

Synthesis of Brominated Acenaphthylenes and Their Flame-Retardant Effects on Ethylene-Propylene-Diene Terpolymer

YOHISUKE MORITA and MIYUKI HAGIWARA, *Japan Atomic Energy Research Institute, Takasaki Radiation Chemistry Research Establishment, Watanuki-Machi, Takasaki, Gunma, Japan 370-12*

Synopsis

Bromoacenaphthylenes and their condensates as flame-retardant reagents were synthesized by bromination of acenaphthylene using $\text{ZnCl}_2\text{-CF}_3\text{COOH}$ or FeCl_3 as catalysts and subsequent dehydrobromination. The chief components were identified as bromoacenaphthylene monomers when $\text{ZnCl}_2\text{-CF}_3\text{COOH}$ were used, and as their condensates (mostly trimers) in the case of FeCl_3 . Their performance as flame-retardant reagents for ethylene-propylene-diene terpolymer (EPDM) was evaluated by measuring the oxygen index of finished compounds, and flammability by a vertical flammability test based on UL-94-VO. Both the monomers and the condensates demonstrated high flame-retardant effectiveness. The high efficiency was attributed to their excellent dispersity in the base polymer and their characteristic thermal decomposition behavior. In TGA, they decomposed in a very wide range of temperature (ca.200–560°C), which covers the decomposition range of EPDM. This was attributed to the existence of bromines of different thermal stabilities in one molecule.

INTRODUCTION

Hydrocarbon polymers such as ethylene-propylene copolymer and polyethylene belong to a class of the most flammable polymers. Because of their excellent electrical and mechanical properties, they are used in a large amount as insulators for wires and cables, and often required to be given flame retardancy. The increased emphasis on the safety of nuclear power plants, where wires and cables are used in an ionizing radiation environment, produces the novel need for radiation stable flame retardants.

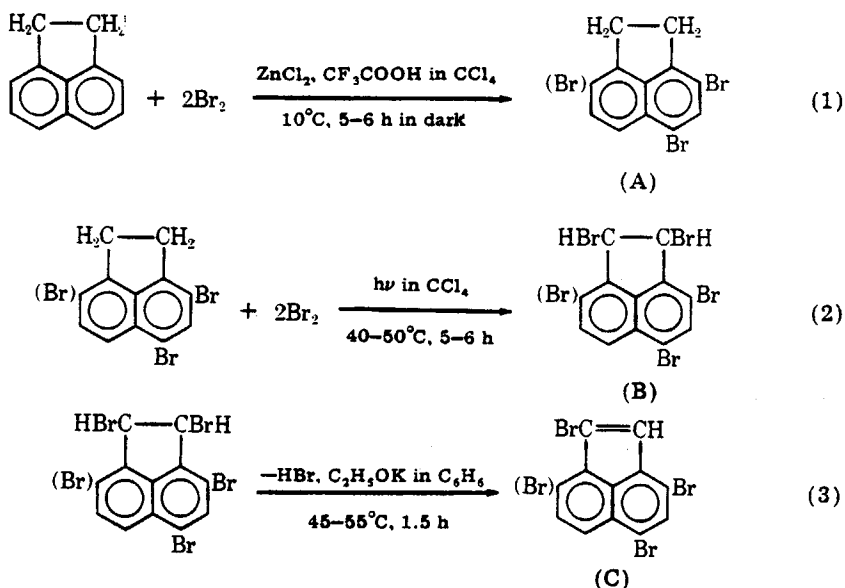
In our previous paper,¹ bromine- and/or phosphorous-containing monomers, which are able to undergo radical polymerization in the matrix of the base polymer during a molding process, demonstrate high flame-retardant properties in ethylene-propylene-diene rubber (EPDM). One of the features of the polymerizable flame retardants is the ease of blending to yield a homogeneous mixture of the base polymer and the flame retardants.

This work is a continuation of the previous paper on the polymerizable flame retardants, and also a part of a series of studies to develop new flame retardants which can give high flame retardancy as well as stability against ionizing radiation to EPDM.

EXPERIMENTAL

Syntheses of Bromoacenaphthylenes and Their Condensates

Brominated acenaphthylenes were prepared by the following steps:



Zinc chloride (ZnCl_2) was ground to a powder and dried at 120°C for ca. 20 h under vacuum before use. Others of chemical reagent grade were used as received. First, [reaction (1)], to 1 mol of acenaphthene were added 1 mol of zinc chloride (ZnCl_2) and 1.75 mol of trifluoroacetic acid (CF_3COOH) as catalysts. A solution of bromine in CCl_4 ($\text{Br}_2:\text{CCl}_4 = 2.5:1$ by weight) was dropped in the dark to the stirred solution containing acenaphthene and the catalysts. The reaction mixture was next exposed to bromine under illumination of cadescend light [reaction (2)] after the catalysts were removed by filtering and washing with water. The brominated intermediate (B) was precipitated into cold acetone (ca. -10 – 0°C) by pouring the reaction mixture which has been condensed to an appropriate concentration by distilling excess CCl_4 under reduced pressure. After dehydrobromination [reaction (3)], bromoacenaphthylenes were obtained in powder form from benzene solution by a similar precipitation procedure. The yield was 61% based on tribromoacenaphthylene. When anhydrous ferric chloride (FeCl_3) was used in the first step as catalysts instead of ZnCl_2 — CF_3COOH , condensed bromoacenaphthylene was obtained. To 1 mol of acenaphthene, 0.5 mol of FeCl_3 and 6 mol of bromine of chemical reagent grade were added. The bromination was done at somewhat higher temperatures than in the case of ZnCl_2 — CF_3COOH , i.e., ranging from 25° to 30°C , and the second step [reaction (2)] was eliminated. The yield of condensed bromoacenaphthylene was 54% based on tetrabrominated acenaphthylene unit.

An additive-type flame-retardant, decabromodiphenyl ether (DBDPE) was used as a reference for evaluating effectiveness of the above flame retardants.

Molding of Flame-Retardant Ethylene-Propylene-Diene Terpolymer

Details of molding of flame-retardant ethylene-propylene-diene terpolymer (EPDM) were described previously.¹ The melting (or softening) temperatures of bromoacenaphthylenes (Table II) used in this work are higher than normal temperature for compounding EPDM. Therefore, they were premixed with necessary ingredients on rolls at 120°C, and rolled again for a short time over the melting points to obtain homogeneous dispersion of the flame retardants.

Measurement

GPC curves of bromoacenaphthylenes were recorded with a Waters ALC/GPC-202/R401 type gel permeation chromatograph using a combination of 1-ft columns, μ -Styragel 100 Å, 500 Å, and 1000 Å, with THF as a solvent: flow rate = 1 cc/min. Fractionation was performed with a Toyo Soda model HLC-827 fractional gel permeation chromatograph using 2 ft, 1 in. columns, G2000-H10 ($\sim 10^2$ Å) and G4000-H10 ($\sim 10^4$ Å), operated at 38°C using chloroform as a solvent: flow rate = 6.2 cc/min; injection volume = 3 cc (concentration, 6.8 wt %). Molecular weight of each component was determined with a vapor pressure osmometer (Hitachi-Perkin-Elmer type 115 osmometer) at 35°C in chloroform solution. NMR spectrum was obtained by a JEOL-PET-100 at 100 MHz for ¹H in a CDCl₃ solution at room temperature.

Flammability tests were carried out as follows: Limiting oxygen index (OI) was measured in conformity to JIS-K7201, in which the use of a 6.5 mm wide and 3 mm thick specimen is specified; another vertical flammability test (VFT) was performed according to UL-94 VO Standard (UL-94 V-0,1,2 Standard for Flammability Test of Plastic Materials for Parts in Devices and Appliances, 1973) using a 127 mm long, 12.7 mm wide, and 3 mm thick specimen with a minor modification in the procedure. The specimen was supported in a three-sided vertical enclosure, and its bottom end was exposed to a propane burner flame 10 times (10 round) repeatedly. The exposure time in each round was 10 s, and flaming time was measured when combustion lasted after the removal of the test flame.

To investigate the homogeneity of the flame retardant in EPDM compound, a cross section of sheet samples was observed by an electron probe X-ray microanalyzer (JEOL, JXA-733).

To estimate the amount of the flame retardant in EPDM compound, a sheet of the compound was immersed in THF at boiling temperature for 24 h. Hydroquinone was added to prevent polymerization of extracted flame retardant. The amount of the extract was determined by the height of the main peak in gel permeation chromatogram.

Thermal volatilization curves of EPDM and the flame retardants were recorded using a thermogravimetric analyzer (Sinku-Riko Co., Ltd., TGD-1500 type). All runs were carried out in air atmosphere at a programmed rate of 2°C/min.

RESULTS AND DISCUSSION

Characterization of Bromoacenaphthylenes and Their Condensates

Figure 1 shows the gel permeation chromatograms of bromoacenaphthylenes synthesized using $\text{ZnCl}_2\text{—CF}_3\text{COOH}$ or FeCl_3 as catalyst. In the case of $\text{ZnCl}_2\text{—CF}_3\text{COOH}$, the highest peak on the chromatogram is located at 31 counts by elution volume, and there are two other lower peaks at the larger molecular weight side. On the other hand, in the case of FeCl_3 , the main peak is situated at 26.5 counts, and there are three other small peaks in the smaller molecular weight side. The location of peaks in the chromatogram (a) agree well with those in chromatogram (b) except for a slight discrepancy between peaks which appeared at 28.7 in (a) and 29.1 in (b). The peak at 32 counts is a ghost, because it is located in a smaller molecular weight region than that of benzene (31.5 counts) used as solvent of the dehydrobromination. From these chromatograms, both bromoacenaphthylenes synthesized using $\text{ZnCl}_2\text{—CF}_3\text{COOH}$ or FeCl_3 consist of three major components on the basis of molecular weight. The smallest molecular weight component was the most abundant with $\text{ZnCl}_2\text{—CF}_3\text{COOH}$, in contrast to the largest one, with FeCl_3 .

For the characterization of each component, the product obtained using $\text{ZnCl}_3\text{—CF}_3\text{COOH}$ was fractionated. The chromatogram after recycling is shown in Figure 2, and Table I lists values of molecular weight, elemental analysis, and the melting point of each fraction. The peaks (I, II, and III) on the analytical GPC curve [Fig. 1(a)] showed further split by recycling. The results (Table I) are caused by a little difference in molecular weight, e.g., the number of substituted bromine. The measurement of molecular weight and bromine content for each fraction suggest that Fr (I) is near equivalent mixture of tri- and tetrabromoacenaphthylene, and Fr (I') is that of tetra- and pentabromoacenaph-

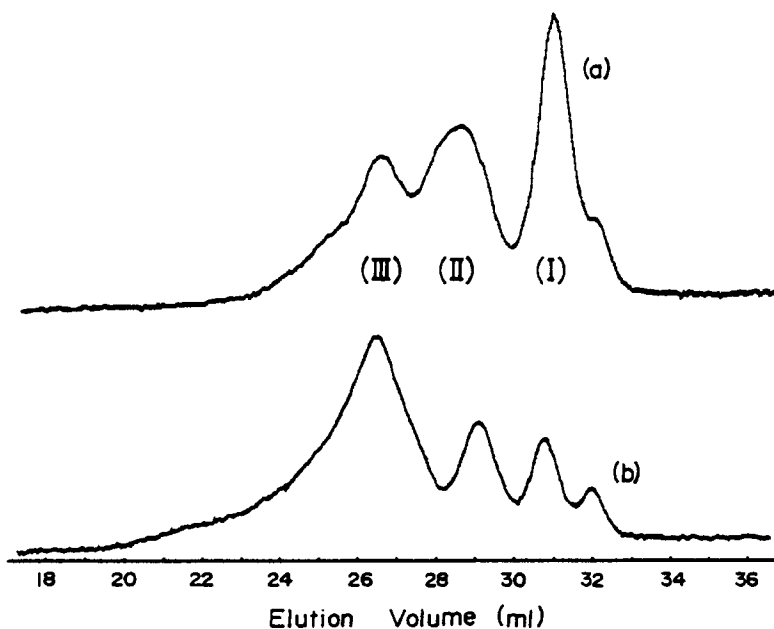


Fig. 1. GPC curves of brominated acenaphthylenes synthesized using (a) $\text{ZnCl}_2\text{—CF}_3\text{COOH}$ and (b) FeCl_3 as catalysts.

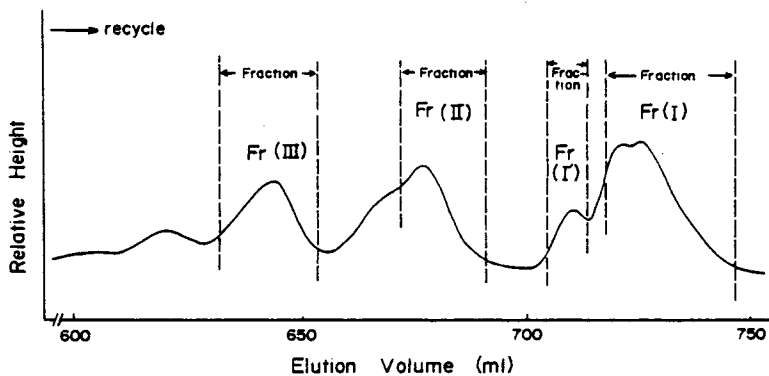


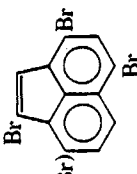
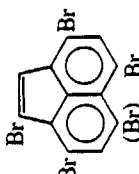
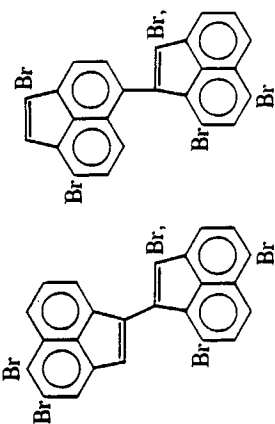
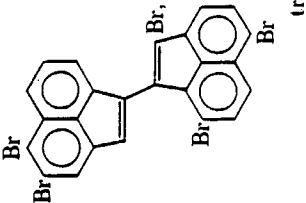
Fig. 2. Fractional GPC curve of brominated acenaphthylenes: catalyst, $\text{ZnCl}_2\text{—CF}_3\text{COOH}$.

thylene. Fr (II) contains less bromine than Fr (I), but its molecular weight is larger than that of Fr (I), and almost equals double of that of tribromoacenaphthylene. Hence, Fr (II) is composed of dimers of bromoacenaphthylenes; Fr (III) is composed of trimers. The dimers and trimers are formed through condensation during the bromination [reaction (1)]. It may take place between carbons at the benzyl positions or between those at the benzyl positions and aromatic rings since the condensation between aromatic carbons needs more severe conditions^{2,3} than those settled in the present work (below 10°C). Possible linkage between structural units in condensates are shown in Table I. Both bromoacenaphthylenes obtained by $\text{ZnCl}_2\text{—CF}_3\text{COOH}$ and by FeCl_3 are similar in components though compositions differ from each other (Fig. 1). According to the results of the fractionation, the slight discrepancy in the position of the peaks observed at 28.7 and 29.1 that fall into Fr (II) is attributable to the difference in ratio of dimers with different degrees of bromination. Hence, bromoacenaphthylene obtained using $\text{ZnCl}_2\text{—CF}_3\text{COOH}$ contains monomers as the most abundant component; on the other hand, that obtained with FeCl_3 consists mainly of condensates (chiefly trimers).

To insure the presence of the double bond between benzyl carbons, $^1\text{H-NMR}$ spectra of the intermediate (B) and the product (C) were measured, and shown in Figure 3. In both spectra, the peaks caused by protons attached on the naphthalene ring are observed at $\delta_{\text{H}} = 7.0\text{--}7.9$ ppm. The intermediate (B) shows peaks at $\delta_{\text{H}} = 5.65\text{--}5.9$ ppm that are caused by protons at benzyl carbons. In the final product, the above peaks shifted to $\delta_{\text{H}} = 6.7\text{--}7.0$ ppm and showed a decrease in peak intensity. A similar shift has been observed between acenaphthene and acenaphthylene.⁴ These changes can be explained by the dehydrobromination of the intermediate (B) to form a double bond between benzyl carbons: The decrease in intensity is due to a removal of one proton, and the peak shift results from a partial resonance of π -electrons between the naphthalene ring and the double bond formed outside the ring. The same change is observed on the condensed bromoacenaphthylene synthesized using FeCl_3 .

Concerning flame retardancy of the ethylene-propylene-diene terpolymer, the one synthesized via bromination using $\text{ZnCl}_2\text{—CF}_3\text{COOH}$ is designated as BACN which contains monomers as the chief component, while the other is obtained using FeCl_3 as con-BACN because it consists mostly of condensed forms. Melting point and bromine content of BACN and con-BACN used in the present work are listed in Table II.

TABLE I
Characterization of Fractionated Bromoacenaphthylenes

Fr No.	MW ^a	Elemental analysis	Summary formula	mp (°C)	Type	Tentative structure
Fr (I)	440 429	C 33.69 H 0.790 Br 64.66	$C_{12}H_{3.4}Br_{3.5}$	70-	Monomer	
Fr (I')	494	C 29.25 H 0.343 Br 69.32	$C_{12}H_{1.7}Br_{4.3}$	171-173	Monomer	
Fr (II)	743 755	C 39.08 H 0.987 Br 54.79 Cl 5.93 ^b	$C_{12}H_{3.6}Br_{2.5}$ $Cl_{0.62}$	100-105	Condensate	
Fr (III)	1117 1140	C 40.04 H 0.815 Br 51.45 Cl 7.41 ^b	$C_{12}H_{2.9}Br_{2.3}$ $Cl_{0.75}$	172-177	Condensate	

^a By vapor pressure osmometer: solvent, $CHCl_3$.

^b Thought to be from the catalyst.

References: calculated MW; $C_{12}H_5Br_3 = 389$, $C_{12}H_4Br_4 = 469$, $C_{12}H_3Br_5 = 548$, $(C_{12}H_5Br_3)_2 = 778$, $(C_{12}H_5Br_3)_3 = 1167$.

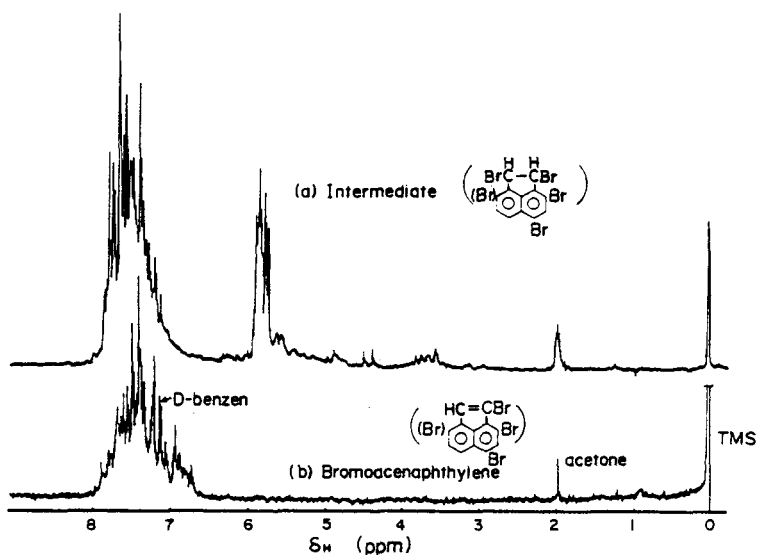


Fig. 3. $^1\text{H-NMR}$ spectra of: (a) intermediates (B) and (b) brominated acenaphthylenes (C); catalyst, $\text{ZnCl}_2\text{-CF}_3\text{COOH}$.

Flame-Retardant Modification of EPDM with BACN or con-BACN

The effectiveness of BACN or con-BACN for the flame-retardant modification of EPDM was evaluated by oxygen index (OI) measurement and the flame test based on the UL-94 standard. Figure 4 shows variation of OI as a function of bromine content in the finished compounds. In these compounds, antimony oxide was added by the amount calculated from the ratio of $\text{Sb/Br} = 1/\text{ca.}3$. OI increases linearly with an increase in bromine content. The effectiveness increases in the following order; $\text{DBDPE} \ll \text{BACN} < \text{con-BACN}$. Oxygen index slopes (OIS) obtained from the lines were as follows: DBDPE, 0.1-; BACN, 0.35; con-BACN, 0.45. BACN and con-BACN are more than twice as effective as DBDPE.

As the combustion of polymeric materials is affected by many factors, it may be better to compare flame resistivity by different methods. In the OI measurement, specimens were ignited at the top end; hence, the flame propagates downwards. It is desirable to carry out a test in which ignition is made at the bottom end of specimen so that flame propagates upwards. Table III shows the results of the test based on UL-94. As described in the experimental section, ignition with a burner flame was repeated 10 times (10 rounds), and self-sustained flaming time was measured in each round. The compound with no flame retardant burned entirely by the first ignition. Specimens with self-extinguishing properties were prepared by regulating bromine content in the range of 0.20–0.30

TABLE II
Br Content and Melting Point of Flame Retardants

Flame retardant	Br (%) ^a	mp (°C)
(I) Bromoacenaphthylene (BACN)	65.0	114–120
(II) Condensed bromoacenaphthylene (con-BACN)	66.7	130–140
Decabromodiphenyl ether (DBDPE)	83.0	315

^a Elemental analysis.

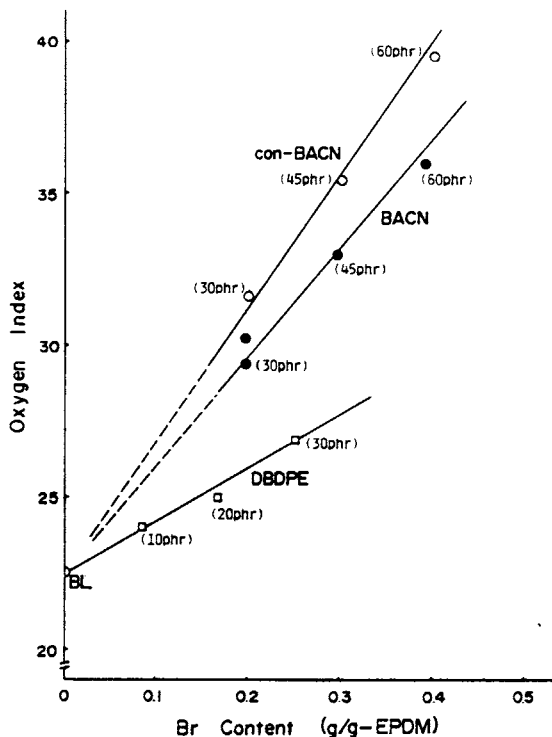


Fig. 4. Oxygen index vs. bromine content of flame-retardant EPDM: EPDM, talc (100 phr), flame retardant (10–60 phr), Sb_2O_3 (3.3–16 phr, Sb:Br = 1:ca. 3), heat stabilizer (polymerized 2,2,4-trimethyl-1,2-dihydroquinoline, 1.5 phr), stearic acid (1 phr), ZnO (5 phr), sulfur (0.4 phr), and DCP (3 phr).

g/g EPDM. From the first to fourth round in the case of DBDPE, the flame went out instantly after the burner was removed. In fifth round, combustion was sustained and spread slowly upward. From the eighth to 10th rounds, the specimen burned completely with dripping. On the other hand, those containing BACN or con-BACN yielded a part still unburned even after the 10th round. The specimen containing 30 phr of BACN (0.20 g/g EPDM) sustained a flame after the fifth round. In contrast to the case of DBDPE, the combustion was confined in a limited area with a very small flame. Con-BACN maintained a self-sustaining flame after several rounds of ignition. This combustion continued for only a very short time with a very small flame. These observations support the fact, obtained previously by the OI measurement, that BACN and con-BACN have high flame retardant effectiveness for EPDM. As mentioned above, since ignition was made at the bottom end, heating of the specimen by flame propagation is very important for sustaining combustion. DBDPE melts at 315°C , and vaporizes simultaneously. This may reduce flame retardancy in the specimen. On the other hand, BACN and con-BACN showed high flame-retardant effectiveness, though their melting temperatures are lower than that of DBDPE. The double bond outside the naphthalene ring can undergo polymerization under the influence of radical initiators.⁵⁻⁷ It is considered that BACN and con-BACN polymerize in the matrix of the base polymer at the molding process and convert to substances of higher molecular weight.

TABLE III
Result of Vertical Flammability Test According to UL-94-VO

Round no. ^a	Flaming time (s)						
	Flame retardant (phr)						
	None	DBDPE (30)		BACN (30)		con-BACN (45)	
	Br content (g/g EPDM)						
	0	0.25		0.20		0.30	
1	burned	0	0	0	0	0	0
2		0	0	0	0	0	0
3		0	0	1	0	0	0
4		0	0	1	0	0	0
5		37	28	34	25	0	0
6		0	11	11	19	0	0
7		1	6 (d)	57	30	1	8
8		15 (d) ^b	12 (d)	0	3	17	12
9		10 (d)	Burned	12	4	5	9
10		Burned		1	0	5	0
Total	—	—	—	117	81	28	29

^a Ignition = 10 s/round.

^b (d) = drip.

Conversion of BACN or con-BACN to such compounds was measured by gel permeation chromatography after extraction, and listed in Table IV. DBDPE, an additive-type flame retardant, was extracted almost entirely. In contrast, BACN and con-BACN extracted only 40–50% of the amount initially added. In other words, about 50–60% of BACN and con-BACN was not extractable. This change may have taken place in the molding process, probably through polymerization and/or grafting initiated by DCP. Polymerizable flame retardants¹ are effective when they yield polymers and/or grafted chains with suitable heat stability. The high flame-retardant effectiveness of BACN and con-BACN may be partly attributed to their conversion to such polymers. The high effectiveness of polymerizable flame retardants results from their good dispersity. They melt at low temperature, mix homogeneously in the base polymer during compounding and are fixed by polymerization during molding. When the monomers were converted to high melting temperature polymers prior to compounding, the effectiveness decreased markedly. This was attributed to less homogeneity during polymer-polymer blending. Reflections of bromine atoms in XMA on a cross section of molded specimen are shown in Figure 5. Con-BACN disperses homogeneously. On the other hand, DBDPE which does not melt at compounding

TABLE IV
Extraction of Flame Retardants with THF

Flame retardant (phr)	Added amount (g/g compound)	Extracted amount (g/g compound)	Extraction (%)
DBDPE (30)	0.121	0.116 ^a	96.3
BACN (30)	0.121	0.046 ^b	38
con-BACN (30)	0.121	0.057 ^b	47

^a Detected at 310 nm (UV).

^b Detected at 340 nm (UV).

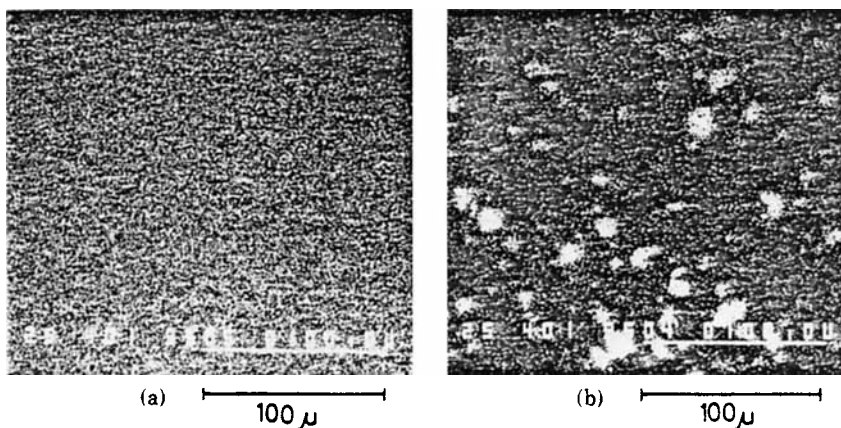


Fig. 5. XMA micrographs (bromine) on cross section of finished compounds containing (a) *con*-BACN (60 phr) and (b) DBDPE (30 phr).

temperature, gave reflections from particles with a size ranging from 5 to 10 μ .

The mechanism^{8,9} of flame retardancy of compounds containing halogens is the deactivation of OH and H radicals that propagate a chain reaction in a flame. For the compounds to function effectively as flame retardants, it is important that they release useful elements at temperatures in a range where decomposition of the base polymer occurs. Figure 6 illustrates the thermogravimetric curves recorded for the flame retardants used in this work and EPDM vulcanized by DCP (2 phr). EPDM decomposes in two stages: the first between 200°C and 305°C, and the second at above 305°C to ca. 500°C. The TG curve of DBDPE shows a rapid decrease in weight beginning at 260°C and continuing to 380°C. BACN and *con*-BACN volatilize in two stages: slow volatilization in a range from 160°C to 335°C for the case of BACN and 200°C to 315°C for *con*-BACN, and a relatively rapid one between ca. 350°C and 560°C for both. It can be estimated from the curves (Fig. 6) that the release of flame-retardant element (Br) from BACN and *con*-BACN begins almost simultaneously with the decomposition of EPDM, and that it continues to a temperature as high as 600°C to cover the whole range of volatilization of EPDM.

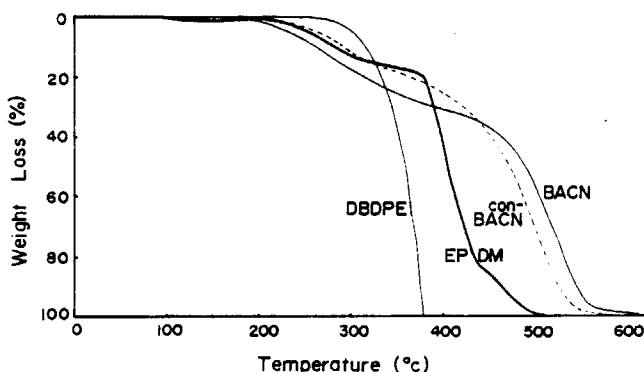


Fig. 6. TG curves of flame retardant and vulcanized EPDM: heating rate = 2°C/min in air.

In the flame-retardant modification of polymers, it is critical to match the timing of the release of flame-retardant elements and the decomposition of base polymer. The decomposition in two stages, that observed in TG curves of BACN and con-BACN, may be caused by the fact that there are two kinds of bromines with different stabilities in one molecule. Further, this may cause the release of flame-retardant element to be sustained over a wide range of temperature which covers that of the decomposition of EPDM. Observed very high flame-retardant effectiveness has a strong relationship to the characteristic decomposition behavior of BACN and con-BACN.

Ionizing radiation resistivity of flame-retardant EPDM with the new flame retardants will be reported shortly in a subsequent paper.

The authors thank Dr. K. Hayashi of Osaka Establishment of JAERI for fractional GPC curves and Mr. Y. Watanabe for obtaining the proton NMR spectra.

References

1. Y. Morita, M. Hagiwara, and K. Araki, *J. Appl. Polym. Sci.*, **25**, 2711 (1980).
2. A. Breuer and T. Zincke, *Ber.*, **11**, 1404 (1878).
3. J. F. Spencer and G. M. Price, *J. Chem. Soc.*, **97**, 338 (1910).
4. C. J. Pouchert and J. R. Campbell, *The Aldrich Library of NMR Spectra*, Aldrich Chemical Co., Inc., Milwaukee, 1974, Vol. IV., pp. 19, (D) A80-5, and 33, (C) A10-4.
5. J. I. Jones, *J. Appl. Chem.*, (*London*), **1**, 568 (1951).
6. K. Ueberreiter and W. Krull, *Makromol. Chem.*, **24**, 50 (1957).
7. J. Springer, K. Ueberreiter, and R. Wenzel, *Makromol. Chem.*, **96**, 122 (1966).
8. W. A. Rosser, H. Wise, and J. Miller, *Seventh International Symposium on Combustion*, Butterworths, London, 1959, p. 175.
9. H. Wise and W. A. Rosser, *Ninth International Symposium on Combustion*, Butterworths, London, 1963, p. 733.

Received September 9, 1981

Accepted February 26, 1982