

## Self-Extinguishing Polystyrene Foaming-in-Place Beads\*

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### Synopsis

The preparation of practical self-extinguishing polystyrene foaming-in-place compositions by suspension polymerization is described. The halogen necessary for self-extinguishing characteristics is incorporated by chain transfer. The synergistic effect of organic peroxides decreases drastically the amount of halogen necessary. For example, 0.3 pph 1,2-dibromotetrachloroethane in the presence of 0.2 pph dicumyl peroxide renders the composition self-extinguishing, while 1.0 pph is necessary without peroxide. The rate of polymerization is unaffected by the presence of this chain transfer agent, while the molecular weight is reduced considerably. The effectiveness of other halogenated chain transfer agents and peroxy compounds has been demonstrated. Silicone mold release agent exerts a deleterious effect on the self-extinguishing properties.

### I. INTRODUCTION

Polystyrene foam is an important commercial product used for construction materials, packaging, refrigeration and other thermal insulation applications, recreational items, buoyancy applications, and novelty and display items. This plastic foam can be prepared in two ways: (1) by extrusion of a molten gel comprised of polystyrene and a blowing agent, and (2) by pre-expansion and molding of polystyrene granules which contain the blowing agent. The extruded foam is produced in the form of logs or sheets which can be cut to the desired shape. The polystyrene granules (foaming-in-place beads) can be molded to a form of any desired intricacy.

For preparing polystyrene foaming-in-place beads in an aqueous dispersing medium, two basic methods can be used: The suspension polymerization of styrene in the presence of blowing agent<sup>1</sup>; and the impregnation of polystyrene granules with blowing agent. This paper concerns the suspension polymerization; the monomer containing suitable free radical initiators and the blowing agent (frequently technical *n*-pentane) is dispersed in water containing the suspending agent, and the mixture is heated to the polymerization temperature. After the polymerization is complete, the

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beads are recovered and screened to give the desired size fraction; for general-purpose molding, the size range usually used is 0.6–2.0 mm.

Many uses of polystyrene foam require that it be self-extinguishing, i.e., the burning foam extinguishes itself after the source of ignition is removed. It has long been known that polystyrene can be rendered self-extinguishing by the addition of halogen, e.g., by incorporating halogenated organic compounds into polystyrene during extrusion.<sup>2</sup> It has also been known for a long time that halogen can be incorporated into the polystyrene molecule by the chain transfer reaction of halogenated organic compounds, e.g., carbon tetrachloride.<sup>3</sup>

This paper shows that the chain transfer reaction can be used to incorporate sufficient halogen into the polymer to produce a practical self-extinguishing composition, provided the effectiveness of the halogen is enhanced by the use of a peroxide synergist.

## II. EXPERIMENTAL DETAILS

### A. Materials

The styrene used was the inhibitor-free plant grade (99.6%). The divinylbenzene was the inhibitor-free technical grade (55:45 divinylbenzene–ethylvinylbenzene). Both monomers were stored at  $-20^{\circ}\text{C}$ . prior to use. Technical benzoyl peroxide (Lucidol Division, Wallace and Tiernan Company) and dicumyl peroxide (Hercules Powder Company) were used. The *n*-pentane used was a purified grade (Commercial Solvents Corporation) which contained a few per cent of lower boiling hydrocarbons. The isooctane used was a commercial grade (Phillips Petroleum Company). The 1,2-dibromotetrachloroethane was recrystallized twice and was found to contain 49.1% bromine (theoretical 49.1%) and 42.7% chlorine (theoretical 43.5%). The other halogenated chain transfer agents were technical grade.

Deionized water was used for all experiments. The suspending agent was the sodium salt of partially sulfonated polyvinyltoluene<sup>4</sup>; it contained 23% active ingredient and 77% sodium sulfate. The potassium dichromate was reagent grade. The pH of the aqueous phase was adjusted to 6 with reagent grade sodium hydroxide.

The hydroquinone, methanol, and methyl ethyl ketone were the usual technical grades.

### B. Preparation of Foaming-in-Place Beads

The polymerizations were carried out in capped 12-oz. bottles under a nitrogen atmosphere. The water/oil phase ratio was 1.25. The bottles were shaken at room temperature to form a stable dispersion; they were then rotated end-over-end in a bath which was quickly heated to the polymerization temperature. After the polymerization was complete, the beads were filtered off, washed with water, and dried in air. The dried beads were screened to separate the 0.6–2.0 mm. size fraction which was used for molding.

The concentrations of active suspending agent and potassium dichromate were 0.035 and 0.05 pph, respectively, based on water.

### C. Preparation of Moldings<sup>5</sup>

The beads were pre-expanded at ca. 100°C. by steam to give a bulk density of ca. 2 lb./ft.<sup>3</sup>. The pre-expanded beads were dried in air for 16–24 hr. and used to fill the 10 × 10 × 1/4 in. cavity of a steam injection mold. Steam was applied to give a molding with an absolute density of ca. 2 lb./ft.<sup>3</sup>; the molding was cooled with water, removed from the mold, dried for 16–20 hr. at 60°C., and cut into 1/4 × 1 × 5 in. test strips.

### D. Self-Extinguishing Test

The test strips, positioned horizontally with the 1 in. side perpendicular, were ignited by a 1 in. microburner flame contacting the lower edge of one end of the strip; the flame was then removed, and the time required for the strip to extinguish itself was measured. The sample was considered self-extinguishing if the time was 2 sec. or less.

### E. Preparation and Recovery of Polymer at Intermediate Conversions

To determine the polymerization parameters as a function of time, individual samples containing 111 g. monomer phase were polymerized for various times and then removed from the bath. All samples except the final ones were shortstopped with ca. 0.1 g. hydroquinone which was added as a 5 or 10% solution in methyl ethyl ketone. The samples were cooled, and the monomer–polymer phase was separated. For all conversions up to ca. 65%, the monomer–polymer beads “creamed” upon standing, i.e., they came to the surface of the samples. In this layer, the clustered beads remained as discrete spheres until the aqueous phase was separated and the beads were washed with successive portions of deionized water; the washing evidently removed the suspending agent because the beads gradually coalesced to a homogeneous monomer–polymer layer, the viscosity of which was greater with increasing conversion. In a few cases, the monomer–polymer layer was separated from the aqueous phase by an emulsion layer; when the aqueous phase was separated, this emulsion layer was combined with the monomer–polymer phase. For the few samples of ca. 80% conversion, the beads creamed but did not coalesce upon washing; instead they formed a sticky, porous mass. For the samples polymerized to complete conversion, the beads sank to the bottom (except for a few which contained bubbles). After washing, the monomer–polymer phases, still containing some residual water, were diluted with methyl ethyl ketone to give 600–3000 g. solution; the amount of methyl ethyl ketone added was that necessary to form a homogeneous solution, i.e., without a separate water layer. Most of the solutions contained a few brown specks which were attributed to the hydroquinone; these were removed by filtration.

Before precipitation, all polymer solutions which contained more than 2.5% solids were diluted to this concentration with additional methyl ethyl

ketone. To precipitate the polymer, one part (by weight) of solution was poured into six parts of methanol. The precipitated polymer was filtered, washed with four 200 g. portions of methanol, and dried under vacuum for 68 hr. at 35°C. The samples were then weighed to determine the percent conversion. These samples were used for the molecular weight determinations. The polymer halogen contents were determined on a part of the foregoing sample which was dissolved and reprecipitated twice by the same procedure. In the text, this sample is designated as fraction A, whether it was precipitated once or thrice.

For some samples which contained chain transfer agent, the mother liquor from the first precipitation, combined with the methanol used for washing, was evaporated to dryness, first at room temperature in a hood and then at 50°C. under vacuum to constant weight (ca. one week). These samples, designated as fraction B, were analyzed for halogen content and, in some cases, for polystyrene.

### F. Analysis of Polymers

The polymer molecular weights were determined by a variety of methods: Intrinsic viscosity, 10% toluene solution viscosity, ultracentrifugation, boiling point elevation, and osmometry. The viscosity measurements were carried out at 25°C. in benzene or toluene solution using modified Ostwald viscometers. The intrinsic viscosities were determined by extrapolation of the triple reciprocal plot.<sup>6</sup> The values for the number-average molecular weight  $\bar{M}_n$  were calculated according to<sup>7</sup>:

$$[\eta]_{\text{benzene}} = 1.13 \times 10^{-4} \bar{M}_n^{0.73}$$

$$[\eta]_{\text{toluene}} = 1.34 \times 10^{-4} \bar{M}_n^{0.71}$$

Since the polymers were not fractionated, the measured intrinsic viscosities were divided by the factor  $\Gamma(\alpha + 2)$ ,<sup>8</sup> where  $\alpha$  is the exponent of  $\bar{M}_n$ , or 1.582 and 1.557 for the benzene and toluene measurements, respectively. The equivalence of the two equations is shown in this paper by the measurement of one sample in both solvents; the value of  $\bar{M}_n$  was 60,400 in benzene and 62,400 in toluene. The 10% toluene viscosity is a one-point determination; the values of  $\bar{M}_n$  were interpolated from a  $\bar{M}_n$ -10% toluene viscosity calibration curve determined from polymers prepared in this study.

The ultracentrifuge measurements were carried out in a Spinco Model E ultracentrifuge and analyzed by sedimentation velocity analysis.<sup>9</sup>

The boiling point elevation measurements<sup>10</sup> were carried out in methylcyclohexane solution; the boiling point elevation was determined as a function of increasing concentrations of polystyrene. The values of  $\bar{M}_n$  were calculated according to

$$\bar{M}_n = Kw/\Delta T$$

where  $w$  is the weight of polystyrene,  $\Delta T$ , the elevation of the boiling point due to the addition of polystyrene, and  $K$ , a constant characteristic of the

solute in a given solvent; the value of  $K$  was previously determined to be 2476. The values of  $\bar{M}_n$  were plotted against cumulative per cent polystyrene; this relationship was extrapolated to zero concentration to give the value of  $\bar{M}_n$  which was used.

The osmometry measurements were carried out in toluene solution with a Mechrolab high speed membrane osmometer, Model 501.<sup>11</sup> The osmotic pressure was determined as a function of polystyrene concentration. The reduced osmotic pressure was plotted against concentration, and the straight line formed was extrapolated to zero concentration. The values of  $\bar{M}_n$  were calculated according to

$$\bar{M}_n = RT(\pi/c)_0$$

where  $R$  is the gas constant,  $T$ , the temperature, and  $(\pi/c)_0$ , the reduced osmotic pressure at zero concentration.

### III. EXPERIMENTAL RESULTS AND DISCUSSION

#### A. Self-Extinguishing Compositions

Many halogenated organic compounds were evaluated as chain transfer agents by adding them to the styrene monomer, carrying out the suspension polymerization to high conversion, and then comparing the polymer solution viscosity (10% in toluene) with that of samples prepared without the halogenated compound. The monomer phase of the polymerization contained 0.20–0.43 pph benzoyl peroxide, 0.00–0.50 pph dicumyl peroxide, 0.00–0.08 pph divinylbenzene, and 7.67 pph *n*-pentane; the polymerization schedule was 11 hr. at 90°C. followed by 5 hr. at 103°C. Some of these compounds, arranged in order of their increasing effect on the polymer solution viscosity, are: 1,2,3-tribromobutane; 1,2,3,4-tetrabromobutane; pentabromomonochlorocyclohexane; hexabromocyclohexane; 1,2-dibromotetrachloroethane; 1,1,2,2-tetrabromoethane; pentabromoethane; and carbon tetrabromide. These results were obtained from comparable polymerization recipes; therefore, if it is assumed that these compounds function as chain transfer agents in the classical sense, this order would be one of increasing chain transfer activity. The numerical values of the chain transfer constants of these compounds cannot be derived from these data, however, primarily because of the high conversion of the polymer samples.

After many tests, it was observed that an unexpectedly small concentration of chain transfer agent was sufficient to render the polystyrene foam self-extinguishing. For example, a composition prepared from a recipe containing 0.20 pph 1,1,2,2-tetrabromoethane, 0.43 pph benzoyl peroxide and 0.20 pph dicumyl peroxide was self-extinguishing, while the same halogenated compound in a concentration of 1 pph was ineffective when added to polystyrene. It was shown at Dow<sup>12</sup> that a synergistic correlation exists between the organic peroxide and the halogen concentrations in the composition. From the peroxide decomposition rates measured in benzene solution,<sup>13</sup> all of the benzoyl peroxide but only a small part of the dicumyl

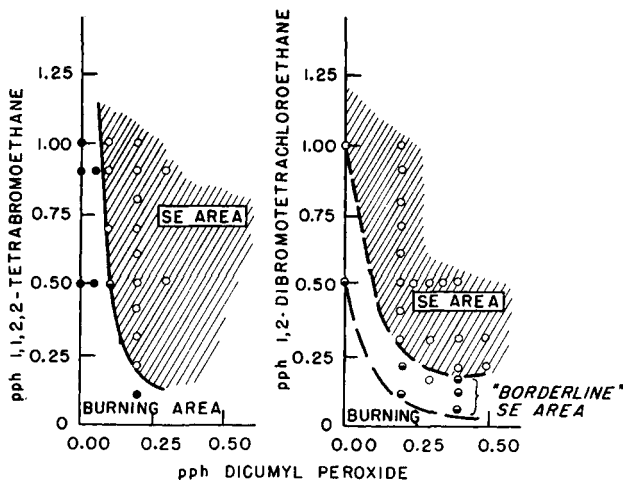


Fig. 1. Variation of self-extinguishing characteristics with the concentrations of chain transfer agent and dicumyl peroxide.

peroxide is decomposed during the polymerization; the half-life of dicumyl peroxide is 80 hr. at 103°C. Thus the polystyrene is rendered self-extinguishing by the synergistic action of the residual peroxide on the halogen incorporated into the polymer by chain transfer.

This synergistic effect is shown for 1,1,2,2-tetrabromoethane and 1,2-dibromotetrachloroethane in Figure 1; the polymerization recipe contained 0.43 pph benzoyl peroxide and 7.67 pph *n*-pentane; the polymerization schedule was 11 hr. at 90°C. followed by 5 hr. at 103°C. For the 1,1,2,2-tetrabromoethane, without dicumyl peroxide, compositions containing 1 pph burned, while with 0.20 pph dicumyl peroxide, compositions containing only 0.20 pph were self-extinguishing. For the 1,2-dibromotetrachloroethane, without dicumyl peroxide, 1.00 pph was necessary to confer self-extinguishing characteristics, while with 0.20 pph dicumyl peroxide, 0.30 pph was sufficient. In general, the residual peroxide reduces the amount of halogen necessary to about one-third that necessary without the peroxide.

There is an upper limit to the concentration of dicumyl peroxide synergist which may be used successfully. Table I gives the results for samples prepared with 2–5 pph dicumyl peroxide; the residual peroxide concentration is calculated<sup>13</sup> to be 93% of the amount originally charged. It can be seen that samples prepared with 5 pph dicumyl peroxide and 0.5 pph 1,1,2,2-tetrabromoethane or 1,2-dibromotetrachloroethane burned, whereas samples prepared with only 2 or 3 pph dicumyl peroxide were self-extinguishing. These data show that the combustion-promoting effect expected from peroxides prevails at the higher peroxide concentrations; this effect can be offset to a certain extent by an increased amount of halogen.

In general, any organic peroxy compound may be used in place of the dicumyl peroxide; however, those with more rapid decomposition rates are frequently decomposed so completely during the polymerization that the

residual concentration is insufficient to confer self-extinguishing characteristics. Table II shows the results for several peroxy compounds which have been substituted successfully for the dicumyl peroxide. The calculated concentration of residual peroxy compound<sup>13</sup> is given along with the average self-extinguishing times of 4–7 specimens. In general, the average self-extinguishing times decreased with increasing concentration of peroxy compound. The values of the product moment correlation coefficient  $r$  calculated from the individual self-extinguishing times are given in the last column. Except for the di-*tert*-butyl peroxide, these correlation coefficients are significant, i.e., the probability  $P$  that this correlation could have occurred by chance is <5%. The correlation coefficient for di-*tert*-butyl

TABLE I  
Variation of Self-Extinguishing Characteristics with Higher Dicumyl Peroxide Concentrations\*

Dicumyl peroxide, pph	1,1,2,2-Tetra-bromoethane, pph	1,2-Dibromo-tetrachloro-ethane, pph	Self-extinguishing times, sec.	
			Individual	Average
2.0	0.5	—	1,1,1,1,1,1	1.0
3.0	0.5	—	1,1,1,1,1,1	1.0
5.0	0.5	—	1,6,>20,2,>20,>20	Burns
2.0	1.0	—	1,1,1,1,1,1	1.0
3.0	1.0	—	1,1,1,1,1,1	1.0
5.0	1.0	—	2,1,1,1,1,1	1.2
2.0	—	0.5	1,1,1,1,1,1	1.0
3.0	—	0.5	2,2,1,2,1,2	1.7
5.0	—	0.5	>20,>20,>20,>20,6,>20	Burns
2.0	—	1.0	1,1,1,1,1,1	1.0
3.0	—	1.0	1,2,1,1,1,1	1.2
5.0	—	1.0	10,2,1,3,1,1	3.0

\* 0.43 pph benzoyl peroxide; 0.08 pph divinylbenzene; 7.7 pph *n*-pentane; 15 hr. at 90°C. and 5 hr. at 103°C.

peroxide ( $-0.29$ ) is not significant; in this case, the individual self-extinguishing times showed considerable scatter, e.g., for 0.3 pph di-*tert*-butyl peroxide, the average time was 3.0 sec., but the individual values ranged from 1 to 8 sec. It can be seen from the calculated concentrations of residual peroxy compound that dicumyl peroxide is the most effective of these synergists. The lesser effectiveness of the hydroperoxides may be attributed to their greater sensitivity to acid-catalyzed decomposition, e.g., by hydrogen bromide.<sup>14</sup> In addition, the decomposition rate of cumene hydroperoxide has been shown to be ca. 30-fold greater in bulk styrene than in benzene;<sup>15</sup> moreover, an additional 10-fold increase has been observed for styrene in emulsion.<sup>16</sup> This was attributed to decomposition occurring at the styrene-water interface. Using these latter data, the calculated residual cumene hydroperoxide concentration is  $0.64\text{--}2.2 \times 10^{-3}$  moles/100 g. styrene as compared to the  $1.3\text{--}4.6 \times 10^{-3}$  range shown in Table II.

TABLE II  
 Synergistic Effect of Peroxy Compounds<sup>a</sup>

Peroxyl compound charged		pph	Half-life, hr.	Calculated residual peroxy compound, moles/100 g. styrene × 10 <sup>3</sup>	Average self-extinguishing time, sec.	<i>r</i>
Conditions	Type					
A <sup>b</sup>	<i>tert</i> -Butyl peracetate	0.2	370(75°C.)	1.3	3.2	-0.75
		0.5		3.2	2.3	
		1.0		6.4	1.5	
A <sup>b</sup>	<i>tert</i> -Butyl perbenzoate	0.2	560(75°C.)	0.92	2.5	-0.77
		0.5		2.3	2.3	
		1.0		4.6	1.0	
B <sup>c</sup>	Dicumyl peroxide	0.2	500(90°C.)	0.70	1.0	—
B <sup>c</sup>	Di- <i>tert</i> -butyl peroxide	0.2	840(90°C.)	1.3	2.0	-0.29
		0.3		2.0	3.0	
		0.5		3.3	2.4	
		0.7		4.6	1.8	
		1.0		6.6	1.2	
B <sup>c</sup>	<i>p</i> -Menthane hydroperoxide	0.2	720(90°C.)	1.1	5.8	-0.61
		0.3		1.7	4.8	
		0.5		2.8	1.8	
		0.7		3.9	1.5	
B <sup>c</sup>	Pinane hydroperoxide	0.2	1800(90°C.)	1.2	13.2	-0.57
		0.3		1.7	4.8	
		0.5		2.9	3.0	
		0.7		4.1	3.0	
B <sup>c</sup>	Cumene hydroperoxide	0.2	7000(90°C.)	1.3	5.2	-0.61
		0.3		2.0	3.5	
		0.5		3.3	2.5	
		0.7		4.6	1.3	

<sup>a</sup> 0.50 pph 1,2-dibromotetrachloroethane; 7.67 pph *n*-pentane.

<sup>b</sup> 0.40 pph benzoyl peroxide; 48 hr. at 75°C. and 5 hr. at 90°C.

<sup>c</sup> 0.43 pph benzoyl peroxide; 0.08 pph divinylbenzene; 11 hr. at 90°C. and 5 hr. at 10<sup>3</sup> °C.



## B. The Reaction of 1,2-Dibromotetrachloroethane

That these self-extinguishing properties are the result of halogen incorporated into the polymer by chain transfer is shown for 1,2-dibromotetrachloroethane by the following set of experiments. Samples containing 0–2.00 pph 1,2-dibromotetrachloroethane were polymerized for 2 hr. at 90°C. to a conversion of 20–25%; the blowing agent was omitted, and the initiator was 0.20 pph benzoyl peroxide. Table III gives the values of  $\bar{M}_n$  determined from intrinsic viscosities and of  $\bar{M}_w$  and  $\bar{M}_n$  determined by ultracentrifugation. In general, the values of  $\bar{M}_n$  for the two methods are in good agreement. The values of  $\bar{M}_n$  and  $\bar{M}_w$  decreased consistently with increasing concentration of 1,2-dibromotetrachloroethane. The ratio  $\bar{M}_w/\bar{M}_n$  decreased slightly with increasing concentration of 1,2-dibromotetrachloroethane.

Figure 2 shows the molecular weight distribution curves for some of the foregoing samples. The decrease in average molecular weight with increasing concentration of 1,2-dibromotetrachloroethane can readily be seen. At first glance, it would appear that the variation of  $\bar{M}_w/\bar{M}_n$  should be greater than that actually found (see Table III); this misapprehension can be attributed to the great sensitivity of the ratio  $\bar{M}_w/\bar{M}_n$  to the amount of very low molecular weight polymer, which is not delineated accurately in Figure 2 because of the scale used.

Table IV gives the halogen content of these samples. As expected, the halogen content increased with increasing concentration of 1,2-dibromotetrachloroethane. The bromine/chlorine ratio decreased from 1.7<sub>0</sub> to 1.3<sub>1</sub> with increasing concentration of 1,2-dibromotetrachloroethane, but did not reach the theoretical value of 1.13. Obviously some of chlorine is lost during the polymerization.

In another set of experiments, individual samples containing 0.50 pph 1,2-dibromotetrachloroethane, 0.20 pph benzoyl peroxide, and 0.20 pph dicumyl peroxide were polymerized to different conversions. For comparison, similar polymerizations were carried out omitting the 1,2-dibromotetrachloroethane. The total polymerization schedule was 11 hr. at 90°C. followed by 5 hr. at 103°C. The *n*-pentane commonly used in foaming-in-place compositions was replaced by isooctane (7.67 pph) which is less volatile and, therefore, more convenient to use in this type of experiment. Figure 3 shows the variation of per cent conversion with time for samples prepared with and without chain transfer agent. The data shown in Figure 3 are those determined from the amount of polymer recovered by precipitation (fraction A). For some samples, with and without chain transfer agent, the conversions were also determined by gravimetric solids analyses. A comparison of the two methods (Table V) shows that the agreement is reasonably good; at all but the lowest conversions, the gravimetric solids analyses gave slightly higher values than those determined from the recovery of the polymer; when the latter values (fraction A) were corrected by the amount of fraction B, the results were still slightly lower at all conversions greater than ca. 20%. In Figure 3, the points for all the samples,

TABLE III  
 Variation of Polymer Molecular Weight with 1,2-Dibromotetrachloroethane Concentration

1,2-Dibromotetrachloroethane, pph	Intrinsic viscosity		Ultracentrifugation		$\bar{M}_w/\bar{M}_n$
	$[\eta]$	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	
—	0.554	6.07	—	—	—
—	0.553	6.05	12.3	5.44	2.26
0.25	0.439	4.41	8.75	4.08	2.14
0.50	0.383	3.65	—	—	—
0.75	0.348	3.20	7.62	3.25	2.34
1.00	0.320	2.86	5.91	2.90	2.04
1.50	0.294	2.54	5.74	2.82	2.04
2.00	0.254	2.09	3.81	1.99	1.91

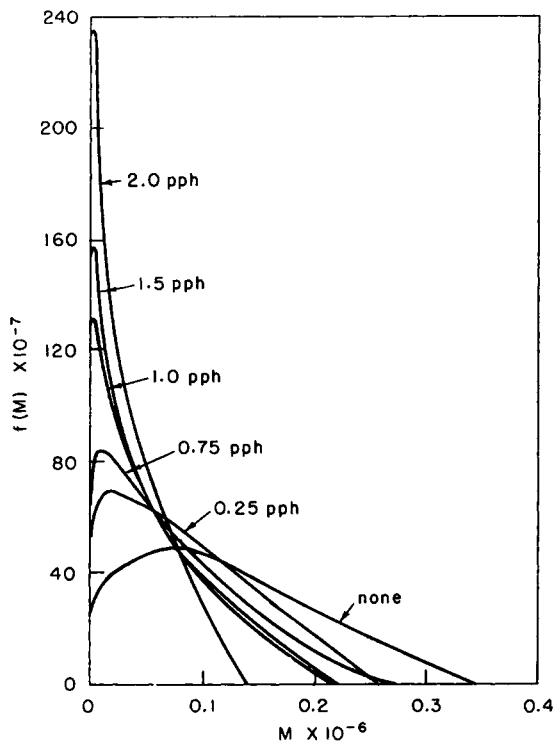


Fig. 2. Variation of molecular weight distribution at 20–25% conversion with 1,2-dibromotetrachloroethane concentration.

with and without chain transfer agent, fall on the same line for all times up to ca. 7 hr.; thus the 1,2-dibromotetrachloroethane acts as an “ideal” chain transfer agent, i.e., it alters the molecular weight of the polymer without affecting the polymerization rate. At times greater than 7 hr., the points diverge slightly, i.e., the samples without chain transfer agent display a slightly higher conversion. This discrepancy may be attributed to the effect of the chain transfer agent on the polymer molecular weight; the onset of the Trommsdorff effect (gel effect) with its accelerative effect on the polymerization rate would be expected to occur at a higher conversion in the less viscous medium. The polymerization rate, initially ca. 16%/hr., decreased with increasing time to ca. 7%/hr. at 5 hr.

Figure 4 shows the molecular weight data for the samples prepared with and without 1,2-dibromotetrachloroethane. The values of  $\bar{M}_n$  were calculated from the intrinsic viscosities, and some from ultracentrifugation, boiling point elevation, and osmotic pressure. The boiling point elevation method is applicable to molecular weights up to ca. 12,000, and the osmotic pressure method to ca. 30,000 or greater. Both of these methods measure  $\bar{M}_n$  directly and can be used to check the values calculated from the viscosity measurements. In the range 12,000–30,000, both methods have been used in the past with varying degree of success; several samples of Figure

TABLE IV  
Variation of Polymer Halogen Content with 1,2-Dibromotetrachloroethane  
Concentration

1,2-Dibromotetra- chloroethane, pph	Br, %	Cl, %	% Br/% Cl
0.25	0.22	0.13	1.6 <sub>9</sub>
0.50	0.39	0.23	1.7 <sub>0</sub>
0.75	0.49	0.31	1.5 <sub>8</sub>
1.00	0.58	0.40	1.4 <sub>5</sub>
1.50	0.73	0.54	1.3 <sub>5</sub>
2.00	0.84	0.64	1.3 <sub>1</sub>

4 fall within this range. For the samples prepared without 1,2-dibromotetrachloroethane, the values of  $\bar{M}_n$  are relatively constant up to ca. 30% conversion and then increase at an accelerating rate up to ca. 80% conversion. This sharp rise may be attributed to two factors: (1) the rapid decrease in initiator concentration—at 90°C., the half-life of benzoyl peroxide is only 80 min.,<sup>13</sup> and the concentration remaining undecomposed after 11 hr. is calculated to be only ca. 0.03% of that initially charged; and (2) the Trommsdorf effect according to which the termination reaction becomes diffusion-controlled when the viscosity of the polymerization medium is great. For the samples prepared with 1,2-dibromotetrachloroethane, the values of  $\bar{M}_n$  increase almost linearly up to ca. 50% conversion and then level off at higher conversions. The lowering of the molecular weight due to the chain transfer agent is greatest at the lowest conversions and decreases with increasing conversion. In this case, the effect of the rapidly-decreasing initiator concentration should be the same, but the Trommsdorf effect should be modified somewhat by the lower viscosity of the polymerization medium arising from the smaller values of  $\bar{M}_n$ . A comparison of the

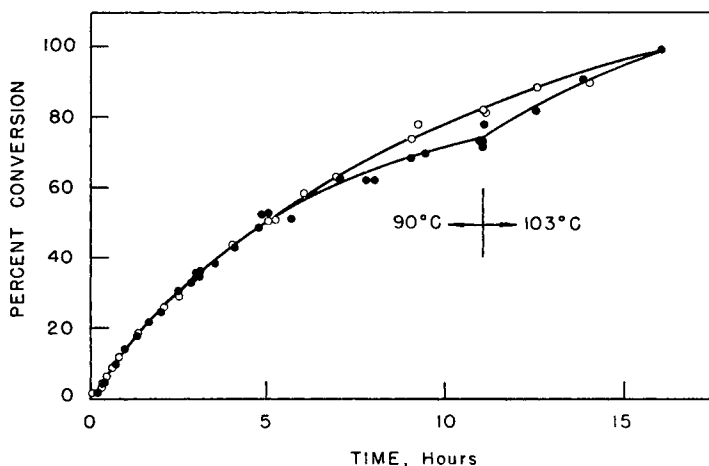


Fig. 3. Variation of per cent conversion with time: (●) 0.50 pph 1,2-dibromotetrachloroethane; (○) without 1,2-dibromotetrachloroethane.

TABLE V  
Comparison of Conversion Data Determined from Gravimetric Solids and the Amount  
of Polymer Recovered

Time, hr.	Conversion, %			Gravimetric solids
	Fraction A	Fraction B	A + B	
With 0.50 pph 1,2-dibromotetrachloroethane				
0.25	0.91	2.35	3.26	0.71
0.50	4.62	0.93	5.55	4.93
0.75	9.33	1.14	10.5	9.92
1.00	13.5	0.91	14.4	12.9
1.33	17.7	1.05	18.8	18.5
1.66	21.5	0.99	22.5	23.4
2.00	24.7	0.88	25.6	26.8
2.50	30.5	0.98	31.5	32.7
3.00	33.9	1.05	34.9	36.7
3.50	38.1	1.06	39.2	40.9
4.08	43.2	1.10	44.3	47.3
4.75	48.8	1.11	50.0	50.6
5.66	51.5	1.09	52.6	57.0
8.00	62.6	1.26	63.9	66.6
11.00	77.9	1.14	79.0	81.6
16.00	(100)	1.10	—	(100)
Without 1,2-dibromotetrachloroethane				
0.17	1.63	—	—	0.29
0.25	1.79	—	—	1.61
0.33	2.95	—	—	3.00
0.42	4.31	—	—	4.40
0.50	6.06	—	—	6.17
0.67	8.43	—	—	8.77
0.83	11.5	—	—	11.9
1.00	13.6	—	—	14.2
1.33	18.3	—	—	18.8
1.67	21.5	—	—	23.1
2.00	26.0	—	—	26.7
2.50	28.7	—	—	32.2
3.00	35.7	—	—	37.4
4.00	43.7	—	—	45.0
5.00	50.5	—	—	52.5
6.00	58.5	—	—	58.9
7.00	62.4	—	—	66.0
9.00	73.9	—	—	75.9
11.00	82.6	—	—	86.1
16.00	(100)	—	—	(100)

values of  $\bar{M}_n$  determined from the viscosity measurements with those determined from the boiling point elevation and the osmotic pressure shows that, for the samples prepared without 1,2-dibromotetrachloroethane, the osmotic pressure values are larger except for the point at 82.6% conversion, while, for the samples prepared with 1,2-dibromotetrachloroethane, the boiling point elevation and osmotic pressure values are smaller except for the point at 4.6% conversion. A possible explanation for this discrepancy

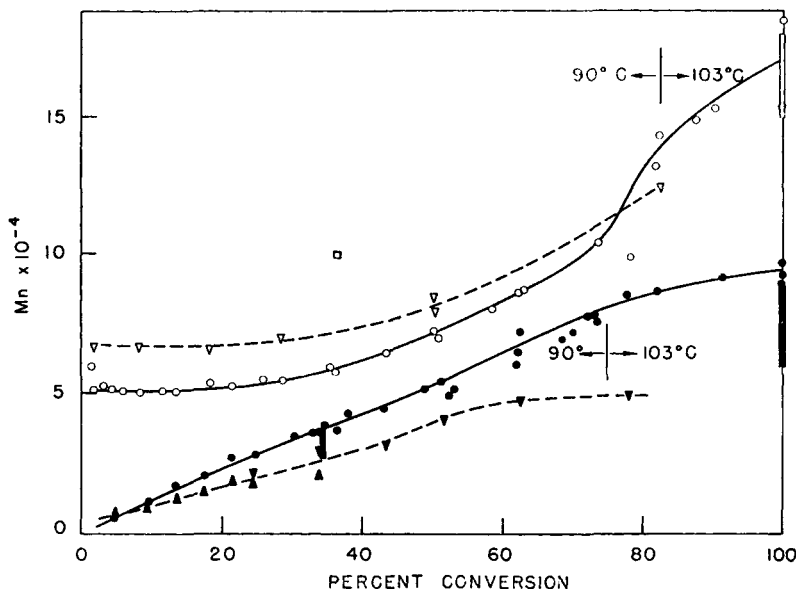


Fig. 4. Variation of  $\bar{M}_n$  with per cent conversion: with 0.50 pph 1,2-dibromotetrachloroethane, (●) from intrinsic viscosity, (▲) from boiling point elevation, (▼) from osmotic pressure, (■) from ultracentrifugation; without 1,2-dibromotetrachloroethane, (○) from intrinsic viscosity, (▽) from osmotic pressure, (□) from ultracentrifugation.

is as follows. Let us assume that the boiling point elevation and osmotic pressure methods yield a more accurate value for  $\bar{M}_n$ . Then the calculation of  $\bar{M}_n$  from the viscosity measurements must be evaluated critically. Many of the samples of this investigation are of lower molecular weight than those used to determine the  $\bar{M}_n$ - $[\eta]$  calibration equation.<sup>7</sup> In addition, the correction factor applied to the measured intrinsic viscosities was calculated assuming  $\bar{M}_w/\bar{M}_n = 2$ . (It should be emphasized that the omission of this correction factor results in discrepancies which are much greater.) The validity of this assumption may be assessed from the available ultracentrifugation data shown in Figure 4. For the samples prepared without 1,2-dibromotetrachloroethane,  $\bar{M}_w/\bar{M}_n$  is 1.47 at 36% conversion and 2.6–3.1 at 100% conversion; for the samples prepared with 1,2-dibromotetrachloroethane,  $\bar{M}_w/\bar{M}_n$  is 2.3–3.1 at 35% conversion and 2.2–3.4 at 100% conversion. Thus, in the general region where  $\bar{M}_w/\bar{M}_n$  is smaller than 2, the viscosity values of  $\bar{M}_n$  are smaller than the osmotic pressure values, and, where  $\bar{M}_w/\bar{M}_n$  is greater than 2, the viscosity values of  $\bar{M}_n$  are larger than the boiling point elevation and osmotic pressure values. This explanation is supported by the data given in Table III; here  $\bar{M}_w/\bar{M}_n$  is ca. 2, and the agreement between the values of  $\bar{M}_n$  determined from intrinsic viscosities and ultracentrifugation is good.

Figure 5 shows the effect of 0.50 pph 1,2-dibromotetrachloroethane on the molecular weight distribution curves determined by ultracentrifugation for the samples at ca. 35 and 100% conversion. The broadening of the

molecular weight distribution with increasing conversion is greater for the samples without chain transfer agent.

Figure 6 shows the variation of halogen content with per cent conversion for the polymer samples recovered by precipitation (fraction A). The halogen content is relatively great at ca. 1% conversion, but decreases progressively with increasing conversion to approach limiting values of ca. 0.16% bromine and ca. 0.11% chlorine. The variation of the bromine/chlorine ratio is also shown in Figure 6: at ca. 1% conversion, this ratio is high, ca. 2.5, but decreases rapidly with increasing conversion to approach a relatively constant value of 1.3–1.6 at ca. 20% conversion. This limiting value is greater than the theoretical value of 1.13 (dashed line in Figure 7) calculated for 1,2-dibromotetrachloroethane, which indicates that some chlorine is lost during the polymerization reaction.

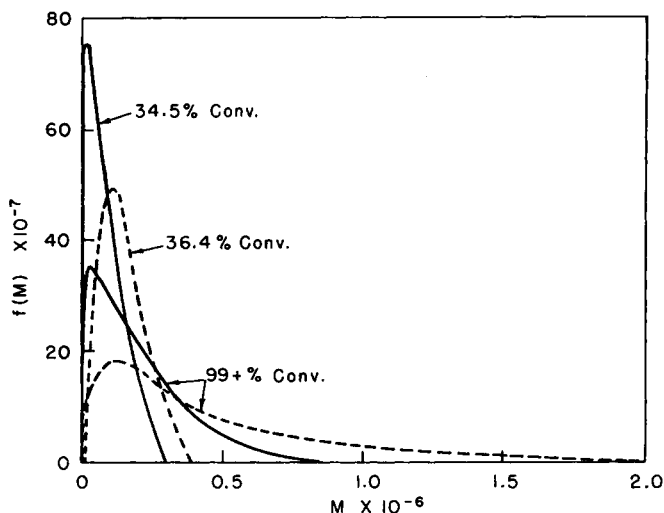


Fig. 5. Molecular weight distributions at ca. 35 and 100% conversion: (—) 0.50 pph 1,2-dibromotetrachloroethane; (---) without 1,2-dibromotetrachloroethane.

Figure 7 shows the variation of halogen content with per cent conversion for fraction B. The values are considerably greater than those of fraction A. Although the experimental points are scattered, the decrease in halogen content with increasing per cent conversion is statistically significant; the values of  $r$  for the bromine and chlorine contents are  $-0.77$  ( $P < 1\%$ ) and  $-0.53$  ( $P < 5\%$ ). The solid lines shown in Figure 7 are the calculated linear regression equations:  $\% \text{ Br} = 3.66 - 0.0168 (\% \text{ conversion})$  and  $\% \text{ Cl} = 2.79 - 0.00662 (\% \text{ conversion})$ . The values for the bromine/chlorine ratio were more consistent than the halogen contents, decreasing from ca. 1.6 at 4.6% conversion to approach a limiting value of ca. 1 at high conversions. Their agreement with the theoretical value of 1.13 (dashed line) calculated for 1,2-dibromotetrachloroethane is much better than for fraction A.

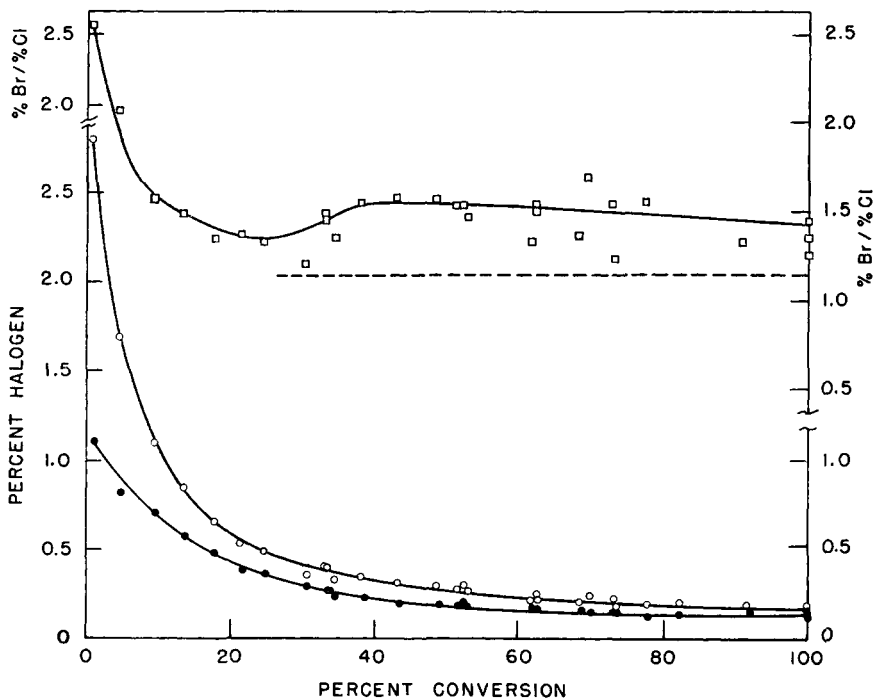


Fig. 6. Variation of halogen content and bromine/chlorine ratio with per cent conversion for fraction A: (O) Br, %; (●) Cl, %; (□) % Br/%Cl.

TABLE VI  
Variation of Halogen Content with Per Cent Conversion for Fractions A and B  
(Weight Based on Initial 100 g. Styrene)

Time, hr.	Fraction A				Fraction B			
	Wt., g.	Br, %	Cl, %	% Br/ % Cl	Wt., g.	Br, %	Cl, %	% Br/ % Cl
0.25	0.91	2.8	1.1	2.5 <sub>5</sub>	2.35	—	—	—
0.50	4.62	1.7	0.82	2.0 <sub>7</sub>	0.93	3.3	2.1	1.5 <sub>8</sub>
0.75	9.33	1.1	0.70	1.5 <sub>7</sub>	1.14	3.5	2.4	1.4 <sub>8</sub>
1.00	13.5	0.85	0.57	1.4 <sub>9</sub>	0.91	3.9	2.9	1.3 <sub>3</sub>
1.33	17.7	0.65	0.48	1.3 <sub>6</sub>	1.05	3.3	2.5	1.3 <sub>2</sub>
1.66	21.5	0.53	0.39	1.3 <sub>6</sub>	0.99	3.5	2.6	1.3 <sub>3</sub>
2.00	24.7	0.48	0.36	1.3 <sub>3</sub>	0.88	3.2	2.8	1.1 <sub>3</sub>
2.50	30.5	0.35	0.29	1.2 <sub>1</sub>	0.98	3.2	2.8	1.1 <sub>1</sub>
3.00	33.9	0.39	0.27	1.4 <sub>4</sub>	1.05	3.0	2.7	1.1 <sub>4</sub>
3.50	38.1	0.34	0.22	1.5 <sub>6</sub>	1.06	3.5	2.9	1.2 <sub>1</sub>
4.08	43.2	0.30	0.19	1.5 <sub>8</sub>	1.10	2.9	2.6	1.1 <sub>0</sub>
4.75	48.8	0.28	0.18	1.5 <sub>6</sub>	1.11	2.3	2.6	0.91 <sub>4</sub>
5.66	51.5	0.26	0.17	1.5 <sub>3</sub>	1.09	2.7	2.3	1.1 <sub>6</sub>
8.00	62.6	0.21	0.14	1.5 <sub>0</sub>	1.26	2.2	2.3	0.97 <sub>0</sub>
11.00	77.9	0.17	0.11	1.5 <sub>5</sub>	1.14	3.0	2.8	1.0 <sub>6</sub>
16.00	99. +	0.13	0.09	1.4 <sub>4</sub>	1.10	1.7	1.7	1.0 <sub>0</sub>



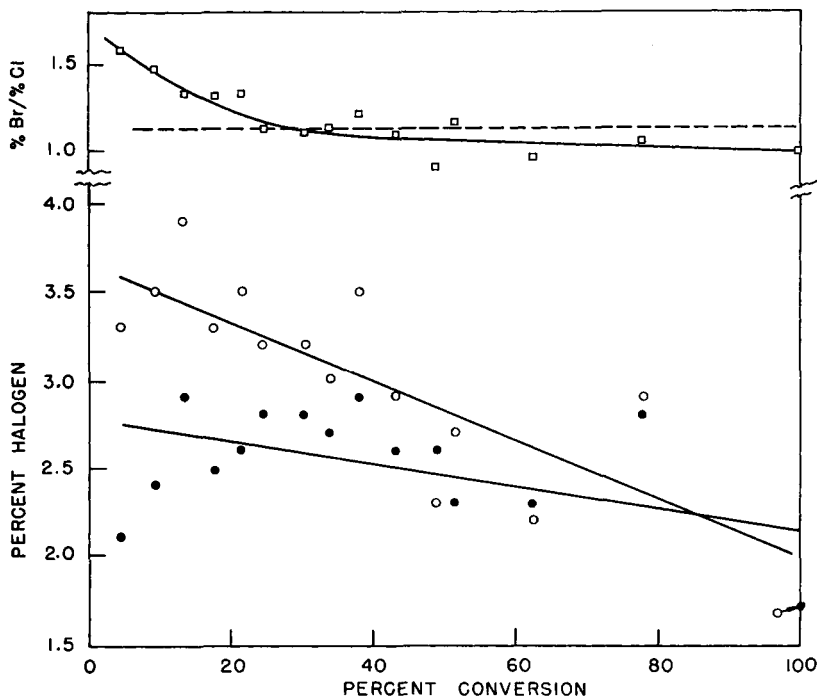


Fig. 7. Variation of halogen content and bromine/chlorine ratio with per cent conversion for fraction B: (O) Br, %; (●) Cl, %; (□) % Br/% Cl.

Table VI summarizes the halogen contents and relative weights of fractions A (original precipitate) and B (from the mother liquor) for some samples. For fraction A, the halogen contents are the same as shown in Figure 6, and the weights are equivalent to the values of Figure 3. For fraction B, the weight was relatively constant at ca. 1 gram except for the first sample (0.25 hr.) which amounted to 2.35 g. Infrared analysis showed that the first sample (0.25 hr.) contained ca. 30% polystyrene, while the next seven (0.50–2.50 hr.) contained 70–80%. Thus the amount of polystyrene recovered from the mother liquor was a relatively constant 0.7–0.8 g. This implies that the loss of polymer during the precipitation process is more dependent upon the relative proportions of polystyrene, methyl ethyl ketone solvent, and methanol precipitant than upon the average molecular weight and the molecular weight distribution. The infrared analyses showed no evidence for the presence of styrene monomer, dimer, trimer, or tetramer, dicumyl peroxide or its derivatives, unreacted 1,2-dibromotetrachloroethane, hydroquinone, or methyl ethyl ketone. These compounds, if present initially, were probably removed during the prolonged vacuum treatment (ca. one week at 50°C.) which was necessary to dry the samples to constant weight.

The foregoing experiments were carried out to determine the chain transfer constant of 1,2-dibromotetrachloroethane; indeed, in an earlier report,<sup>17</sup>

values for the chain transfer constant were given. Later, however, it was learned that the correct elemental analyses of the sample of 1,2-dibromotetrachloroethane used, which were regarded as indicative of its purity, were actually not representative of a pure sample. Rather, the sample contained some halogenated analogs of 1,2-dibromotetrachloroethane, fortuitously combined in such proportions that the elemental analyses agreed well with those calculated for the pure compound. Therefore, it is our intent to submit new results on the chain transfer reaction of this compound at a later time, rather than describing our present results and conclusions as to the possible reaction mechanism. However, the foregoing experiments which used the impure sample of 1,2-dibromotetrachloroethane are cited to illustrate that chain transfer does occur as evidenced by the decrease of the polymer molecular weight and the chemical combination of halogen into the polymer chain.

### C. The Deleterious Effects of Finely-Divided Solids

The self-extinguishing characteristics of these compositions are damaged by the presence of very small concentrations of certain substances, e.g., the silicone resins used in mold release agents. The concentration of silicone resin (e.g., polydimethylsiloxane) necessary to make these self-extinguishing compositions burn is not known accurately, but it must be very small, e.g., when a mold is sprayed with silicone mold release, the first molding burns, and 5-7 successive moldings must be made without further spraying before the self-extinguishing characteristics of the composition are realized. Apparently the small amount of silicone resin which is picked up by the molding is sufficient to destroy the self-extinguishing characteristics completely. This is a surface effect; test strips cut from the surface of the molding burn, while those from the interior are self-extinguishing. The combustion of silicone resin produces silicon dioxide. The adventitious distribution of mold release agent over the molding surface would be expected to give, upon combustion, an extremely fine dispersion of silicon dioxide. This silicon dioxide was believed to be the cause of the deleterious effect. Therefore, finely divided silicon dioxide was sprinkled on a test strip cut from the interior of a self-extinguishing molding; the excess was blown off with compressed air. It was found that silicon dioxide applied in this manner was as effective as the silicone mold release agent. Other substances, e.g., diatomaceous earth and cigarette ash, were judged less effective but still severely impaired the self-extinguishing characteristics of the foam. A third group of compounds comprising magnesium oxide, zinc oxide, nickel sesquioxide, cobaltic oxide, as well as floor dust, were also found to be effective, but to a lesser extent than the foregoing materials. This deleterious effect was also observed when 1 pph polydimethyl siloxane was added to the monomer prior to the polymerization; moldings made from this composition burned violently. The mechanism of this effect is not known at the present time; however, it has been pointed out by R. E. Skochdopole (The Dow Chemical Company) that the foregoing materials,

insofar as their composition is known, are good absorbers of radiant energy,<sup>18</sup> and that this property may be the reason for their effectiveness. To test this hypothesis, zinc sulfide and powdered aluminum, both poor absorbers of radiant energy,<sup>18</sup> were tried; neither one affected the self-extinguishing characteristics adversely. Polylease 77 (Barrett Division, Allied Chemical and Dye Corporation), which reputedly contains a low molecular weight polyethylene, is an effective mold release agent which, when used sparingly, does not damage the self-extinguishing characteristics. This deleterious effect of the silicone resins and related substances has been demonstrated for self-extinguishing polystyrene foam of different origin and composition.

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### Résumé

La préparation par polymérisation en suspension, de compositions de mousse de polystyrène dont la combustion s'arrête d'elle-même est décrite. L'halogène nécessaire pour les propriétés d'auto-extinction est incorporé par transfert de chaîne. L'effet synergétique de peroxydes organiques diminue fortement la quantité d'halogène nécessaire. Par exemple, 0,3 pph de 1,2-dibromotétrachloroéthane en présence de 0,2 pph de peroxyde de dicumyle rend le mélange auto-extinctible, alors que 1,0 pph est nécessaire en absence de peroxyde. La vitesse de polymérisation n'est pas influencée par la présence de cet agent de transfert de chaîne, tandis que le poids moléculaire est réduit considérablement. On a mis en évidence l'efficacité d'autres agents halogénés de transfert de chaîne et des peroxydes. Des résidus de silicone exercent nocif sur les propriétés d'auto-extinction.

### Zusammenfassung

Die Darstellung von praktischen, flammwidrigen Schaumpolystyrolmassen durch Suspensionspolymerisation ist beschrieben. Das zur Erzielung der Flammwidrigkeit nötige Halogen wird durch Kettenübertragung eingebaut. Die synergetische Wirkung organischer Peroxyde setzt die notwendige Menge Halogen stark herab. Die Polymerisationsgeschwindigkeit wird durch die Anwesenheit dieses Überträgers nicht beeinflusst, während das Molekulargewicht beträchtlich herabgesetzt wird. Zum Beispiel machen 0,3% 1,2-Dibromtetrachloräthan in Gegenwart von 0,2% Dicumylperoxyd die Masse selbstauslöschend, während ohne Peroxyd 1,0% notwendig ist. Die Wirksamkeit anderer halogener Kettenüberträger und Peroxydverbindungen wurde gezeigt. Siliconformgleitmittel hat einen schädlichen Einfluss auf die flammwidrigen Eigenschaften des Schaumkunststoffes.

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