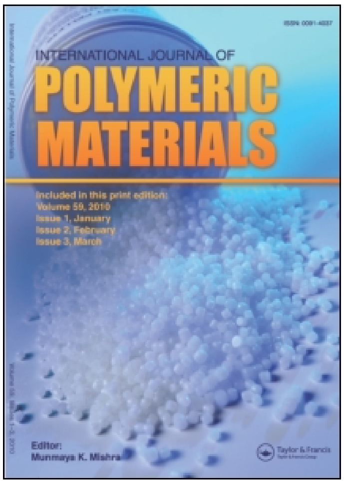

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High Molecular Weight Halogenated Fire Retardants

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Fire retardant characteristics of high molecular weight halogenated compounds are reviewed.

KEY WORDS Fire retardants, halogenated compounds.

RESULTS AND DISCUSSION

High molecular weight fire retardants are the polymeric and oligomeric products containing chemical elements that assist ignition in some way. It is known that chlorine, bromine, phosphorus and to a lesser degree nitrogen and sulfur are such elements. The high molecular nature of fire retardants provides some general properties that are superior compared to low molecular weight fire retardants of similar chemical structure.

High molecular weight fire retardants do not migrate from the volume of polymeric material to its surface, often seen when low molecular weight fire retardants are used. Because high molecular fire retardants are not volatile, sanitary-hygenic conditions improve both in the manufacturing and exploitation of articles made from fire retardant polymers. Finally, in some cases high molecular fire retardants exhibit thermodynamic compatibility with protected polymers that is positively affected by the number of properties of polymeric materials. These advantages may be responsible for the current enhanced interest in high molecular fire retardants.

Poly (vinyl chloride) (PVC) is the best-known example of a high molecular weight fire retardant. There are other known polymeric materials that are mixtures of poly (vinyl chloride) with PP, poly (methyle methacrylate) (PMMA), copolymer butadiene with akrylonitril and some other polymers.[1,2] However the application of PVC as a high molecular weight fire retardant is limited by the elimination of hydrogen chloride at low temperatures (140–160°C). It will be attributed to high molecular weight fire retardants, the chlorinated paraffines (CP) with more than 20 carbon atoms in the chains. Such CPs are employed for flame retardance of polyolephines, PMMA, polyepoxides, and polyurethanes.[3] As in the case of PVC, the field of the application of CP is limited by low thermal stability.

A number of more thermally stable halogen and phosphorus containing polymers have been synthesized for use as high molecular weight fire retardants. For example, brominated epoxy resin of diane type containing up to 52 wt. % of bromine loses 5 wt. % only when heated to about 380°C. This epoxy resin is more effective as a fire retardant for polyester, nylon, and thermoplastic polyurethanes.[4,5] In order to lower flammability, glass-reinforcement based on nylon and polybutadiene terephthalate polypentabrombenzylacrylate is used.[6] The polymer contains 75 wt. % of bromine and loses about 20 wt. % when heated up to 344°C. Its softening temperature is 205–215°C.

One of the best known high molecular weight fire retardants, Pyrochec 68 PB, consists of brominated polystyrene containing 67 wt. % bromine with molecular mass of about 80,000. The softening temperature of Pyrochec 68 PB is 215–225°C and initial decomposition temperature is 375°C. The application of this high molecular weight fire retardant allows us to obtain polymeric material based on different polymers having a V-O rating on the UL-94 test. The most successful Pyrochec 68 PB is employed for flame retardance of styrene plastic, polyester, unsaturated polyesters, and polyamides.[7]

The high molecular weight fire retardant PO 64 P is by nature brominated poly-1,4-phenyleneoxide containing about 62 wt. % bromine and is characterized by increased thermal stability.[8] The softening temperature of this polymer is 230°C and initial decomposition temperature is about 300°C. PO 64 P is employed for flame retardance of different structural plastics. High thermal stability permits us to use this fire retardant in materials based on the polymers with high processing temperatures, for example, polypenyleneoxide.

Together with halogen containing high molecular weight fire retardants, phosphorus and halogen-phosphorus containing polymers are employed as fire retardants, for example, the polyester based on phenylphosphonic and di(chloralcyl)phosphoric acids. Finally, the polyphosphazenes are employed for flame retardance of a number of polymers, first of all polyepoxides.[9]

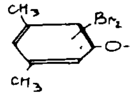
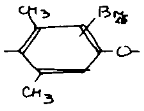
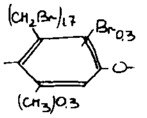
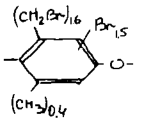
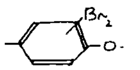
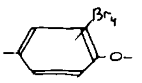
Despite the fact that high molecular weight fire retardants—based on the different chemical nature of the polymers—are employed to create flame retardant polymeric materials, there is not much information about the peculiarity of the action of this type of fire retardant. At the same time, the differences in thermal destruction mechanisms of low and high molecular weight substances permit us to expect differences in the mechanisms of the action of these compounds as fire retardants.

In relations to this, it has been of interest to us to investigate the peculiarity of the action of brominated polyphenyleneoxides and polystyrene as high molecular weight fire retardants and to compare them with a similar low molecular weight fire retardant, decabromdiphenyloxide (DBDO). The investigations were carried out using the oxygen index (OI) test and thermogravimetric analysis (TGA). Sample size for TGA was 100 mg; the samples were subjected to a temperature rise of 5°C/min. The methods of gas chromatography and infrared and mass spectrometry were used to analyze the thermal degradation products.

Brominated polyphenyleneoxides (BPPO) were synthesized either by poly-2,6-dimethyl-1,4-phenyleneoxide bromination—BPPO Ia-d—or oxidative coupling of 2,4,6-tribromphenol and pentabromphenol—BPPO IIa,b. The properties of syn-

TABLE I

The structure and properties of brominated polyphenyleneoxides

Code	Structure	Bromine content, wt. %	Molecular mass	Initial decomposition temperature, °C
Ia		57,0	-	215
Ib		50,3	22,000	245
Ic		58,0	45,000	200
Id		68,1	33,000	215
IIa		63,5	6,000	300
IIb		77,9	3,500	260

thesized BPPO were described previously in detail. The structure and properties of BPPO are shown in Table I.

Brominated polystyrenes (BPS) with different bromine content were obtained by treatment of polystyrene solution in dichloroethane by bromine or bromine chloride in the presence of the catalyst antimony trichloride.[11] The properties of synthesized BPS are given in Table II.

BPPO and BPS were introduced in low density polyethylene (LDPE), polystyrene (PS) and styrene plastics—high impact polystyrene (HIPS) and acrylonitrile-butadiene-styrene (ABS)—together with the synergistic additive antimony trioxide. The content of high molecular weight fire retardants in the mixture corresponded to a bromine concentration of 10 wt %. The quantity of antimony trioxide corresponded to an atomic ratio of Br/Sb = 3.

Oxygen index (OI) data of the mixtures LDPE with BPPO and antimony trioxide are shown in Table III.

The mixtures based on LDPE containing BPPOs as fire retardants have the same

TABLE II

The properties of brominated polystyrenes

Code[a]	Bromine content in the aliphatic part of macromolecules, wt. %	Molecular mass	Glass temperature, °C	Initial decomposition temperature, °C
BPS-45	0	2,000,000	156	325
BPS-60	0,7	2,100,000	167	310
BPS-68	0,09	4,300,000	184	315
BPS-71	–	–	245	300

[a] The numbers signify total bromine content in BPS.

TABLE III

OI data of the mixtures LDPE with BPPO and antimony trioxide

BPPO	Content BPPO, wt. %	OI	Character of the burning
Ia	17,5	22	Charring
Ib	19,9	24	Charring
Ic	17,2	24	High viscous melt
Id	14,7	24	Charring
IIa	15,9	24	Charring
IIb	12,6	22	Dripping
DBDO	12,0	24	Dripping

TABLE IV

OI data of the mixtures PS with BPPO and antimony trioxide

Code	Content BPPO, wt. %	OI	Character of the burning
la	17,5	28	Charring
lb	19,9	27,0	Charring
lc	17,2	27,5	High viscous melt
ld	14,2	28,0	Charring
IIa	15,9	26,0	Charring
IIb	12,6	24	Dripping
DBDO	12,0	24,0	Dripping

or a little smaller OI (the mixtures with BPPO 1a, 1b) as those with DBDP—a similar low molecular weight fire retardant. However when comparing the effectiveness of BPPO with DBDO it should be taken into account that the burning of the mixtures containing BPPO is accompanied by charring (with the exception of the mixture with BPPO IIb), while the burning of LDPE containing DBDO is accompanied by intensive dripping. While the dripping at candle burning brings an increase in the OI,[12] we can be sure that the effectiveness of BPPO Ia-d and BPPO IIa in LDPE is not worse than that of DBDO. Oxygen index data of the mixtures PS with BPPO and antimony trioxide are given in Table IV.

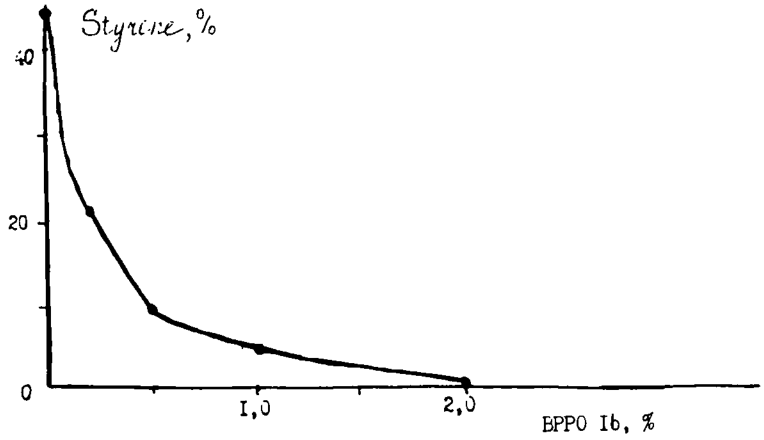


FIGURE 1 Influence of BPPO Ib on styrene yield at the thermal destruction of the mixture based on PS.

TABLE V

OI data for the mixtures PS with BPS and antimony trioxide

BPS[a]	Content BPS, wt. %	OI	Character of the burning
BPS-45	22,2	22,0	Charring
BPS-60	16,7	24,5	Charring
BPS-68	14,7	24,5	Charring
BPS-71	14,1	25,0	Charring
DBDO	12,0	24,0	Dripping

[a] The numbers signify the content of bromine in BPS.

Apart from BPPO IIb, all BPPOs have shown themselves to be more effective fire retardants than DBDO in PS. The thermal degradation of BPPOs and their influence on the thermal destruction of PS has been investigated in order to clear up the reason for the greater effectiveness of BPPO. It was discovered that deep dehydrobromination occurs by heating BPPO Ia-d at a temperature interval of 200–400°C and a result was that the polymer lost about 70–80% of its bromine. The degree of dehydrobromination in BPPO IIa, b was significantly lower in an analogous condition (10–20%). According to TGA, BPPO Ia-d lost 10–30% weight but BPPO IIa, b lost only 3–5% weight by temperature of initial thermal degradation of PS. The weight loss of BPPO Ia-d was 40–70%, thereby most of the thermal destruction product is HBr in temperature intervals conforming to maximum velocity of formation of volatile combustible destruction products of PS. Apparently one of the reasons for the higher effectiveness of BPPO Ia-d in comparison with BPPO IIa, b as the fire retardants for PS is a larger concentration of combustion inhibitors in the gas phase: HBr and $SbBr_3$. Quantitative data on the yield of these compounds as a result of pyrolysis of the PS mixtures with BPPO and antimony trioxide are given in Table VI.

The comparison TGA curves of the mixtures PS-BPPO Ib and PS-BPPO Ib-Sb

TABLE VI

The formulation of pyrolysis products of PS mixtures with high molecular weight brominated fire retardants and antimony trioxide

Fire retardants	Unvolatile residue	Oligomers and other low volatile compounds	Styrene	HBr	$SbBr_3$
		wt %			
–	23 (43)	20 (31)	44 (24)	–	–
BPS-45	53 (38)	20 (39)	27 (20)	0.5 (0)	2,4
BPS-60	65 (67)	15 (19)	17 (14)	0,3 (0)	1,6
BPS-71	65 (73)	12 (7)	23 (8)	0,1 (0)	2,1
BPPO Ia	72 (59)	21 (32)	0 (0)	7,0 (1,9)	7,0
BPPO Ib	62 (69)	32 (25)	0 (0)	5,4 (2,2)	3,4
BPPO Ic	59 (84)	29 (3)	3 (2)	8,6 (1,4)	10,2
BPPO Id	67 (80)	19 (8)	7 (4)	7,2 (2,2)	5,8
BPPO IIa	65 (67)	33 (26)	0 (0)	1,5 (0.6)	6,0
BPPO IIb	59 (62)	34 (32)	6 (2)	1,5 (0,7)	3,0
DBDO	52 (48)	19 (27)	28 (25)	0,2 (0)	0,4

TABLE VII

Fractional formulation of thermal destruction products of mixtures of styrene plastics with high molecular weight fire retardants and antimony trioxide

Styrene plastic	Fire retardant	Unvolatile residue	High boiling destruction products	Low boiling destruction products
		wt. %		
HIPS	–	35	35	30
	BPPO-Ib	51 (56)	39 (27)	7 (17)
	BPPO IYa	36 (44)	50 (40)	12 (15)
	BPPO IYb	45 (40)	44 (43)	10 (17)
	BPS-68	40 (44)	32 (46)	27 (20)
	DBDO	54 (35)	33 (41)	12 (23)
ABS	–	61	25	14
	BPPO Ib	60 (70)	28 (19)	11 (10)
	BPPO Ib	60 (70)	28 (19)	11 (10)
	BPPO Ib	60 (70)	28 (19)	11 (10)
	BPPO IYa	60 (70)	32 (22)	7 (7)
	BPPO IYb	58 (67)	33 (25)	8 (7)
	BPS-68	53 (54)	41 (39)	5 (6)
	DBDO	65 (50)	24 (45)	10 (5)

[a] Data for the mixtures containing Sb_2O_3 are shown in brackets.

[b] In this fraction styrene content is equal to 97% for mixtures based on HIPS and 72% for mixtures based on ABS.

O with calculated curves built on TGA data for individual components where additive summary weight loss was allowed, showed that in the presence of BPPO Ib thermal stability of PS increased. Apart from BPPO IIa another BPPO exerts analogous influence on the thermal stability of PS. The analysis of thermal destruction products of the mixtures PS-BPPO and PS-BPPO-Sb_2O_3 showed that

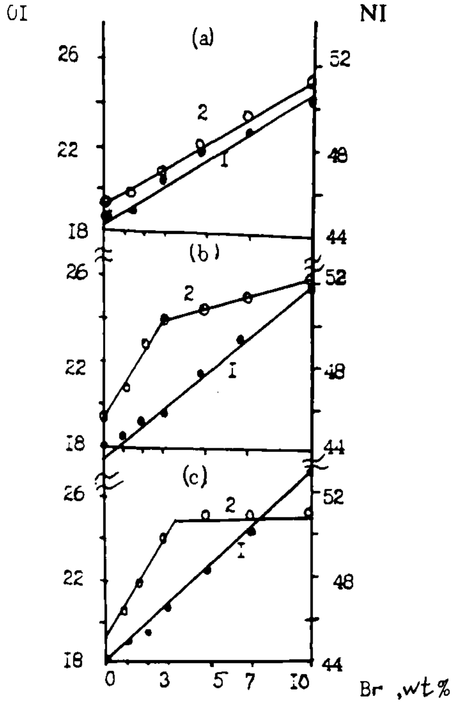


FIGURE 2 Dependence of OI (1) and NI (2) on bromine content in styrene plastics containing BPPO Ib. (a) ABS, (b) HIPS, (c) PS.

styrene, where it is the principle product of the thermal destruction of PS, was not generally formed or was formed in a much smaller quantity (the mixtures with BPPO Ic, d and BPPO IIb) in the presence of BPPO. The influence of BPPO on the styrene content in thermal destruction products of PS mixtures is exhibited even with a very small quantity of additive (Figure 1).

Based on these results, it can be concluded that thermal destruction products of BPPO inhibit the reaction of thermal depolymerization of PS, which is a major reaction of the thermal destruction process of PS. Thus the influence of BPPO on direct destructive processes in PS resulting in a significant decrease in the quantity of volatile combustible destruction product, i.e., fuel for the burning of PS evidently represents the added factor of the action of BPPOs as fire retardants. The higher effectiveness in PS rather than in LDPE is accorded with supposition about the inhibition of the depolymerization process as an additional factor of the action of BPPOs as fire retardants. In LDPE the mechanism of the action of BPPO is not basically different from that of DBDO inasmuch as the reaction of thermal depolymerization is not characteristic for this polymer, namely, this reaction can be inhibited by thermal destruction products of BPPO.

Oxygen index data for the mixtures PS with BPS and antimony trioxide are shown in Table V.

With the exception of BPS-45, the effectiveness of BPS is close to that of DBDO. In the case where BPSs are used as fire retardants, the burning is accompanied by formation of char as with BPPO. Apparently high molecular destruction products

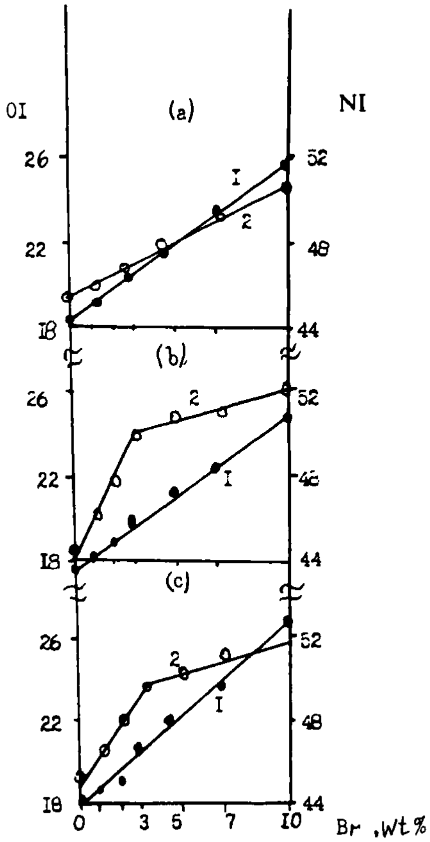


FIGURE 3 Dependence of OI (1) and NI (2) on bromine content in styrene plastics containing BPPO IYa. (a) ABS, (b) HIPS, (c) PS.

of BPS and BPPO participate in thermal cross-linking processes of PS macromolecules. The effectiveness BPS is lower than that of BPPO.

Data about formulation of destruction products of the PS mixture with high molecular weight fire retardants are presented in Table VI. It is shown that in the presence of BPS the quantity of styrene formed by pyrolysis is decreased to a level approximately the same as that in the presence of DBDO, while BPPO inhibits formation of styrene completely or reduces the yield of styrene to a significantly lower level compared to BPS and DBDO. Also, by pyrolysis of mixtures containing BPPO, HBr is formed ($SbBr_3$ where the mixture contains Sb_2O_3) on the somefold more than that by pyrolysis of the PS mixtures with BPS and DBDO. This means that the greater effectiveness of BPPO in PS is conditioned just as much by the essential influence of this group of fire retardants on the direct destruction processes in PS as a consequence of the significant decrease of volatile combustible destruction products, so that there is formation of larger quantities of gas-phase inhibitor of the burning.

It should be noted that the action of BPPO and BPS in PS is somewhat different from that in the styrene plastics HIPS and ABS. Therefore, the oxygen index data of the HIPS mixtures with different-by-type BPPO and BPS containing over 60%

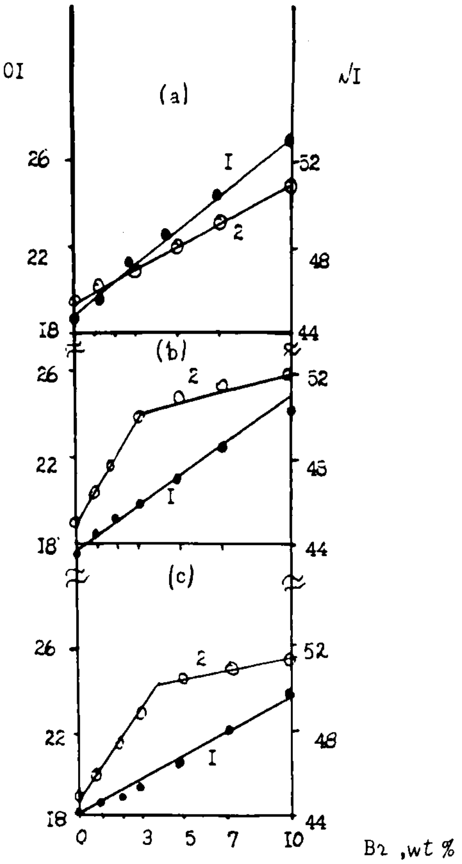


FIGURE 4 Dependence of OI (1) and NI (2) on bromine content in styrene plastics containing BPPO IYb. (a) ABS, (b) HIPS, (c) PS.

bromine equal 24–25, i.e., they do not depend on the structural peculiarity of high molecular weight fire retardants and are close to the OI of the HIPS mixture with DBDO.[3] The effectiveness of different-by-type BPPO is also nearly identical in ABS (OI = 25–26), the effectiveness of BPS is somewhat higher (OI = 27), but DBDO surpassed the high molecular weight fire retardants in effectiveness (OI = 28). These results agree with those on the influence of BPPO and BPS on the formulation of thermal destruction products HIPS and ABS. This influence on correlating Table VI and VII is lower than that on PS.

The results given above permit us to propose that relation of the factors controlling the action of high molecular weight fire retardants changes according to the type of styrene plastic. This proposal is supported by the character of dependence of the OI and NI (the limit of the burning on an oxidizer other than oxygen-nitrous oxide) against the bromine content in the mixtures of styrene plastics with fire retardants (Figures 2–6).

It is known that if the action of a fire retardant is controlled by the inhibition of the gas-phase process of the burning, then the inclination of a straight line expressing the dependence of the oxidizer limit on fire retardant concentration

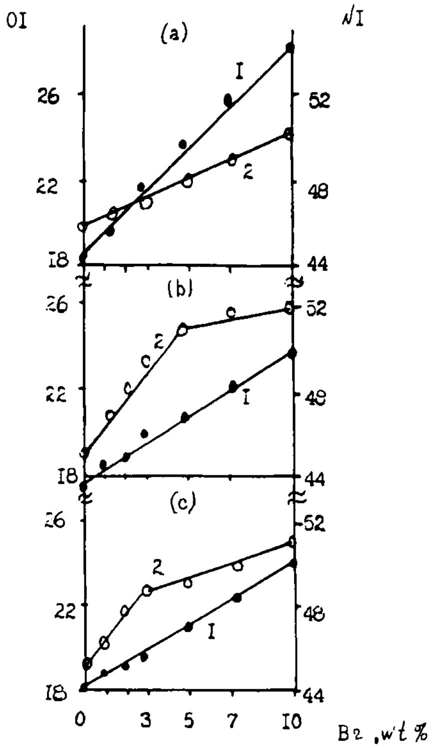


FIGURE 5 Dependence of OI (1) and NI (2) on bromine content in styrene plastics containing BPS-68. (a) ABS, (b) HIPS, (c) PS.

(tgα) will be greater during burning in oxygen than in nitrous oxide, while the inverse is observed for the action of fire retardants in the condensed phase.

The dependence of the OI and the NI on the concentration of high molecular weight fire retardants and DBDO is linear for the mixtures based on ABS, therefore taα is the same (the mixture with BPPO Ib) or more (the mixtures with BPPO IYa, BPPO IYb, BPS-68, DBDO) at burning in an atmosphere containing oxygen. Thus the action of BPPO, BPS and DBDO is mainly controlled by inhibition of the gas-phase burning in ABS.

The dependence of the NI on the concentration of fire retardants has a break at a bromine content of approximately 3% in the case of mixtures based on PS and HIPS with all investigated fire retardants, but the analogous dependence of the OI is linear. At burning in the atmosphere containing nitrogen tgα for the mixtures with a low concentration of fire retardants is higher than at burning in the atmosphere containing oxygen. However for mixtures with a high concentration of fire retardants the inverse is true.

Thus high molecular weight fire retardants and DBDO act basically in the condensed phase at low concentrations of PS and HIPS, but a gas-phase mechanism of inhibition predominates at high concentrations.

The results of this study allow us to conclude that the principle difference between the action of high molecular weight fire retardants and those of low molecular

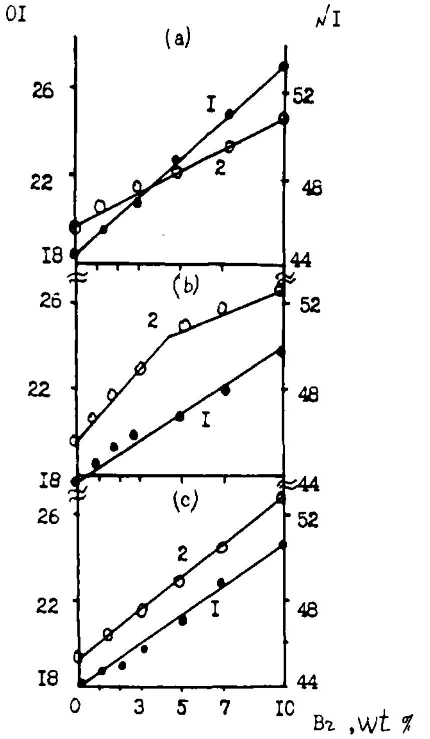


FIGURE 6 Dependence of OI (1) and NI (2) on bromine content in styrene plastics containing DBDO. (a) ABS, (b) HIPS, (c) PS.

weight is in their influence on the nature of processes of thermal destruction of polymers. This leads to changes in formation and quantity of volatile combustible destruction products. The degree of this influence depends on the character of the thermal destruction process of one or another polymer. This influence is exhibited to a greater degree in PS and therefore the effectiveness of high molecular weight fire retardants is greater compared to low molecular weight DBDO. On the contrary high molecular weight fire retardants have lesser influence on the thermal destruction of LDPE and ABS and their effectiveness is equal or lower compared to DBDO in these polymers.

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