

Mechanism of Flame-Retardant Action of Tris(2,3-Dichloropropyl) Phosphate on Epoxy Resin

LI JIANZONG and CHEN SHIYUAN, *Polymeric Material Division, Chemistry Department, Hubei University, Wuhan, The People's Republic of China*, and XU XIAOMING, *Applied Chemistry Division, Wuhan Institute of Water Transportation Engineering, Wuhan, The People's Republic of China*

Synopsis

The use of tris(2,3-dichloropropyl) phosphate (TCPP) as a flame retardant in epoxy resin cured by methyltetrahydrophthalic anhydride was studied. Although TCPP is an organophosphorus flame retardant containing chlorine, the data obtained from LOI measurements showed that TCPP was not more effective compared to other flame retardants containing only phosphorus. In order to understand the mechanism of flame retardant action of TCPP on epoxy resin, the effect of TCPP on the thermal degradation of the resin was investigated using thermogravimetry, differential scanning calorimetry, infrared spectroscopy, and elemental analysis. TCPP was shown to act predominantly by condensed phase mechanism, to catalyze decomposition, and to enhance char formation. A mode of flame retardant action of TCPP on epoxy resin by phosphorus in condensed-phase was proposed.

INTRODUCTION

Haloalkyl phosphorus esters are quite commonly employed in flame-retardant polymeric materials. In order to research more effectual flame retardants, attention has been directed to the mode of flame-retardant action for these additives. The comprehensive studies were made of the action of tris(2,3-dibromopropyl) phosphate (TBPP) on a variety of polymers. In studies by Steutz et al.¹ TBPP was found not to change the activation energy of thermooxidation degradation of polypropylene, although it raised the oxygen index. A vapor-phase physical shielding effect was postulated for the flame retardant in this polymer. It was shown by Inagaki² that the presence of TBPP lowered the temperature of the burning surface and increased the thermal stability of polystyrene. The observations tended to substantiate the view that both physical and chemical flame inhibition involved in the vapor-phase activity. There was also some evidence that TBPP worked by the condensed-phase mechanism. Several workers have reported that the flame retardants act to a significant degree by condensed phase action in polymers such as polystyrene, polyester, and rigid foams.³⁻⁶ Obviously, generalization as to the mechanism must be made with care as the behavior can be, and in fact is in many cases, greatly dependent upon the individual polymers. On the other hand, extrapolation of the behavior of bromo compounds to chloro compounds should also be undertaken with caution in view of the well-known differences in bond strengths.

TABLE I
Flame-Retardant Effect of Tris(2,3-Dichloropropyl) Phosphate on Epoxy Resin

Sample	TCPP (phr)	LOI (%)
EP-0	0	21.2
EP-1	5	23.8
EP-2	10	28.9
EP-3	15	29.7
EP-4	20	30.1
EP-5	30	31.7
EP-6	50	32.5

Information in the literature concerning flame retardant action of tris(2,3-dichloropropyl) phosphate (TCPP) on polymers is slight. This paper describes the use of TCPP in epoxy resin cured by methyltetrahydrophthalic anhydride and elucidation of its mode of action.

EXPERIMENTAL

Materials

Diglycidyl ether of bisphenol A (DGEBA) was used as epoxy resin, methyltetrahydrophthalic anhydride (Me-THPA) as curing agent, and 2-ethyl-4-

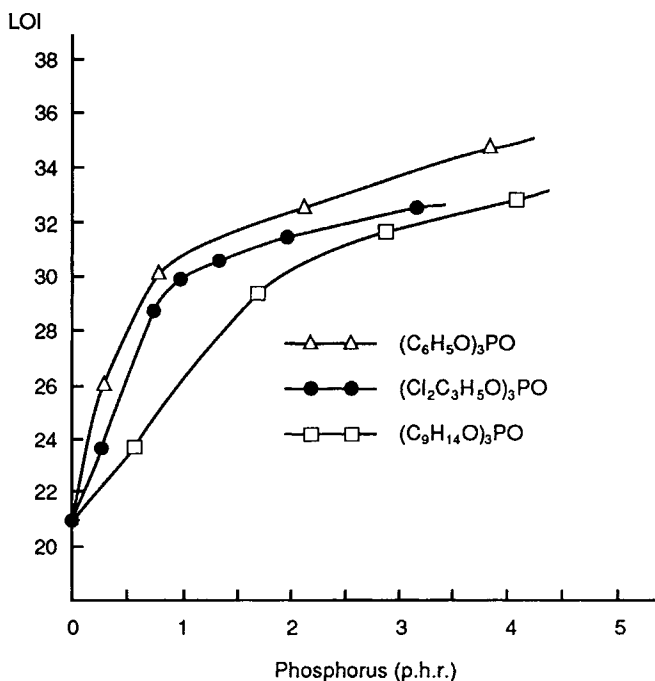


Fig. 1. The limiting oxygen index values for epoxy resin samples treated with phosphorus-containing flame retardants as a function of phosphorus content.

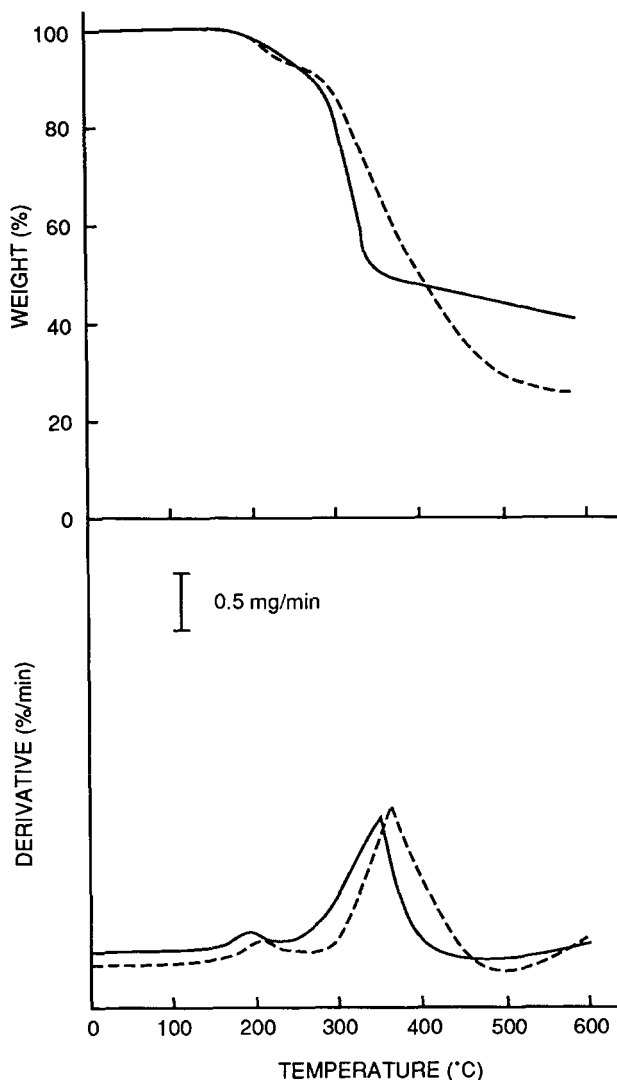


Fig. 2. TG-DTG curves for epoxy resin samples in nitrogen: (—) sample treated with 15 phr TCPP; (---) sample untreated. Heating rate: $10^{\circ}\text{C}/\text{min}$.

methylimidazole (EMI) as catalytic curing agent. The above materials including the flame retardants used here are all commercially available. The samples were not purified before use and the flame retardants studied are chemical purity.

Preparation of Samples

The resin formulation for casting were mixed at elevated temperatures ($70\text{--}80^{\circ}\text{C}$) by an agitator. The mixture was cast into the molds consisting of two glass plates. The cure cycle was as follows: $90^{\circ}\text{C}/2\text{ h}$, $120^{\circ}\text{C}/1\text{ h}$. The curing process was under atmosphere.

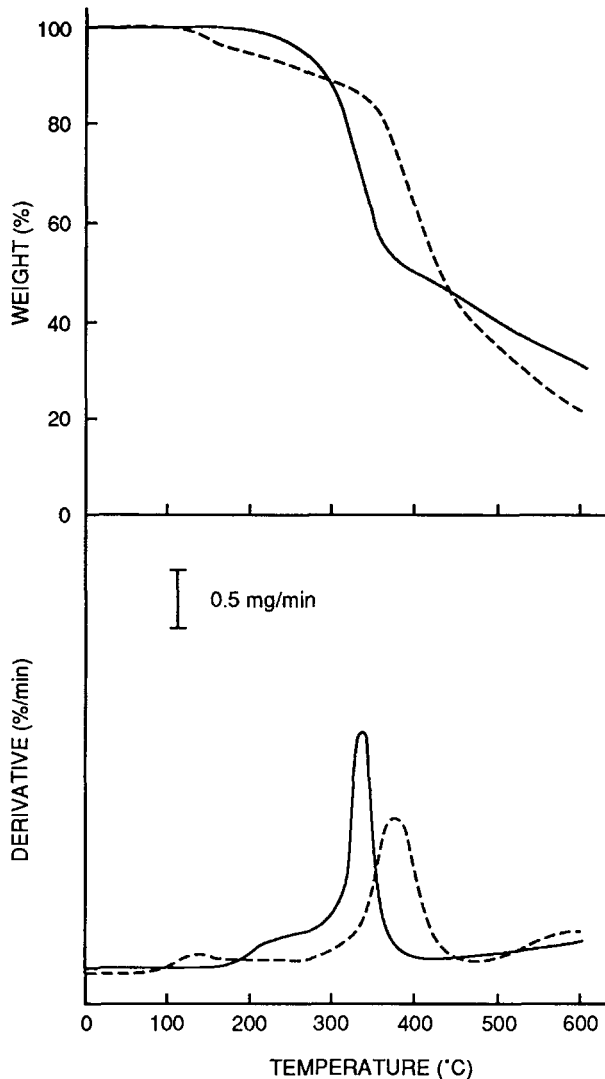


Fig. 3. TG-DTG curves for epoxy resin samples in air: (—) sample treated with 15 phr TCPP; (---) sample untreated. Heating rate: $10^{\circ}\text{C}/\text{min}$.

Flammability Test

The limiting oxygen index (LOI) was determined on a HC-2 oxygen index apparatus (Scientific Instrument Factory, Tenjing, P.R. China) in accordance with standard procedure.⁷

Thermogravimetry

The thermogravimetric analysis was performed in air or nitrogen with a Shimadzu thermogravimetric analyzer DT-30B. The samples of about 10 mg were heated at a heating rate of $10^{\circ}\text{C}/\text{min}$ from room temperature to 600°C . The DTG curves were obtained electronically.

TABLE II
Thermogravimetric Data for TCP-Containing Epoxy Resin in Air

TCP (phr)	Initial stage		Major stage		Weight loss at 600°C
	T (°C) ^a	Loss (%)	T (°C) ^a	Loss (%)	
0	175	5.6	364	24.2	82.5
5	187	5.1	329	26.5	75.7
10	191	5.3	324	27.3	72.2
15	198	4.9	322	29.1	70.3
20	197	4.8	320	30.5	70.1
30	197	4.8	317	30.5	70.1

^a Temperature of DTG peak maximum.

Differential Scanning Calorimetry

A Model CDR-1 differential scanning calorimetry (Scientific instrument Factory, Shanghai, P.R. China) was used. The samples of about 5 mg were heated at heating rate of 10°C/min from room temperature to 600°C in air.

Infrared Spectroscopy

A Shimadzu spectrometer IR-440 was used. Infrared spectra were examined as KBr discs. The concentrations of the samples were 1% by weight in KBr discs.

Elemental Analysis

Chlorine contents of the samples were determined by a titration method. Samples were burned in an oxygen combustion flask. The resulting hydrogen

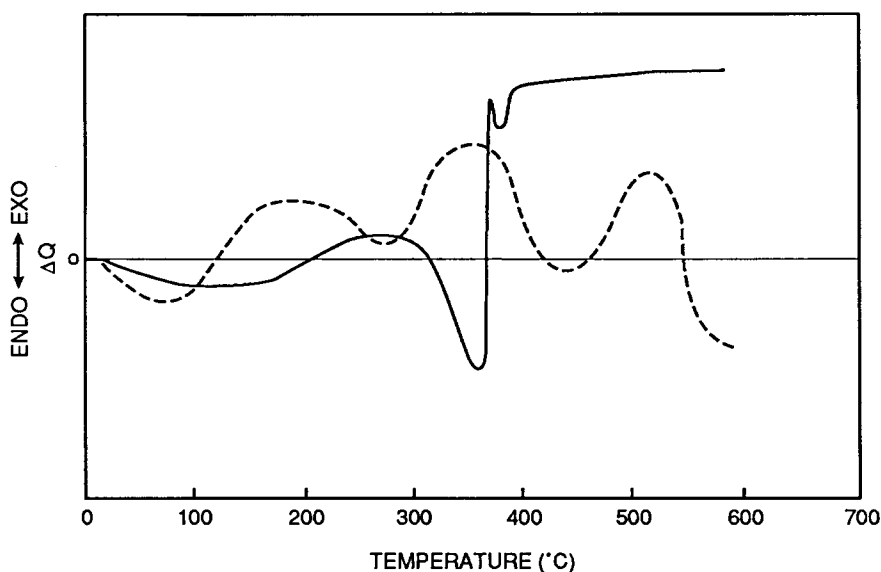


Fig. 4. DSC curves for epoxy resin samples in air: (—) sample treated with 15 phr TCP; (---) sample untreated. Heating rate: 10°C/min.

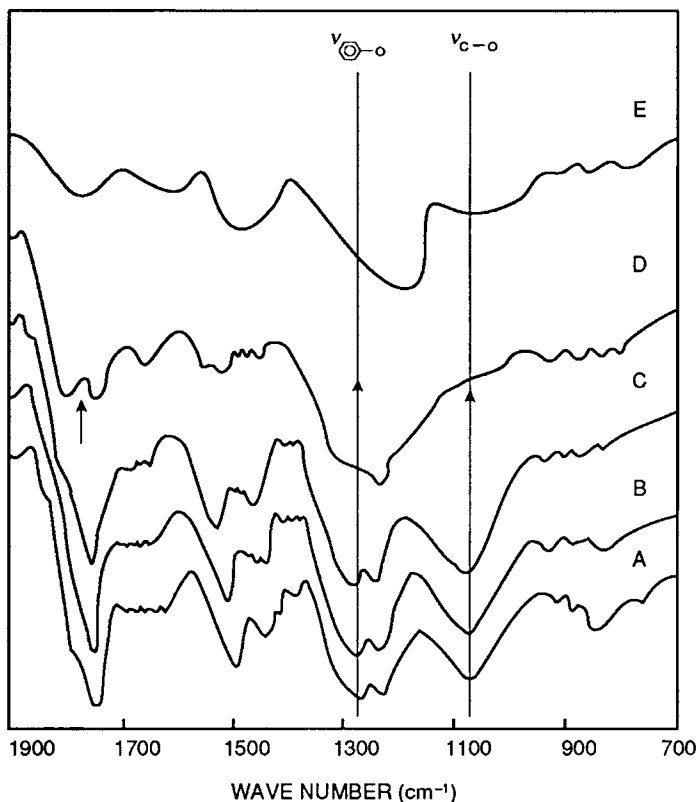


Fig. 5. Infrared spectra of untreated samples after heating for 30 min in air: (A) untreated; (B) at 200°C; (C) at 250°C; (D) at 300°C; (E) at 350°C.

chlorine was absorbed in an aqueous solution of sodium hydrogen and hydrazine sulfate. The solution was titrated with a silver nitrate.

Phosphorus contents of the samples were determined by a titration method. Samples were burned in an oxygen combustion flask. The resulting products were absorbed in an aqueous solution of sodium hydroxide. The solution added $\text{La}(\text{NO}_3)_3$ was titrated with EDTA.

RESULTS AND DISCUSSION

Flammability Characteristics

The effect of TCPP on the LOI of the epoxy resin was listed in Table I. A significant increase with increasing TCPP concentration is noted up to 10 phr; it raised the LOI of epoxy resin to 28.9 from 21.2. TCPP at greater than 10 phr increases the LOI slightly.

The effect of phosphorus content of TCPP on the LOI of the epoxy resin was shown in Figure 1, together with the results obtained using triphenyl phosphate and trimethylphenol phosphate given for comparison. As seen in Figure 1, a similar significant increase in flame retardation with increasing phosphorus

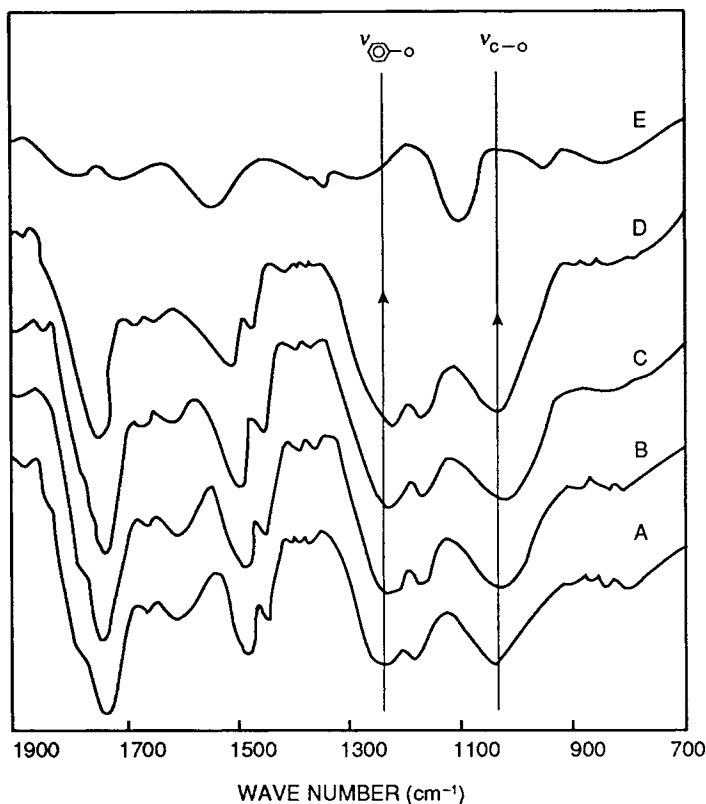


Fig. 6. Infrared spectra of samples treated with 15 phr TCPP after heating for 30 min in air. (A) untreated; (B) at 200°C; (C) at 250°C; (D) at 300°C; (E) at 350°C.

concentration is noted up to 2 phr; it raised the LOI of the three epoxy resin systems to 30–32 from 21.2. In the regions of phosphorus concentration of 2–4 phr the phosphoruses with and without chlorine are nearly effective in raising the LOI. The combined result in Figure 1 shows that the power of the retardation of the three resin systems are approximately dependent on phosphorus concentration, although the chlorine content of the TCPP–epoxy resin system is greatly increased with the phosphorus progressively increased. It appears quite possible that TCPP mainly works by phosphorus alone despite the presence of halogen. It is commonly suggested from many studies^{8–10} that organophosphorus flame retardants containing halogen are more effective than those not containing halogen through a synergistic combination of phosphorus and halogen. However, this does not hold true for the TCPP–epoxy resin system. Thus the mode of action of TCPP on epoxy resin should be investigated.

Thermal Degradation Studies

Thermogravimetric curve and the corresponding DTG trace in nitrogen show the difference brought about by incorporating TCPP into epoxy resin, presented in Figure 2. The weight of loss for the two resin samples were initiated at the same temperature. The major degradation of the two resin samples took place

TABLE III
Elemental Analysis of TCPP-Containing Epoxy Resin after Heating Treatments

Sample ^a	Temperature (°C)	Residual weight (%)	P %	Cl %
EP-3-1	Untreated	—	1.05	9.28
EP-3-2	200	97.5	0.87	8.48
EP-3-3	250	88.1	0.87	6.81
EP-3-4	300	74.6	1.17	6.49
EP-3-5	350	58.5	3.15	0

^a Samples containing 15 phr TCPP and heated in air for 30 min.

in the same temperature range (300–400°C), but the resin sample containing 15 phr TCPP broke down more rapidly in this temperature range, and left a higher residuals about 40% at 600°C, compared to about 25% residues for the resin sample uncontained TCPP. The TG result in N₂ suggests that TCPP operates by condensed phase activity.

The degradation of the epoxy resin in air is more relevant to flame retardance and gave the TG curves of Figure 3 and the data in Table II. These showed that the decomposition of epoxy resin was affected by adding TCPP. The initial step was moved to slightly higher temperature with similar weight loss. The major step was shifted to lower temperatures and degraded more rapidly with less weight loss when TCPP was present. Up to 600°C the resin added TCPP produced more char.

Thermal analysis by DSC in air (Fig. 4) exhibits a much larger exothermic peak at about 360°C, suggesting that a simultaneous process involving catalytic reaction of the additive with the substrate took place in the major degradation stage, corresponding well with TG results.

The influence of TCPP on the thermooxidation of epoxy resin thermoset was further examined by using infrared spectroscopy. The infrared spectra for residuals of the two resin samples after heating in the temperature range from 200 to 350°C for 30 min were shown in Figures 5. and 6, respectively.

As shown in the infrared spectra of resin sample uncontained TCPP, two absorption bands at 1250 cm⁻¹ due to C—O group and at 1040 cm⁻¹ due to C—O—C group, respectively, disappeared at 300°C and could not be detected at 350°C, it was demonstrated that ether bondings were scissioned in initiative fashion to the degradation of epoxy resin cured by anhydride, as has been reported by many previous studies.^{11,12} At elevated temperature, the bands observed at 1780 and 1850 cm⁻¹ in the infrared spectra of the degradation residues in our studies might arise from anhydride units in the cured epoxy resin chain. These bands fall well within the region of the symmetric and asymmetric stretching frequencies of the carbonyl groups of anhydrides which could be expected as degradation products of epoxy resin cured by anhydrides. This conclusion was also previously reported by Anderson¹³ and Fisch and Hofman.¹⁴

For the resin sample containing 15 phr TCPP, disappearance of the bands at 1250 and 1040 cm⁻¹ could be observed up to 300°C, as was demonstrated for the sample uncontained TCPP. When it was heated to 350°C, the sample was so carbonized that we could not detect the characteristic spectral bands of

the epoxy resin. A spectral comparison of the two resin samples confirmed the TG results.

Regarding the characterisation of the thermooxidative degradation for the TCPP-epoxy resin system, the observed flame retardancy by TCPP could be adequately accounted for by a condensed-phase mode of flame inhibition.

Elemental Analysis

Elemental analysis of the residues extends our studies to establish the mode of flame-retardant action of TCPP on epoxy resin. It can be seen from Table III that the amount of chlorine atoms was lost steadily throughout after heating in air for 30 min from 200 to 350°C, but a comparable amount of phosphorus atoms to that initially added was present in residual products; even at 350°C, it is inferred that phosphorus atoms could not vaporize from the surface, but sink into the polymer. It is not unlikely that TCPP incorporated into epoxy resin could be transformed into phosphoric acid or pyrophosphoric acid before the resin is degraded.

Mechanism of phosphorus flame retardants on polymers has been reviewed by Weil.¹⁵ He pointed out that phosphorus flame retardants function in oxygenated polymers by a condensed-phase activity of inducing char, and that the acid-catalyzed char-forming mode of action of phosphorus plays an evident role. In our studies TCPP acts to a significant degree by a similar mechanism, although it is phosphorus flame retardant containing chlorine. The chlorine atoms in TCPP could play a minor role in the flame-retardant action combined with LOI results reported here.

CONCLUSION

In epoxy resin, TCPP appears to act as a catalyst that chemically promotes the carbonization reaction of the resin, and thus decreases the formation of flammable, carbon-containing gas; on the other hand, the char coat which is formed acts physically as a barrier to passage for heat, oxygen, or fuel. The overall effect in the condensed phase results in a flame inhibition.

The authors wish to thank Professor Oian Baogong for instruction on this paper, and also express thanks to Mr. S. P. Chen, Mrs. M. Wu and Mrs. R. Quan for experimental assistance. Our thanks also go to Mr. Y. Feng of Wuhan University for the thermogravimetric analysis.

References

1. D. Steutz, B. Barnes, A. Diedwardwardo, and F. Zitomer, paper presented at University of Utah Polymer Conference, Salt Lake City, June 8, 1970.
2. N. Inagaki, S. Sakurai, and K. Katsuura, *J. Appl. Polym. Sci.*, **23**, 2023 (1979).
3. A. W. Benbow and C. F. Cullis, *Combust. Flame*, **24**, 217 (1975).
4. R. Sanders, *Text. Chem. Color.*, **5**, 48 (1973).
5. J. E. Kresta and K. C. Frisch, *J. Cell. Plast.*, **11**, 68 (1975).
6. J. D. Cooney, M. Day, and D. M. Wiles, *J. Appl. Polym. Sci.*, **29**, 911 (1984).
7. Test Method D2863-77, American Society for Testing and Materials, Philadelphia, 1977.
8. L. N. Gordon, *Int. J. Polym. Mater.*, **7**, 140 (1979).
9. N. K. Jha et al., *J. Appl. Polym. Sci.*, **32**, 4393 (1986).

10. J. W. Lyons, *The Chemistry and Use of Fire Retardants*, Wiley-Interscience, New York, 1970.
11. M. B. Noiman et al., *Dokl. Akad. Sci. SSSR*, **135**, 1419 (1960).
12. L. H. Lee, *J. Appl. Polym. Sci., Part A*, **3**, 859 (1956).
13. H. C. Anderson, *J. Appl. Polym. Sci.*, **6**, 486 (1962).
14. W. Fisch and W. Hofman, paper presented at 136th American Chemical Society Meeting, Atlantic City, NJ, Sep. 1959; *Plast. Print. Ink Chem.*, **19**(2), (Sep. 1959).
15. E. D. Weil, in *Flame Retardancy of Polymeric Materials*, W. C. Kuryla and A. V. Papa, Eds., Dekker, New York, 1976, p. 123.

Received August 16, 1989

Accepted December 21, 1989