containing both phosphorus and silicon: (—) P-Si-4 in N_2, (_ . _) P-Si-4 in air, (. . .) Si-P-4 in N_2, (_ . . _) Si-P-4 in air.

Table III   Compositions and LOI Enhancement of Epoxy Resins Based on BGPPO and Siloxane Curing Agent PDMS-NH$_2$

Sample	P Compound (wt %)	Si Compound (wt %)	P Content (wt %)	Si Content (wt %)	LOI
P-Si	—	PDMS-NH$_2$ (29.4)	0	10.8	26
P-Si-I	BGPPO (44.3)	PDMS-NH$_2$ (34.6)	4.8	12.7	45
P-Si-II	BGPPO (44.3)	PDMS-NH$_2$ (24.3)	4.8	8.9	43
P-Si-III	BGPPO (44.3)	PDMS-NH$_2$ (17.2)	4.8	6.3	40
P-Si-IV	BGPPO (44.3)	PDMS-NH$_2$ (10.4)	4.8	3.8	38
P-DDM	BGPPO (44.3)	—	4.8	0	33

ment, i.e., flame-retardant efficiency, is demonstrated.

However, the above-mentioned LOI enhancement of silicon on phosphorus-containing epoxy resins is not as conspicuous. Therefore, a siloxane diamine aminopropyl-terminated polydimethylsiloxane (PDMS-NH$_2$) is chose to replace the silane epoxide TGPS for composing the phosphorus/silicon-containing epoxy resins. This performance is based on the concept that siloxanes produce a lot of silica (SiO$_2$) during degradation, and the silicon enhancement of the thermal stability of the char is mainly from the formation of silica layers that retards oxidation of the char.[18]

Another series of phosphorus/silicon-containing epoxy resins are prepared basing on the compositions of bis(3-glycidyloxy)phenyl phosphine oxide (BGPPO) and PDMS-NH$_2$ (Table III). The TGA thermograms of the resins are first examined, and shown as Figure 4. The char protection from the introduction of silicon is also observed at a high-temperature region. Furthermore, the pro-
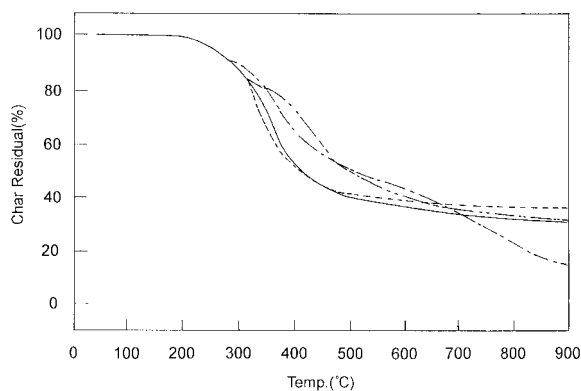
tection starts to perform at about 500°C to result in very high char yields of about 35%. Therefore, the relatively high tendency of silica formation of siloxane is demonstrated. Owing to the low surface energy of silica, the formed silica from the siloxane degradation migrates to the surface of the char, and then to form a continuous protection layer of the char.[18,19] The phosphorous moiety decomposes to bring a high yield of phosphorus-rich char, and the silica from siloxane degradation provides a protection mechanism of the char. The flame-retardant efficiency is thus enhanced by composing these two mechanisms. Therefore, high LOI values are reasonably expected for the siloxane–phosphorus-based epoxy resins. The results of LOI measurement for the resins are listed in Table III. A high LOI value of 45 is found for the resin with a phosphorus content of 4.8% and a silicon content of 12.7%. Furthermore, the LOI values increase with the increase in silicon content. Therefore, these outstanding LOI values and corresponding excellent flame retardants certainly bring some benefits for the resins in application. The success in simulating the LOI values via changing the compositions of silicon and phosphorus contents also gives some convenience in resin formulation.

Figure 4   The TGA thermograms of phosphorus containing epoxy resins cured by a silane-based amine curing agent: (—) P-DDM in N$_2$, (_ _ _) P-DDM in air, (_ . _) P-Si-IV in N$_2$, (. . .) P-Si-IV in air.

CONCLUSIONS

Phosphorus and silicon exhibit their individual effects on flame-retardating epoxy resins. While both phosphorus and silicon are combined in the epoxy resin compositions, a synergistic effect on the flame retardancy of phosphorus and silicon is found. Furthermore, a siloxane reagent provides a much higher synergistic efficiency than a silane reagent while associated with phosphorus in the epoxy resin compositions. This highly synergistic

flame retardation efficiency of siloxane with phosphorus mainly comes from the formation of a continuous silica layer, which reduces thermal oxidation of the phosphorus char. Epoxy resins with a high LOI value of about 41 is thus obtained. For epoxy resins, a phosphorus content of about 5–6% is needed for sufficient flame-retardant properties.[25] In addition, such a high phosphorus content is not convenient for epoxy resin utilization. Therefore, this high efficiency in fire resistance certainly brings effective benefits and convenience in resin formulation.

REFERENCES

1. Nair, C. P. N.; Glouet, G.; Brosses, J. J Polym Sci Polym Chem 1988, 26, 1791.
2. Nair, C. P. N.; Glouet, G.; Guilbert, Y. Polym Degrad Stabil 1989, 26, 205.
3. Liu, Y. L.; Hsiue, G. H.; Chiu, Y. S.; Jeng, R. J.; Ma, C. J Appl Polym Sci 1996, 59, 1619.
4. Liu, Y. L.; Hsiue, G. H.; Chiu, Y. S.; Jeng, R. J.; Perng, L. H. J Appl Polym Sci 1996, 61, 613.
5. Liu, Y. L.; Hsiue, G. H.; Chiu, Y. S. J Polym Sci Polym Chem 1997, 35, 565.
6. Liu, Y. L.; Hsiue, G. H.; Lan, C. W.; Chiu, Y. S. J Polym Sci Polym Chem 1997, 35, 1769.
7. Liu, Y. L.; Hsiue, G. H.; Lan, C. W.; Chiu, Y. S. J Polym Dedrad Stabil 1997, 56, 291.
8. Banerjee, S.; Palit, S. K.; Maiti, S. J Polym Sci Polym Chem 1994, 32, 219.
9. Banks, M.; Ebdon, J. R.; Johnson, M. Polymer 1994, 35, 3470.
10. Banks, M.; Ebdon, J. R.; Johnson, M. Polymer 1993, 35, 4547.
11. Cellis, C. F.; Hirschler, M. M. The Cumbustion of Organic Polymers; Clarendon Press: Oxford, 1981, p. 241.
12. Kishore, K.; Annakutty, K. S.; Mallick, I. M. Polymer 1988, 29, 762.
13. Kannan, P.; Kishore, K. Polymer 1991, 32, 1909.
14. Krevelen, D. W. V. Polymer 1975, 16, 615.
15. Sato, M.; Yokoyama, M. Eur Polym J 1979, 15, 75.
16. Liu, Y. L.; Hsiue, G. H.; Lee, R. H.; Chiu, Y. S. J Appl Polym Sci 1997, 63, 895.
17. Hsiue, G. H.; Wang, W. J.; Chang, F. C. J Appl Polym Sci 1999, 73, 1231.
18. Kambour, R. P.; Klopfer, H. J.; Smith, S. A. J Appl Polym Sci 1981, 26, 847.
19. Kambour, R. P.; Ligon, W. V.; Russell, R. R. J Polym Sci Polym Lett 1978, 16, 327.
20. Inoue, H.; Ueda, A.; Nagai, S. J Polym Sci Polym Chem 1988, 26, 1077.
21. Imai, S.; Aoki, O. U.S. Pat. 5102960 (1992).
22. Zheng, S.; Wang, H.; Dai, Q.; Kuo, X.; Ma, D.; Wang, K. Macromol Chem Phys 1995, 196, 269.
23. Crivello, J. V.; Narayan, R. Macromolecules 1996, 29, 433.
24. Crivello, J. V.; Bi, D. J Polym Sci Polym Chem 1993, 31, 3109.
25. Polyfile, specially report for flame retardation techniques, Japan, pp 31, September, 1998.