The flame-retardant effect of diethyl vinyl phosphonate in copolymers with styrene, methyl methacrylate, acrylonitrile and acrylamide

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Diethyl vinyl phosphonate has been free-radically copolymerized with styrene, methyl methacrylate, acrylonitrile and acrylamide to give copolymers containing roughly equal amounts of covalently bound phosphorus. The flammabilities of these copolymers have been assessed, principally by measurements of limiting oxygen index, and compared with those of the corresponding homopolymers: polystyrene, poly(methyl methacrylate), polyacrylonitrile and polyacrylamide. It has been found that all the copolymers are more flame retardant than the corresponding homopolymers, especially the copolymer with acrylamide which appears to display considerable nitrogen–phosphorus synergism.

(Keywords: copolymer; diethyl vinyl phosphonate; flame retardance)

INTRODUCTION

Increasing interest in, and concern about, flame retardance in polymers is being expressed as a consequence of the increased use of polymers in situations where they pose a potential fire hazard, e.g. in structural and decorative applications in domestic, office and transport environments. Conventionally, flame retardance in polymers is achieved through the use of additives, many of which can themselves present hazards in the form of emissions of toxic gases or dense and suffocating smokes, or of which very high concentrations are required in order to be fully effective, with concomitant deleterious effects upon other properties. Consequently, there is a continuing search for flame-retardant systems that do not suffer these disadvantages.

In particular, we have been attracted to searching for ways of chemically modifying polymers to improve flame retardance in the belief that low levels of modification may lead to improvements comparable with those currently achieved by high levels of additives. Initially, we have been looking at modifications with phosphorus-containing groups and have already reported encouraging results from the phosphorylation of poly(vinyl alcohol) and ethylene–vinyl alcohol copolymers and from the phosphonylation of low density polyethylene[1]. Phosphorus-based flame-retardant additives have already been shown by others[2] to offer advantages over, for example, the widely used halogenated flame retardants, some of which can give rise to dense, acidic smokes in a fire.

In this paper we report the results of a study of the influence of covalently bound phosphorus on the flame retardance of polystyrene (PS), poly(methyl methacrylate) (PMMA), polyacrylonitrile (PAN) and polyacrylamide (PAM). On this occasion, the phosphorus has been introduced into the polymers not by chemical modification but by copolymerizations with diethyl vinyl phosphonate (DEVP). PS and PMMA were chosen for study in part because they are important thermoplastic moulding materials but also because they tend to depolymerize in a fire with the consequent production of large quantities of highly volatile and flammable monomers and oligomers[3]. PAN and PAM, on the other hand, tend to decompose by a chain-stripping mechanism in which nitrogen-containing fragments are eliminated from the side-groups, leaving behind, in some circumstances, significant quantities of a carbon-rich char[4]. The choice of PAN and PAM also allows potential phosphorus–nitrogen synergism in flame retardance to be explored; such synergism is not uncommon in additive-based flame-retardant systems[5–7].

EXPERIMENTAL

Materials

All monomers were obtained from the Aldrich Chemical Co. S was freed from 4-*tert*-butylcatechol inhibitor (10–15 ppm) by repeated washing with 10% w/v aqueous NaOH and then with water until the washings were neutral. After drying over $CaSO_4$ for 2 h the S was then distilled under a reduced pressure of nitrogen and stored in the dark at $<0°C$ over molecular sieves until required for use. Similar procedures to those

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outlined above were used to remove the inhibitor (hydroquinone, 10 ppm) from MMA and to further purify the monomer. The hydroquinone monomethyl ether inhibitor (35–45 ppm) in AN was removed by passing the monomer down a column of activated basic alumina. AM was purified by recrystallization from dry dioxane (m.p. 84–86°C) and was then stored in a desiccator until required. DEVP was supplied uninhibited (it shows little tendency to homopolymerize) and was used without purification. Azoisobutyronitrile (AIBN), from BDH, was purified by recrystallization from ethanol. Benzoyl peroxide (BPO) and *tert*-butyl hydroperoxide (TBHP), both from Aldrich, were used without purification; the latter was supplied as a 3 M solution in 2,2,4-trimethylpentane.

Copolymerizations

Copolymers of S, MMA, AN and AM with DEVP were prepared by free-radical copolymerizations, in ampoules *in vacuo*, of monomer mixtures in toluene (for S, MMA and AM) or dioxane (for AN), using either AIBN at 60°C or TBHP at 100°C as initiator, for periods of up to 60 h. The copolymers were recovered by precipitation in absolute alcohol and were dried to constant weight in a vacuum oven. The details of preparation and recovery are summarized in *Table 1*. In attempting to make copolymers containing the desired amount of DEVP (10 mol%), feeds were initially chosen based upon reactivity ratios calculated from published Alfrey-Price Q and e values for the relevant monomers[8]. However, as will be seen below, for AN–DEVP and AM–DEVP the calculated reactivity ratios are not a good guide to the actual behaviour, and for this reason a trial and error approach was adopted to find the optimum feeds to produce copolymers of the desired composition.

Analytical methods

^{1}H n.m.r. spectra were recorded on solutions of copolymers in CDCl$_3$ (for S–DEVP and MMA–DEVP), d$_6$-DMSO (for AN–DEVP) and D$_2$O (for AM–DEVP) using a Jeol PMX 60 MHz n.m.r. spectrometer. From these spectra, the compositions of the copolymers were determined. For S–DEVP this was done by comparing the area of the S phenyl peaks at 6.5–8.0 ppm with the total proton peak area, whilst for MMA–DEVP it was done by comparing the area of the MMA methoxyl peak at 3.7 ppm with the total proton peak area. For both AN–DEVP and AM–DEVP, the compositions were determined by comparing the areas of the DEVP methyleneoxy peaks at 3.8–4.3 ppm with the total proton peak areas.

Thermogravimetric analyses (t.g.a.s, carried out on a Perkin–Elmer TGA-7 thermogravimetric analyser), elemental analyses of copolymers for phosphorus, determinations of heats of combustion by bomb calorimetry and measurements of limiting oxygen index (LOI) were all carried out as described previously[1]. Copolymer sheets for LOI measurements were prepared by pressing samples of the copolymers between mould release papers or Teflon films in a hot press at temperatures of up to 170°C. In order to press satisfactory samples from the S–DEVP copolymer it was necessary to mix it intimately with 27% w/w of the plasticizer, dioctylphthalate. The flame-retardant properties of these samples were therefore compared with those of PS containing the same concentration of plasticizer.

RESULTS

Table 2 lists the compositions of the copolymers determined both by n.m.r. spectroscopy and by phosphorus analysis, and also 'theoretical' compositions calculated

Table 1 Preparation of copolymers

Copolymer	DEVP (g)	Comonomer (g)	Solvent (g)	Initiator (g)	Temp. (°C)	Time (h)	Conversion (% w/w)
S–DEVP	10	25	Toluene, 35	TBHP, 0.46	100	69	78
MMA–DEVP	17	30	Toluene, 48	AIBN, 0.15	60	30	64
AN–DEVP	50	24	Dioxane, 74	AIBN, 0.15	60	3	42
AM–DEVP	50	32	Toluene, 83	AIBN, 0.15	60	5	40

Table 2 Characterization data for copolymers with DEVP and for the parent homopolymers

Polymer	Mol. fract. DEVP in polymer		P content of polymer (wt%)	Mol. fract. DEVP by P anal.	T.g.a. residue (wt%)		P in residue from burning (wt%)	LOI (vol% O$_2$)	ΔH_{comb} (kJ g^{-1})
	Theor.	N.m.r.			in N$_2$	in air			
PS	0	0	–	–	–	0	–	19.0	–
S–DEVP	0.07	0.10	2.6	0.09	0	0	–	–	–
PS(plast.)	0	0	–	–	–	–	–	21.5	–
S–DEVP(plast.)	0.07	0.10	2.0	–	–	–	2.5	28.0	–
PMMA	0	0	–	–	0	0	–	17.1	24.5
MMA–DEVP	0.13	0.18	4.2	0.15	1.3	0	6.2	23.7	18.5
PAN	0	0	–	–	–	0	–	18.3	16.2
AN–DEVP	0.47	0.14	5.7	0.12	23.0	8.8	8.9	27.5	10.9
PAM	0	0	–	–	–	0	–	27.3	15.0
AM–DEVP	0.46	0.19	5.3	0.14	18.0	3.6	9.6	57.9	13.2

from reactivity ratios and allowing for the degree of conversion. Also in *Table 2* are the measured LOI values, heats of combustion, and char yields from t.g.a. runs carried out both in air and in N_2. *Table 2* also contains LOI values for the homopolymers, PS, PMMA, PAN and PAM, and heats of combustion for PMMA, PAN and PAM.

DISCUSSION

Copolymer compositions

In order to assist in making copolymers containing the required amount of DEVP (~10 mol%), reactivity ratios for S-DEVP, MMA-DEVP, AN-DEVP and AM-DEVP were calculated from published Alfrey-Price Q and e values[8] of 1.0 and −0.8 (for S), 0.78 and 0.40 (for MMA), 0.48 and 1.23 (for AN), 0.23 and 0.54 (for AM) and 0.27 and 0.04 (for DEVP). The reactivity ratios so calculated are 2.689 and 0.317 (for S-DEVP), 2.098 and 0.251 (for MMA-DEVP), 0.239 and 0.293 (for AN-DEVP), and 0.513 and 0.806 (for AM-DEVP). Scrutiny of *Table 2* shows that for S-DEVP and MMA-DEVP the measured compositions are not significantly different from those calculated using the reactivity ratios. However, for both AN-DEVP and AM-DEVP, the calculated contents of DEVP are greater than achieved in practice, even allowing for conversion, showing that for these two systems the true reactivity ratios are significantly different from those calculated from the Q and e values.

Flammabilities

As can be seen from *Table 2*, the LOI values for the copolymers are all greater than those for the corresponding homopolymers, indicating that the incorporation of DEVP has a significant effect upon the flame retardance of the polymers. The increase in LOI for the S and MMA copolymers are relatively small (from 21.5 to 28.0 for plasticized PS and from 17.1 to 23.7 for PMMA), probably because both PS and PMMA tend to undergo random and chain-end scission when heated, followed by depolymerization. Under these circumstances, DEVP will tend to be lost from the copolymers and therefore will have a reduced flame-retardant effect. This is reflected also in the negligible char yields for these polymers in the t.g.a. experiments under both nitrogen and air atmospheres and, in the case of PMMA, by the relatively small reduction in the heat of combustion produced by incorporating DEVP. Small amounts of char are, however, obtained when both S-DEVP and MMA-DEVP are burnt, and these chars show some retention of phosphorus, indicating that there may be a small condensed-phase component of the flame-retardant effect of DEVP.

In PS, the main effect of DEVP may be to slightly increase the temperature at which substantial depolymerization occurs and thus to restrict, to a certain extent, the supply of volatile fuel to the locus of combustion. This effect can be seen by comparing the t.g.a. traces of PS and S-DEVP (*Figure 1*) recorded in air. Although S-DEVP appears to begin degrading at about 120°C compared with 250°C for PS, the temperature at which 50% weight loss has occurred in S-DEVP is 470°C, whereas for PS it is 450°C. For PMMA and MMA-DEVP, a similar effect is observed (*Figure 2*),
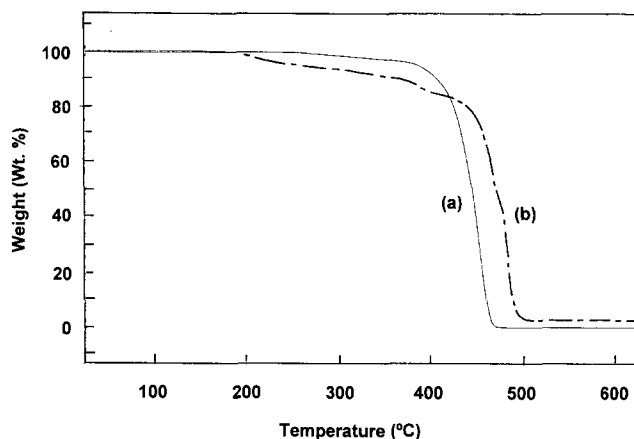
Figure 1 T.g.a. traces recorded with heating in air at 20°C for (a) polystyrene and (b) styrene-diethyl vinyl phosphonate copolymer
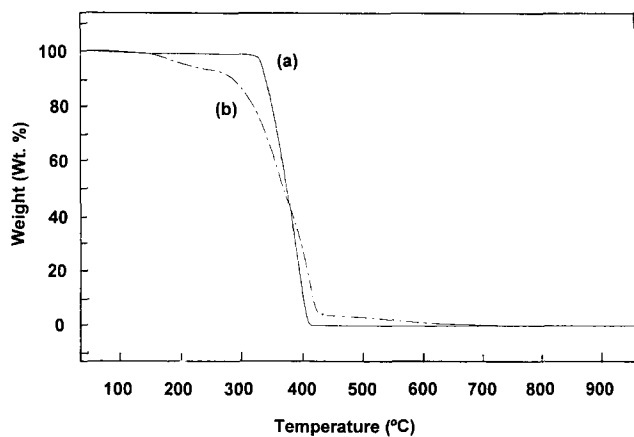
Figure 2 T.g.a. traces recorded with heating in air at 30°C for (a) poly(methyl methacrylate) and (b) methyl methacrylate-diethyl vinyl phosphonate copolymer

with MMA-DEVP beginning to degrade at a lower temperature than PMMA but degrading less precipitously as the temperature is raised.

With AN and AM, the effects of incorporating DEVP are more pronounced. In both cases, comparisons of the t.g.a. traces recorded in air for the copolymers and for the parent homopolymers (*Figures 3* and *4*) indicate pronounced increases in thermo-oxidative stability brought about by the incorporation of DEVP. In both t.g.a. and combustion experiments on the copolymers, significant quantities of incombustible char are produced, and these chars have phosphorus contents significantly greater than those of the starting copolymers (see *Table 2*). Here, there would seem to be a clear indication of a flame-retardant effect of DEVP involving, in part at least, a condensed-phase mechanism, i.e. some protection of the polymer from the advancing flame front by the formation, during combustion, of a phosphorus-rich incombustible char layer. Such a mechanism of flame-retardation is well known in phosphorus-based additive flame-retardant systems[2]. Nevertheless, as we have shown with phosphorylated poly(vinyl alcohol) and ethylene-vinyl alcohol copolymers[1], there must also be a significant gas-phase component to flame retardation; the amounts of char produced in both the t.g.a. and the combustion experiments are relatively small and yet the effects on LOI are quite large (particularly for AM-DEVP).
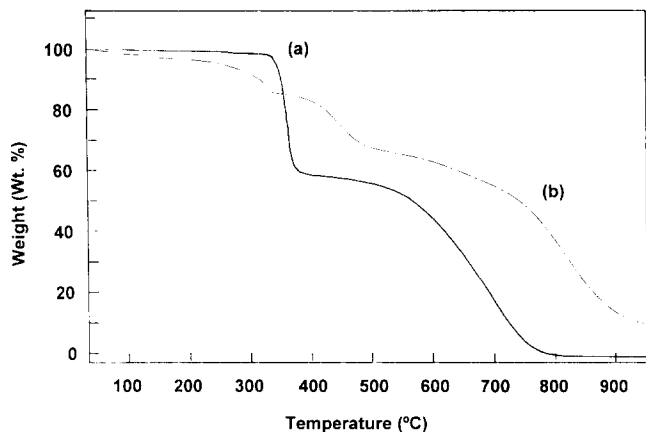
Figure 3 T.g.a. traces recorded with heating in air at 30°C for (a) polyacrylonitrile and (b) acrylonitrile–diethyl vinyl phosphonate copolymer
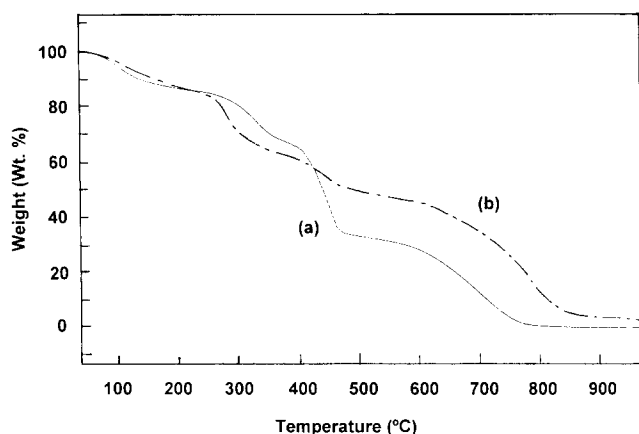

Figure 4 T.g.a. traces recorded with heating in air at 30°C for (a) polyacrylamide and (b) acrylamide–diethyl vinyl phosphonate copolymer

With AM–DEVP there is also clear evidence of nitrogen–phosphorus synergism. Whereas the addition of 5.7% by weight of phosphorus in the form of DEVP to PAN increases the LOI by 51% (i.e. from 18.3 to 27.5), the incorporation of a slightly smaller amount of phosphorus (5.3% by weight), in the form of DEVP in PAM, raises the LOI by 112% (i.e. from 27.3 to 57.9). Nitrogen–phosphorus synergism is well known in flame retardance, as pointed out above, and has been exploited in such flame-retardant additives as N-methylolacetamide/phosphonate combinations[9,10]. In AM–DEVP, the formation of an incombustible char and hence the

increase in flame retardance may be aided by the formation of phosphoramide structures which serve to crosslink the polymer chains and help to maintain their integrity during the early stages of combustion (*Scheme 1*).
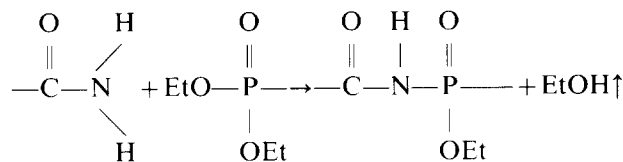
Scheme 1

CONCLUSIONS

The incorporation of DEVP into PS and PMMA has only a very small effect upon flame retardance as gauged from LOI measurements. With PAN, and especially with PAM, the effect of DEVP is much more significant, with clear evidence for a pronounced flame-retardant effect operating probably through both condensed-phase and gas-phase mechanisms. In AM–DEVP, there is also evidence for nitrogen–phosphorus synergism.

ACKNOWLEDGEMENTS

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