Eur. Polym. J. Vol. 28, No. 5, pp. 493–497, 1992
Printed in Great Britain. All rights reserved

0014-3057/92 $5.00 + 0.00

STUDIES OF THE EFFECTS OF PHOSPHORUS AND ITS COMPOUNDS ON THE COMBUSTION OF CELLULOSE

C. F. CULLIS, M. M. HIRSCHLER* and R. G. MADDEN
Department of Chemistry, City University, London EC1V 0HB, England

(Received 22 August 1991)

Abstract—Cellulose cotton cloth has been treated with phosphorus, both by direct phosphorylation and by addition of various compounds containing up to 98.6% P. Studies have been made of the effects of these treatments on thermal decomposition and flammability of the cloth. It has been shown that, in terms of unit weight of phosphorus introduced, phosphorylation is a more efficient method of imparting flame retardance than incorporation of additives. When the various additives used were compared on this basis, tritolyl phosphate and triphenyl phosphine were the most effective, while red phosphorus was the least so. Flame retardance of cellulosic materials is generally related to the extent of increased charring. However no such generalization can be made with regard to the phosphorus-based additives studied in this work, since some function primarily in the gas phase and others in the condensed phase. There is thus no obvious correlation between degree of flame retardant effectiveness and mechanism of flame retardance. The predominant effect of nitrogen compounds, both on their own and when used in conjunction with phosphorus compounds, was to decrease flammability, but there appeared to be no simple connection between the magnitude of their effect and any particular mode of action.

INTRODUCTION

The incorporation of phosphorus into organic polymers generally inhibits the combustion of these materials. In this paper, some studies have been made of the influence of phosphorus and its compounds on the combustion behaviour of cellulose cotton cloth. Included among the additives studied was red phosphorus (RP), which has been shown to be a potentially useful flame retardant for certain nitrogen-containing [1, 2] and oxygen-containing [3–6] thermoplastic polymers. The effects produced by most additive flame retardants on textiles are, however, often only temporary, since the additives tend to be removed by leaching, laundering and dry-cleaning. Thus, in order to obtain a truly durable flame-retardant finish, it is desirable for the active species to be chemically bonded to the polymer. Parallel studies have therefore been made of the effects on flammability of directly phosphorylating cellulose beforehand.

EXPERIMENTAL PROCEDURES

Cellulose was in the form of Egyptian cotton cloth [7]; its phosphorylation was carried out where necessary by a modification of the method used by Gupta *et al.* [8]. Unmercerized cotton cloth was first treated with a 2.5 wt% aqueous solution of NaOH for 2 min, washed with water and dried. The cloth was then refluxed with pyridine in a dry N_2 atmosphere for 30 min, after which phosphorus oxychloride was added dropwise over 1 hr; the resulting mixture was heated to a range of temperatures for different periods of time in order to vary the degree of phosphorylation of the cloth. It was found that the optimum conditions for obtaining a cloth containing 5 wt% of phosphorus involved refluxing the mixture at 55° for 72 hr. Details have been given elsewhere [9, 10] of the sources of most of the additives; good-quality samples of the remainder were obtained from BDH or Aldrich.

Methods of incorporating both soluble and insoluble additives into the cotton have already been described [7]; RP, sieved to a particle size of 90 μm, was "ironed-on" to the cloth, which had previously been impregnated with neoprene to act as an adhesive. The iron was covered with a perforated teflon sleeve to prevent adhesion of the phosphorus to it. The experimental techniques for measuring flammability and studying thermal behaviour have been fully described elsewhere [7]. An account has also been given [9] of methods for the computation of the limiting oxygen index (LOI) results; it is considered that LOI remains a useful criterion of the influence of additives on the flammability of a given polymer, even though it is not always a reliable measure of fire performance in real systems. In addition, the gaseous combustion products of certain polymer and additive systems were analysed by i.r. spectrometry [10].

RESULTS

Flammability results

(a) Comparison of effects of different forms of phosphorus. The LOI of cotton cloth, measured at room temperature, is 18.2 but it is significantly increased by the presence of phosphorus. In most of the systems studied, the LOI increases with phosphorus loading but quite rapidly reaches a limiting value. Table 1 shows the effects of these limiting concentrations of phosphorus compounds in different oxidation states, as well as those of direct phosphorylation, on the flammability of the cloth. It will be seen that, on an overall weight basis, all the additives used have effects on the LOI of roughly the same magnitude. However, in terms of the weight of phosphorus introduced, pre-phosphorylated cellulose exhibits by far the highest flame resistance; among the additives, tritolyl phosphate (TTP) and triphenyl phosphine (TPN) are, on this latter basis, the most effective flame-retardants and RP is the least.

---

*Present address: Safety Engineering Laboratories, 38 Oak Road, Rocky River, OH 44116, U.S.A.

Table 1. The effects of phosphorus compounds on the flammability of cotton cloth

Phosphorus compound	Oxidation state	Wt% of P compound added	Wt% of P added	LOI	ΔLOI	ΔLOI
					Wt% P compound added	Wt% P added
—	—	—	—	18.2	—	—
TTP	+5	17.4	1.5	22.7	0.26	3.0
DMP	+3	11.9	3.0	24.1	0.50	2.0
TPP	+3	16.0	1.6	22.3	0.26	2.6
RP	0	16.4	16.2	23.1	0.31	0.3
TPO	−1	13.5	1.5	20.9	0.13	1.8
TPN	−3	10.9	1.3	22.0	0.27	2.9
Phosphorylation		—	5.1	31.8	—	6.2

TTP, tritolyl phosphate; DMP, dimethyl methyl phosphonate; TPP, triphenyl phosphite; RP, red phosphorus; TPO, triphenyl phosphine oxide; TPN, triphenyl phosphine.

Table 2. The effects of phosphorus compounds, used in conjunction with MEL, on the flammability of cotton cloth

Phosphorus compound	Wt% of P compound added	Wt% of P added	Wt% of MEL added	LOI	ΔLOI	ΔLOI
					Wt% P compound added	Wt% P added
—	—	—	—	18.2	—	—
—	—	—	11.2	23.4	—	—
TTP	6.1	0.5	12.6	24.8	1.1	13.2
DMP	6.5	1.6	10.2	27.6	1.4	5.8
TPP	9.3	0.9	10.6	26.1	0.8	8.8
P	9.2	9.2	11.3	26.3	0.9	0.9
TPO	5.8	0.6	9.2	23.7	0.9	9.2
TPN	13.8	1.6	5.8	24.4	0.5	3.8
Phosphorylation		5.2	5.0	35.0		6.7

Abbreviations for phosphorus compounds as in Table 1.

(b) Influence of added nitrogen compounds. Since the flame-retardant action of phosphorus is generally enhanced by the simultaneous presence of suitable nitrogen compounds [11], parallel studies were made of systems containing also melamine (MEL). The results in Table 2 show that this nitrogen compound decreases the flammability in all cases. Again, on an overall weight basis, the various phosphorus compounds have broadly similar effects but, judged in terms of the weight of phosphorus introduced, the differences between the individual compounds are even more pronounced, although RP still has by far the smallest influence. Since the flame-retardant action of P—N systems is often significantly enhanced by the presence of halogen [12], some measurements were made of the effects on the flammability of cotton cloth of the presence also of decabromobiphenyl (DBB), an additive previously used in conjunction with phosphorus and nitrogen compounds [10, 13]. These measurements showed however that the highest LOI values are obtained with binary additive systems containing only RP and MEL (Table 3), so that no further work was done involving the halogen compound.

In order to throw further light on the comparatively small flame-retardant action of RP–MEL systems on cotton cloth, a triangular diagram was constructed (Fig. 1). Qualitatively it shows a region of relatively high flame retardance at high MEL levels along the cellulose baseline. At high RP loadings, the flame retardancy is seen to decrease, as is observed experimentally. It can be shown that there is reasonably good synergism between RP and MEL with a coefficient of 235; this is significantly higher than the P–N synergism coefficients found with these same additives for thermoplastic polymers [10].

However, in order to gain a better understanding of possible modes of P–N interaction, several other nitrogen compounds were investigated (Table 4). In terms of the weight of nitrogen introduced, ammonium formate (AMF) is the most effective flame retardant on its own and *N*-methylimidazole (NMI) is the least effective and indeed slightly increases the flammability of cotton cloth. However, all the nitrogen compounds, when used in conjunction with RP, cause some further reduction in flammability.

Table 3. The effects of MEL and DBB on the flammability of cotton cloth–RP systems

RP (wt%)	MEL (wt%)	DBB (wt%)	LOI
—	—	—	18.2
9.8	—	—	22.7
9.2	11.3	—	27.3
8.5	—	13.0	24.6
8.1	7.2	8.1	27.2

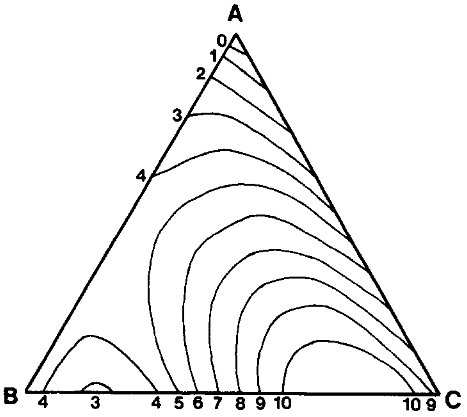

Fig. 1. The effects of RP and MEL on the LOI values of cotton cloth. (A) 100% cellulose; (B) 80% cellulose + 20% RP; (C) 80% cellulose + 20% MEL. LOI values: 0, 18.2; 1, 19.2; 2, 20.2; 3, 21.2; 4, 22.2; 5, 23.2; 6, 24.2; 7, 25.2; 8, 26.2; 9, 27.2; 10, 28.2.

Table 4. The effects of nitrogen compounds, on their own and in conjunction with RP, on the flammability of cotton cloth

Nitrogen compound	Wt% of N compound added	Wt% of N added	Wt% of RP added	LOI	Δ LOI Wt% N compound added	Δ LOI Wt% N added
—	—	—	—	18.2	—	—
	—	—	9.8	22.7	—	—
AMF	9.0	2.0	—	19.4	0.13	0.60
	11.4	2.5	5.1	25.0	0.20	0.92
BTA	14.7	3.5	—	18.8	0.04	0.17
	13.1	3.2	9.2	23.2	0.04	0.16
ETU	15.5	5.1	—	19.5	0.08	0.25
	15.2	4.9	10.6	22.3	−0.03	0.12
HMT	10.0	4.0	—	18.8	0.06	0.15
	9.2	3.7	7.8	22.8	0.01	0.03
MEL	14.9	9.9	—	21.7	0.23	0.35
	11.3	7.5	9.2	26.3	0.31	0.48
NMI	17.8	6.1	—	17.3	−0.05	0.15
	16.4	5.6	8.1	20.4	−0.14	−0.41

AMF, ammonium formate; BTA, barbituric acid; ETU, ethylene urea; HMT, hexamethylenetetramine; MEL, melamine; NMI, *N*-methylimidazole.

A triangular diagram for the cellulose–TTP–MEL system (Fig. 2) shows a region of relatively high flame retardance along the cellulose baseline with a maximum shifted slightly towards the MEL axis; the synergism coefficient is 208. Although, when used at the same overall loading, TTP is slightly less effective than RP as a flame retardant for cotton cloth, it is much more effective on a per unit weight of phosphorus basis (Tables 1 and 2).

Thermoanalytical results

Cellulose breaks down in two stages, a fast main decomposition stage at *ca* 325° and a much slower stage at *ca* 460°, identifiable as the carbon burn-off (CBO) stage and accounting for about 18% of the weight loss [Fig. 3(a)]. When RP is heated on its own, it undergoes a significant (16%) increase in weight at about 420°, presumably because of reaction with oxygen to form a moderately volatile oxidized species such as P_2O_5. However, when RP is added to cotton cloth, the first weight loss stage is observed at a slightly lower temperature than with the cloth on its own [Fig. 3(b)]; the CBO stage occurs at a considerably higher temperature and produces over 30% by weight of carbon. The thermogravimetric trace for phosphorylated cellulose [Fig. 3(c)] shows that the main decomposition starts at *ca* 280° but then occurs much more slowly than with cellulose itself. In contrast to the behaviour observed with untreated cellulose, the decomposition involves two distinct weight losses prior to the CBO stage.

When TTP is incorporated into cotton cloth, there is a significant weight loss between 200 and 270°

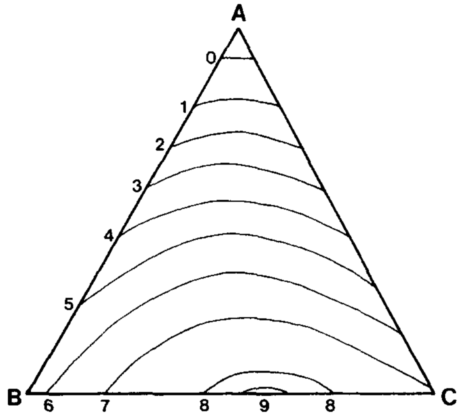

Fig. 2. The effects of TTP and MEL on the LOI values of cotton cloth. (A) 100% cellulose; (B) 80% cellulose + 20% TTP; (C) 80% cellulose + 20% MEL. LOI values: 0, 18.2; 1, 19.2; 2, 20.2; 3, 21.2; 4, 22.2; 5, 23.2; 6, 24.2; 7, 25.2; 8, 26.2; 9, 27.2.

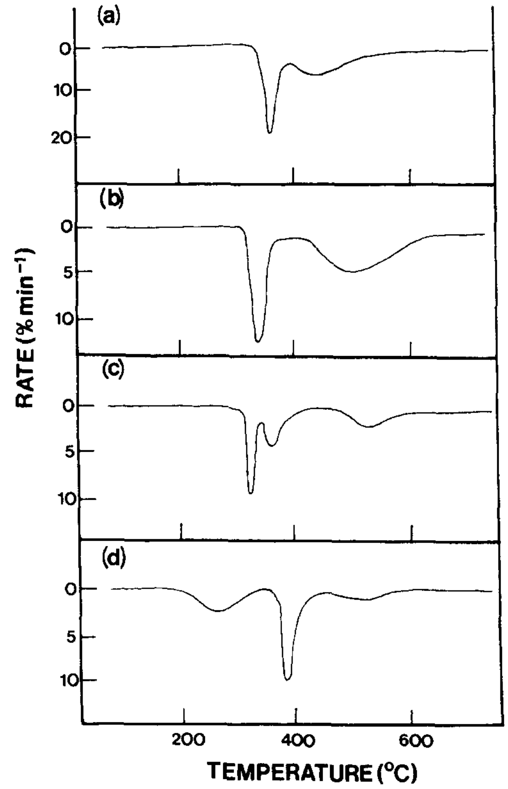

Fig. 3. Differential thermogravimetric analysis curves for cotton cloth–phosphorus systems. (a) Pure cellulose; (b) cellulose + 15 wt% RP; (c) phosphorylated cellulose containing 5.2 wt% P; (d) cellulose + 10 wt% TTP.

Table 5. The effects of phosphorus compounds, in absence and presence of MEL, on the CBO weight loss of cotton cloth

P compound (wt%)	Wt% MEL	CBO weight loss (%)
—	—	18.0
TTP (15.8)	—	15.9
TTP (6.1)	12.6	17.5
DMP (11.8)	—	31.8
DMP (6.5)	10.2	35.8
TPP (16.0)	—	34.2
TPP (9.3)	10.6	38.6
RP (10.0)	—	24.1
RP (15.0)	—	30.6
RP (10.0)	10.0	26.1
TPO (13.5)	—	16.9
TPO (5.8)	9.2	17.8
TPN (10.8)	—	23.0
TPN (6.5)	8.7	21.9

Abbreviations for phosphorus compounds as in Table 1.

[Fig. 3(d)]; it represents *ca* 10% of the total weight and thus corresponds to complete loss of all TTP from the cloth. The second and third weight loss stages correspond to the two weight losses found with the cloth on its own but occur at temperatures some 20° higher. The weight loss at the CBO stage is reduced. Somewhat similar behaviour is observed with samples of cotton cloth containing triphenyl phosphine oxide (TPO). Here again effectively all the additive is lost at quite low temperatures and the size of the CBO weight loss stage is decreased.

The magnitude of the CBO stage is a useful measure of the amount of char phase formed and thus also of the extent to which dehydration of the cellulose has occurred. Table 5 shows the effects of various phosphorus compounds (in the absence and presence of MEL) on the CBO stage and it is clear that, although most the additives increase the associated weight loss, this is not the case for TTP or TPO. Table 6 shows data similar to those in Table 5 for various nitrogen compounds (in absence and presence of RP) and it can be seen that all of these except ethylene urea (ETU) increase the magnitude of the CBO weight loss stage.

Table 6. The effects of nitrogen compounds, in absence and presence of RP, on the CBO weight loss of cotton cloth

N compound (wt%)	Wt% RP	CBO weight loss (%)
—	—	18.0
AMF (9.0)	—	24.8
AMF (13.0)	7.0	27.4
BTA (10.4)	—	21.0
BTA (13.4)	9.4	27.1
ETU (10.0)	—	19.1
ETU (16.0)	7.0	17.5
HMT (14.0)	—	22.0
HMT (11.0)	11.0	26.6
MEL (10.0)	—	24.1
MEL (10.0)	10.0	26.1
NMI (7.4)	—	24.9
NMI (16.4)	8.1	38.6

Abbreviations for nitrogen compounds as in Table 3.

Infrared spectrophotometric results

Analysis was carried out of the gaseous products formed when cellulose, various additives and cellulose-additive systems are heated. In particular, whereas cellulose on its own gives carbon oxides and what is probably laevoglucosan, the addition of RP causes the formation of various low molecular weight compounds such as acetaldehyde. With RP alone and when it is incorporated into cellulose, there are absorption peaks in the region 930–1390 cm^{-1} which are almost certainly ascribable to P—O and P=O stretching modes and are therefore indicative of the formation of oxides such as P_2O_5 and oxyacids such as H_3PO_4. RP also reduces the temperature at which water is formed and would therefore appear to encourage dehydration.

MEL also seems to facilitate dehydration of cellulose. Both this and all the other nitrogen compounds studied, except barbituric acid (BTA) and NMI, yield some ammonia on decomposition.

DISCUSSION

With cellulosic polymers, many phosphorus-containing flame retardants act largely, if not exclusively, in the condensed phase. In such cases the phosphorus is probably converted, during the combustion process, into phosphorus oxyacids which can catalyse dehydration and crosslinking of the cellulose at the expense of its decomposition to yield laevoglucosan and other volatile flammable compounds [14, 15]. Clearly cellulose, with phosphorus firmly incorporated into its structure beforehand, would be expected to undergo dehydration readily, on combustion, and this probably explains why phosphorylated cotton cloth has a relatively high LOI compared with that of untreated cotton (Table 1). It can be seen that all the phosphorus-based additives used in the present work also raise the LOI to some extent and, with many of them, the CBO weight loss is increased (Table 5), showing that dehydration and charring of the cotton cloth are enhanced. Nevertheless TTP and TPO do not behave in this way (Table 5) and, since the thermoanalytical results show that, with cotton samples containing these two additives, almost all the phosphorus is lost in the early stages of decomposition, these two compounds must act mainly in the gase phase. TPO is indeed known to be an efficient inhibitor of premixed flames as a result of its ability to form P and PO radicals which catalyse recombination of free radicals responsible for flame propagation [16]; it is also believed to act in the gas phase during its inhibition of the combustion of certain polymers [17]. However TTP, which is very stable, also operates in the gas phase but probably functions by an essentially physical mechanism, being released as such and in the form of a heavy vapour which "blankets" the flame and thus excludes oxygen [18].

One of the striking findings shown in Table 1 is that RP is so much less efficient as a flame retardant, on a per unit weight of phosphorus basis, than all the other phosphorus compounds. Although the thermoanalytical results show that RP increases the CBO weight loss of cotton cloth and the i.r. measurements suggest that some phosphorus oxides or oxyacids are formed from systems containing this additive, it must be concluded that only an extremely small proportion of the element is converted to compounds with active flame-retardant properties. In this connection, Fig. 1 shows that, although MEL is inherently less effective than RP as a flame retardant for the cotton cloth (compare Tables 1 and 4), the raising of the LOI is nevertheless determined largely by the nitrogen compound. This behaviour contrasts with that exhibited by systems containing both TTP and MEL (Fig. 2), where both additives contribute more or less equally to the overall flame-retardant effect.

There has long been abundant evidence that, with cellulosic materials, nitrogen compounds not only improve the flame-retardant action of phosphoric acid and related compounds [19] but can also cause any phosphorus to be attached more firmly to the polymer [17]. Comparison of Tables 1 and 2 shows that MEL reinforces the action of all the phosphorus-containing additives used. One way in which nitrogen acts is by increasing the ability of phosphorus compounds to phosphorylate cellulose and this is no doubt an important mode of action with many of the additives studied in the present work. Some nitrogen-containing additives can apparently catalyse the thermal condensation of phosphoric acid to polyphosphoric acids which are better phosphorylating agents for cellulose [20]. Alternatively P—N compounds, such as phosphoramides, can be formed which esterify hydroxyl groups more readily than phosphoric acids themselves [15, 21]. However, it is not surprising that, when cellulose has already been phosphorylated, addition of MEL has little further effect (compare Tables 1 and 2). Nevertheless it is interesting that the largest increase in flame retardance is found with TTP and TPO, which appear to act in the gas phase and it is not easy to understand how MEL acts so effectively in conjunction with these two phosphorus-based additives (Table 2).

Table 4 shows that the various nitrogen compounds, both on their own and in conjunction with RP, marginally decrease the flammability of cotton cloth. They are in general less effective flame retardants than the phosphorus compounds (compare Tables 1 and 4). All the nitrogen additives, except ETU which is relatively volatile and therefore probably readily lost from the polymer, increase the CBO weight loss (Table 6); the apparently anomalous behaviour of ETU shows, however, that nitrogen compounds can act as flame retardants other than by catalysing dehydration of the cotton cloth. At the same time, it is clear that increased char formation is not necessarily associated with a reduction in flammability; this effect is shown in particular by the behaviour of NMI (compare Tables 4 and 6). It is of course well known that nitrogen compounds have gas-phase modes of action including, in many cases, the ability to release gases such as nitrogen or ammonia. Such gaseous compounds dilute the volatile decomposition products of the cotton cloth, making them less flammable. However, in the systems studied, there seems to be little or no correlation between the flame-retardant effects of nitrogen-containing additives and their capacity to release ammonia.

Perhaps the principal conclusion which can be safely drawn from the results is that, despite the often superficial similarity of behaviour of many of the phosphorus-based additives studied, several distinct modes of flame-retardant action are involved; the same conclusion seems to apply to the different nitrogen compounds. In particular, it appears that there is no obvious correlation between the flame-retardant effects of the various additive systems and their ability to bring about dehydration of the cotton cloth. This point emphasizes that the enhancement of charring is by no means the only, or even necessarily the most important, mode of flame-retardant action involved when phosphorus is incorporated into cellulosic materials.

Acknowledgement—One of the authors (C. F. C.) thanks the Trustees of the Leverhulme Foundation for the award of an Emeritus Research Fellowship.

REFERENCES

1. J. R. A. Broadbent and M. M. Hirschler. *Eur. Polym. J.* **20,** 187 (1984).
2. H. Staendeke. Red phosphorus—recent developments for safe and efficient flame retardant applications. In *Dynamics of Current Developments in Fire Safety of Polymers, Joint SPE-FRCA Tech. Mtg*, 20–23 March 1988, Grenelefe, FL, pp. 32–46 (1988).
3. A. Granzow and J. F. Cannelongo. *J. appl. Polym. Sci.* **20,** 689.
4. A. Granzow, R. G. Ferrillo and A. Wilson. *J. appl. Polym. Sci.* **21,** 1687 (1977).
5. A. Ballistreri, S. Foti, G. Montaudo, E. Scamporrino, A. Arnesano and S. Calgari. *Makromolek. Chem.* **182,** 1301 (1981).
6. A. Ballistreri, G. Montaudo, C. Puglisi, E. Scamporrino, D. Vitalini and S. Calgari. *J. Polym. Sci., Polym. Chem.* **21,** 679 (1983).
7. C. F. Cullis, M. M. Hirschler and M. A. A. M. Khattab. *Eur. Polym. J.* **20,** 59 (1984).
8. J. C. Gupta, S. Bhatnagar, K. Lal and H. L. Bhatnagar. *Indian J. Textile Res.* **4,** 43 (1979).
9. F. K. Antia, P. J. Baldry and M. M. Hirschler. *Eur. Polym. J.* **18,** 167 (1982).
10. C. F. Cullis, M. M. Hirschler and Q. M. Tao. *Eur. Polym. J.* **27,** 281 (1991).
11. W. C. Kuryla and A. J. Papa. In *Flame Retardancy of Polymeric Materials*, Vol. 3 (edited by W. C. Kuryla and A. J. Papa). Marcel Dekker, New York (1975).
12. E. N. Peters. In *Flame Retardancy of Polymeric Materials*, Vol. 5 (edited by W. C. Kuryla and A. J. Papa), p. 113. Marcel Dekker, New York (1979).
13. C. F. Cullis, M. M. Hirschler and Q. M. Tao. *Eur. Polym. J.* **22,** 161 (1986).
14. E. D. Weil. In *Flame Retardancy of Polymeric Materials*, Vol. 3 (edited by W. C. Kuryla and A. J. Papa), p. 185. Marcel Dekker, New York (1975).
15. J. T. Langley, M. J. Drews and R. H. Barker. *J. appl. Polym. Sci.* **25,** 243 (1980).
16. J. W. Hastie. *J. Res. natn. Bur. Stand.* **77A,** 773 (1973).
17. C. F. Cullis and M. M. Hirschler. *The Combustion of Organic Polymers*. Oxford University Press, Oxford (1981).
18. A. W. Benbow and C. F. Cullis. In *Proc. Comb. Inst. Eur. Symp., Univ. Sheffield*, September 1973, p. 183. Academic Press, New York (1973).
19. A. B. Pepperman, M. F. Margavio and S. L. Vail. *J. Fire Retard. Chem.* **3,** 276 (1976).
20. C. Y. Shen, N. E. Stahlheber and D. R. Dyroff. *J. Am. chem. Soc.* **91,** 62 (1969).
21. G. D. McGinnis, F. Shafizadeh and R. Susott. *Chem. Engng News* **17,** April, 37 (1972).