

# Flame-Retardant Modification of Ethylene-Propylene Copolymer with Monomers Containing Bromine and/or Phosphorus

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## Synopsis

Vinyl-type monomers containing bromine and/or phosphorus were synthesized and used as flame retardants for ethylene-propylene-diene terpolymer. The monomers were mixed with the base polymer,  $Sb_2O_3$  as a synergist, radical initiator, and other additives, and polymerized in the matrix of the base polymer. The monomers act as an effective flame retardants when they form thermally stable polymers comparable to the base polymer. The efficiency was dependent on the amount of flame-retardant polymer formed in the finished compound.

## INTRODUCTION

The need for flame-retardant polymers has increased markedly in recent years. Polymers are required to possess not only flame retardancy, but various other properties, such as weathering stability, high mechanical and electrical properties, and innocuousness of generated smokes at combustion.

In order to obtain flame retardancy in polymers, a large amount of flame retardant is usually added. However, the addition of a large amount of flame retardant lowers the mechanical property of the compound and causes the additives to exude from the compound during its use. These problems could be solved by using a flame retardant of high molecular weight or grafting flame-retardant monomers on the base polymers. Compounds of high molecular weight, however, often lack compatibility with the base polymers. When they do not melt at mixing temperature, their dispersion in the base polymers becomes heterogeneous. In this case, the flame retardancy of the polymers is only slightly improved. On the other hand, the polymerization of the flame-retardant monomer in the matrix of the base polymer may give a homogeneous mixture of polymers of different kinds, since the monomer in a molten state can be well dispersed. For example, there have been, on polyethylene terephthalate and other polyesters,<sup>1-5</sup> attempts to obtain flame-retardant polymers by means of grafting vinyl-type monomers containing halogen or phosphorus. The work of Liepins et al.<sup>6,7</sup> indicated that the uniformly grafted fibers of polyethylene terephthalate with several specified monomers show considerably high flame retardancy.

It is also necessary to develop flame retardants containing less chlorine in order to reduce as much as possible the toxic smoke and the corrosive gas generated during combustion of polymers.

In this study, the flame-retardant monomers containing less corrosive phosphorus and bromine were synthesized. The flame-retardant monomers were

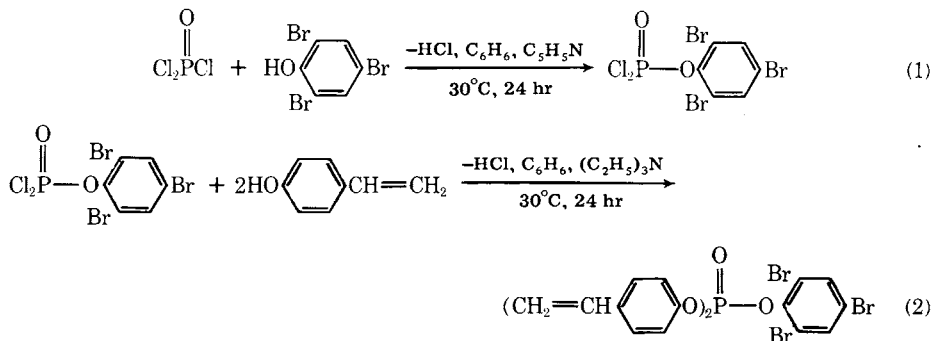
mixed with ethylene-propylene copolymer and polymerized in the matrix of the base polymer. The relationships between flame retardancy and the reactivity of the monomers or the thermal stability of their polymers were discussed.

## EXPERIMENTAL

### Synthesis of Flame-Retardant Monomers

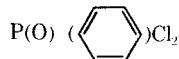
The flame-retardant monomers used in the present work are listed in Table I with their melting points and their bromine and phosphorus contents. There are three types of monomers, i.e., phosphate, phosphonate, and acrylate.

Bis-(*p*-vinylphenyl) tribromophenyl phosphate [III] was prepared by the following dehydrochlorination reactions:



*p*-Vinylphenol (provided by Maruzen Oil Co., Ltd.) was purified by recrystallization from toluene. Benzene (used as a solvent) and amines (used as reagents capturing evolved HCl) were dried and distilled before use. Others of chemical reagent grade were used as obtained. The product was purified twice by recrystallization from ethyl ether and identified by ultimate analysis and IR spectral measurement.

Other phosphorus-containing monomers ([I], [II], and [IV]) were also prepared in two steps similar to the described reactions:



instead of  $\text{P(O)Cl}_3$ , was used in step 1 for the preparation of phosphonate [IV], and

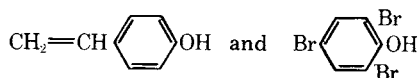
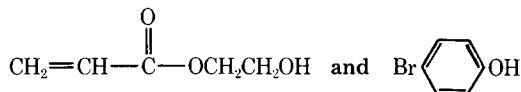


TABLE I  
 Flame-Retardant Monomer

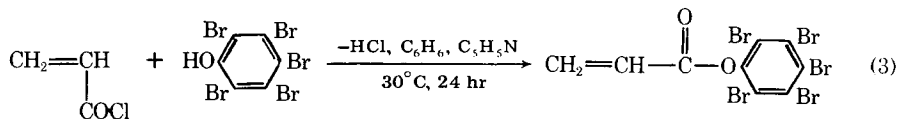
Monomer	Br, %	mp, °C
(I) Bis-(acryloylethoxy) tribromophenyl phosphate $(\text{CH}_2=\text{CH}-\text{C}(=\text{O})-\text{O}-\text{C}_2\text{H}_4\text{O})_2-\text{P}(=\text{O})-\text{O}-\text{C}_6\text{H}_2(\text{Br})_3$	39.4	39
(II) Bis-(bromophenyl) <i>p</i> -vinylphenyl phosphate $\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4-\text{O}-\text{P}(=\text{O})(\text{O}-\text{C}_6\text{H}_4\text{Br})_2$	31.4	49
(III) Bis-( <i>p</i> -vinylphenyl) tribromophenyl phosphate $(\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4\text{O})_2-\text{P}(=\text{O})-\text{O}-\text{C}_6\text{H}_2(\text{Br})_3$	39.0	98
(IV) <i>p</i> -Vinylphenyl tribromophenyl phenyl phosphonate $\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4\text{O}-\text{P}(=\text{O})(\text{C}_6\text{H}_5)(\text{O}-\text{C}_6\text{H}_2(\text{Br})_3)$	41.9	106
(V) Tribromophenyl acrylate (TBPA) $\text{CH}_2=\text{CH}-\text{C}(=\text{O})-\text{O}-\text{C}_6\text{H}_2(\text{Br})_3$	62.3	70.5
(VI) Pentabromophenyl acrylate (PBPA) $\text{CH}_2=\text{CH}-\text{C}(=\text{O})-\text{O}-\text{C}_6\text{H}(\text{Br})_5$	73.7	152
Decabromodiphenyl ether (DBDPE) $\text{Br}-\text{C}_6\text{H}_3(\text{Br})_3-\text{O}-\text{C}_6\text{H}_3(\text{Br})_3-\text{Br}$	83.0	315
Tribromophenyl propionate (TBPP) $\text{CH}_3\text{CH}_2\text{C}(=\text{O})-\text{O}-\text{C}_6\text{H}_2(\text{Br})_3$	62.0	66

instead of



were used for phosphate [I] and phosphate [II], respectively.

Pentabromophenyl acrylate (PBPA) was obtained by dehydrochlorination according to reaction (3).



Commercially available acryloyl chloride was distilled under reduced pressure before use. PBPA was purified by recrystallization from a mixture of methanol and toluene and identified by ultimate analysis.

Tribromophenyl propionate was prepared by the reaction between propionic acid and tribromophenol (dissolved in benzene) using trifluoroacetic acid anhydride<sup>8</sup> as a dehydrator. The product was purified by recrystallization from ethyl ether and identified by IR spectral measurement.

Tribromophenyl acrylate (TBPA) was provided by Osaka Yuhkigohsei Co., Ltd., and was purified by recrystallization from ethyl ether. An additive-type flame retardant, decabromodiphenylether (DBDPE), provided by Hitachi Chemical Industry Co., Ltd., was used as a reference in the measurement of the effectiveness of these flame retardants of monomer type.

### Molding of Flame-Retardant Ethylene-Propylene-Diene Terpolymer

Ethylene-propylene-diene terpolymer [EPDM; propylene content = 34 wt %; iodine value = 19 I<sub>2</sub> (g)/EPDM (100 g)] used as a base polymer was provided by Japan Synthetic Rubber Co., Ltd. Additives such as a heat stabilizer (polymerized 2, 2, 4-trimethyl-1, 2-dihydroquinoline), crosslinking agents (Sulfur, dicumyl peroxide), ZnO, Sb<sub>2</sub>O<sub>3</sub>, talc, etc., were purchased and used as obtained.

EPDM was mixed on a roll mill at 120°C by adding sulfur (0.4 phr) and ZnO (5 phr) as crosslinking agents, heat stabilizer (1.5 phr), stearic acid (1 phr) as a lubricating agent, flame-retardant monomer (12.8 ~ 40 phr), Sb<sub>2</sub>O<sub>3</sub> (6 ~ 10 phr) as a synergist for the flame retardant (molar ratio of Br:Sb = 1:2.0 ~ 3.0) and talc (100 phr), and at 40 ~ 50 °C dicumylperoxide (DCP, 3 ~ 6 phr) was added to the polymer compound. The mixed stock was molded into sheets 3-mm thick and pressed at 160°C under a pressure of 100 kg/cm<sup>2</sup> for 30 min. During the molding process, the polymerization of the flame-retardant monomer is initiated by DCP simultaneously with the crosslinking of the matrix polymer.

### Measurements

Limiting oxygen index (OI) was measured according to JIS-K7201, in which the use of a 6.5-mm wide and 3-mm thick sample is specified.

Thermal volatilization curves of polymerized flame retardants were recorded using a thermogravimetric analyzer (Rigaku-Denki Co., Ltd., TG-DSC standard type). All runs were carried out in air atmosphere at a programmed rate of 2.5°C/min.

## RESULTS AND DISCUSSION

The effectiveness of the monomers as flame retardants was evaluated by measuring OI of the EPDM compounds. Figure 1 shows the relationship between OI and bromine content in the compounds. As shown with phosphate [III], TBPA, and DBDPE, OI increases with an increase in bromine content. TBPA, PBPA, and phosphate [III] were more effective than phosphate [I] and [II], phosphonate [IV], and DBDPE. Phosphate [III] containing both bromine and phosphorus in one molecule gave a very high value of OI. It also gave very

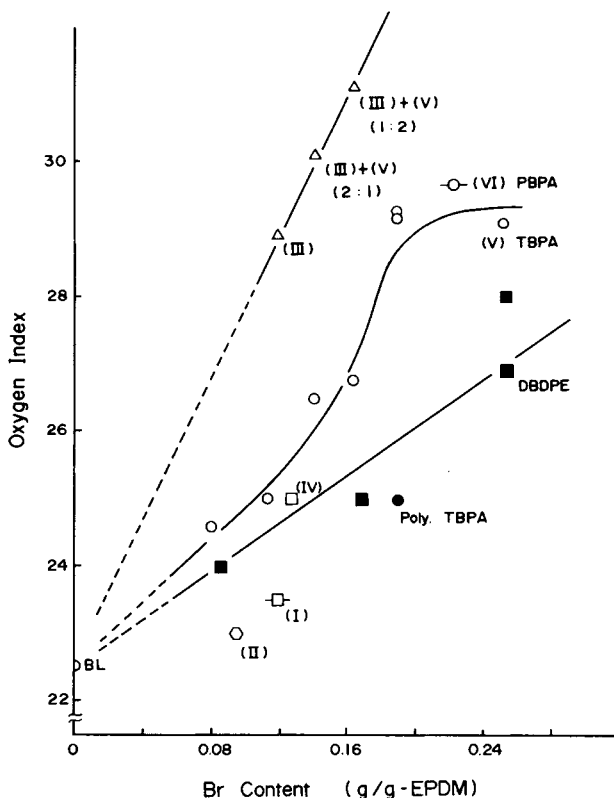


Fig. 1. Oxygen index vs. bromine content of EPDM modified with flame-retardant monomer: [I]  $(\text{CH}_2=\text{CHCOOC}_2\text{H}_4\text{O})_2-\text{P}(\text{O})-\text{OC}_6\text{H}_2\text{Br}_3$ ; [II]  $\text{CH}_2=\text{CHC}_6\text{H}_4\text{O}-\text{P}(\text{O})(\text{OC}_6\text{H}_4\text{Br})_2$ ; [III]  $(\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4\text{O})_2-\text{P}(\text{O})\text{C}_6\text{H}_2\text{Br}_3$ ; [IV]  $\text{CH}_2=\text{CHC}_6\text{H}_4\text{O}-\text{P}(\text{O})(\text{C}_6\text{H}_5)\text{OC}_6\text{H}_2\text{Br}_3$ ; [V]  $\text{CH}_2=\text{CHCOOC}_6\text{H}_2\text{Br}_3$ ; [VI]  $\text{CH}_2=\text{CHCOOC}_6\text{Br}_5$ ; ■,  $\text{C}_6\text{Br}_5\text{OC}_6\text{Br}_5$ ; ●, poly-[V].

high OI when used in combination with a bromine-containing monomer such as TBPA. While, in the cases of phosphate [I] and [II], the obtained values of OI were confined within a region slightly higher than that of the compound with no flame retardant. The effectiveness of phosphonate [IV] was nearly equal to that of DBDPE. As stated later, the effectiveness of the flame-retardant monomers is strongly dependent on their conversion to polymer form and the stability of the resultant polymer to volatilization upon heating. TBPA, PBPA, and phosphate [III] fall into the same class when ranked according to their polymerizability and the thermal stability of the polymers. Very high measured OI using phosphate [III] may be due to a synergistic action of Br and P. The slight effect of phosphate [I], [II], and phosphonate [IV] on the flame retardancy is due to their low conversion to the polymer or the thermal instability of their polymers.

As shown by a closed circle in Figure 1, OI was lower when polymer of TBPA was added in powder form than when TBPA was first mixed in monomer form and then polymerized in the matrix of EPDM. In order to explain the difference in the effectiveness between these two cases, it is important to note that molten TBPA disperses homogeneously and is fixed by the subsequent polymerization in the base polymer. Since poly-TBPA does not melt on the mixing roll at  $120^\circ\text{C}$ ,

its dispersion in the base polymer is assumed to be less homogeneous. Hence, the greater the homogeneity of dispersion of flame retardant in the base polymer, the higher the flame retardancy of the obtained compounds.

The use of DBDPE or phosphate [III] combined with TBPA gives a linear relationship between OI and the content of bromine (Fig. 1). While, in the case of TBPA alone, the linear relationship is not maintained when the bromine content exceeds 0.20 g/g EPDM. The reason for this phenomenon will be discussed later.

In order to examine their reactivity in radical polymerization, the flame-retardant monomers were polymerized in purified benzene at 80°C under oxygen-free conditions using benzoyl peroxide as an initiator (weight ratio of benzene, monomer, and benzoyl peroxide = 8.7:1:0.005). Polymer yield was determined gravimetrically. Figure 2 shows time-yield relationships obtained for each monomer. The initial polymerization rate (average rate within 30 min) was found to decrease in the following order; phosphate [I]  $\gg$  TBPA, PBPA, phosphate [III]  $>$  phosphonate [IV], phosphate [II]. Thus, phosphate [I] having two acryloyloxy groups yielded the highest rate. On the other hand, phosphate [II] and phosphonate [IV] having a *p*-vinyl phenyl group gave the lowest rate, but bifunctional phosphate [III] polymerized at an intermediate rate as rapidly as TBPA and PBPA.

The relationship between the initial polymerization rate and OI of the compounds treated with each monomer was shown in Figure 3. The values of OI were obtained from Figure 1 by estimating those at bromine content of 0.14 g/g EPDM. OI increases with increasing monomer reactivity except in the case of phosphate [I], suggesting that the efficiency of the flame retardant depends on the amount of the monomer converted into polymer.

To determine the amount of the monomer polymerized in the matrix of the base polymer, a sheet of the compound treated with TBPA was cut into chips and immersed in hot toluene for 50 hr using Soxhlet's extraction apparatus. Hydroquinone was used to inhibit the polymerization of extracted TBPA. Extracted polymer was precipitated by adding an excess amount of methanol to the toluene solution. The amount of flame-retardant polymer remaining in

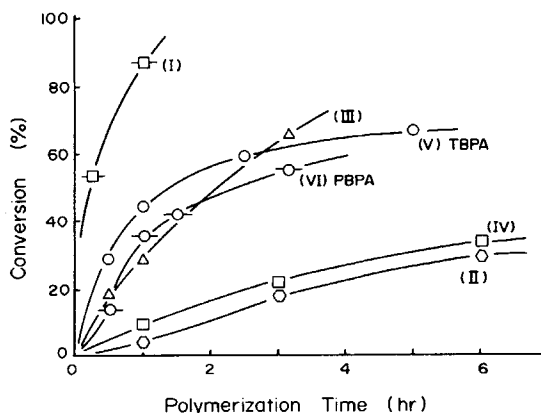


Fig. 2. Time-conversion curve in the polymerization of flame-retardant monomer: benzene: monomer: benzoyl peroxide = 8.7:1:0.005 (by weight); temperature at 80°C; [I] ~ [VI] represent the same as in Fig. 1.

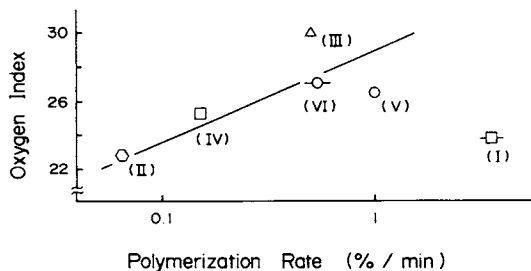


Fig. 3. Relationship between oxygen index of flame-retardant EPDM (estimated for bromine content of 0.14 g/g EPDM) and initial polymerization rate of flame retardant: [I] ~ [VI] represent the same as in Fig. 1.

the matrix of the base polymer is calculated by taking the difference between the weights of the specimen before and after extraction. Hence, the total amount of polymerized monomer is obtained by adding the amount of the extracted polymer to that of the unextracted one. OI (solid line) (Fig. 4) of the compound before extraction is plotted as a function of the amount of polymerized TBPA. The number in parentheses beside each point is the percent conversion. OI increases linearly with an increase in the amount of polymerized TBPA.

Polymerization conversion of TBPA increases with the amount of DCP initiator. OIs obtained at different concentrations of DCP with a constant TBPA (22 phr) are plotted in Figure 4. OI increases with an increase in the amount of DCP because of an increase in the amount of polymerized TBPA. On the other hand, when the polymerization conversion is low, the observed OI is not as high, even when the concentration of TBPA is as high as 40 phr. These observations may explain the deviation from linearity in the plot of OI versus bromine content. TBPA monomer vaporizes rapidly before poly-TBPA and

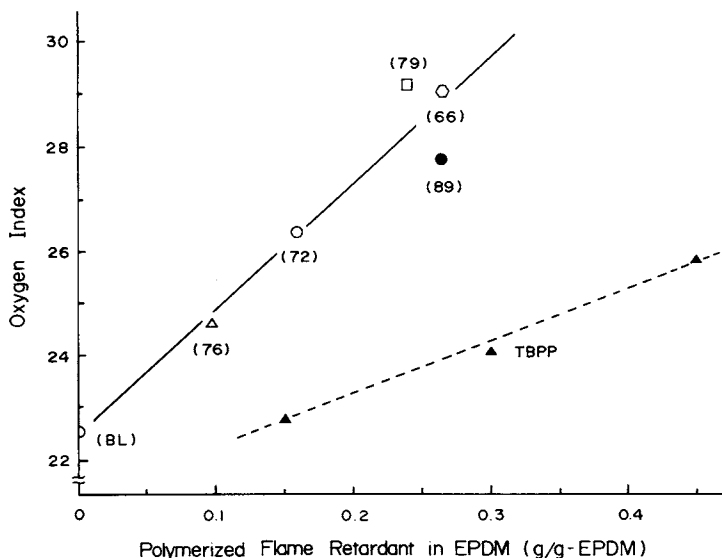


Fig. 4. Relationship between oxygen index and amount of polymerized TBPA in EPDM:  $\Delta$ , TBPA 13 phr;  $\circ$ , TBPA 22 phr;  $\bullet$ , TBPA 22 phr, DCP 6 phr;  $\square$ , TBPA 30 phr;  $\circ$ , TBPA 40 phr. The number in parentheses beside each point is a percentage conversion. And, (—  $\blacktriangle$  —) TBPP; the numbers on the abscissa indicate the amount of TBPP added in the EPDM compound.

the base polymer decomposes in contact with the flame. The slight effect of the unpolymerized TBPA on the flame retardancy may be caused by its rapid release from the system at an early stage of heating.

The dashed line in Figure 4 shows the change in OI of the compound treated with tribromophenyl propionate (TBPP). The numbers on the abscissa indicate the amount of TBPP added to the compound. The difference in the observed effects between TBPA and TBPP elucidate the effectiveness of the flame retardants of monomer type. Both resemble each other in molecular weight, melting point, and bromine content, except TBPP does not undergo polymerization during the compounding process. Low flame-retardant effectiveness of TBPP may be attributed to its rapid release of TBPP from the system on heating. Because of the same reason, the monomeric TBPA is less effective than the polymeric form.

The relationship between OI and the initial polymerization rate in Figure 3 may lead to the conclusion that most flame-retardant monomers used are more effective when they are converted into polymers. However, phosphate [I], having two acryloyloxy groups, shows very low efficiency in spite of having the highest polymerization rate. This fact suggests the existence of other important factors governing the effectiveness of the flame-retardant monomer.

Figure 5 illustrates the thermogravimetric curves recorded for the polymers of each monomer. The polymer of phosphate [I] begins to degrade at a temperature extremely low compared to polymers of the other monomers. Einhorn<sup>9</sup> has reported that, in the case of halogen (Cl, Br) containing flame retardants, optimum efficiency is obtained when the flame retardants decompose within a range of  $\pm 50^\circ\text{C}$  around the decomposition temperature of the base polymer. As seen in Figure 5, maximum slope on the TG curve for EPDM exists at near  $400^\circ\text{C}$ . The polymer of phosphate [I] degrades in two stages. The decomposition with the maximum slope in the first stage (elimination of tribromophenyl group) occurs at  $210^\circ\text{C}$ , lower by about  $200^\circ\text{C}$  than that of EPDM. The observed low efficiency of phosphate [I] can be attributed to the insufficient thermal stability of its polymer. Owing to the rapid splitting off of bromine containing fragments, occurring at a low temperature, the polymer of phosphate [I] loses its effect before the base polymer undergoes decomposition to combustible gases.

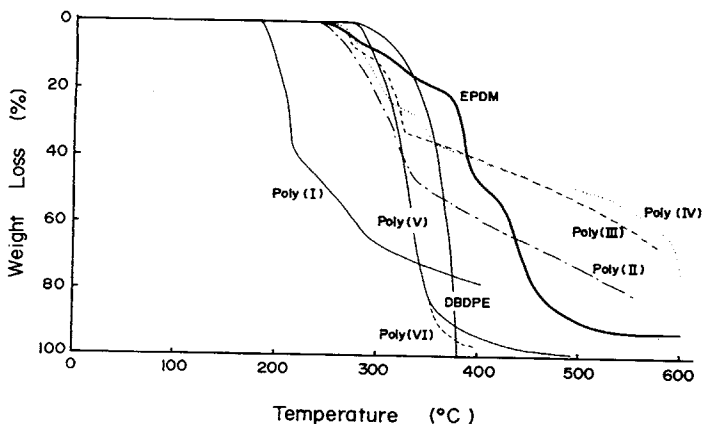


Fig. 5. TG curve for polymerized flame retardant: heating rate  $2.5^\circ\text{C}/\text{min}$  in air; poly[I] ~ [VI] were obtained by solution polymerization near saturation yield in the same condition as in Fig. 2.



In the cases of phosphate [II], [III], and phosphonate [IV], the first rapid degradation of their polymers occurs in the range of 290 ~ 360°C, and both polymers of TBPA and PBPA decompose in one stage with the maximum slope on the TG curve in the range of 320 ~ 330°C. The polymers, except phosphate [I], decompose in almost the same temperature range, and high enough to act as flame retardants for EPDM. Under these conditions, the effectiveness of flame-retardant monomers depends mostly on polymerization reactivity rather than on the stability of their polymers in thermal decomposition.

Consequently, in order to select an effective flame-retardant monomer, one must consider (1) its reactivity to polymerization, and (2) thermal decomposition behavior of its polymer in connection with that of base polymer. Furthermore, it is preferable that the monomer melt below the molding temperature so that it can be dispersed homogeneously in the base polymer.

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