

A new polymeric flame retardant additive for vinyl polymers

Subramanian Sundarrajan, Kaushal Kishore & Kannan Ganesh*

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India

Received 29 May 2000; revised 10 October 2000

Diethyl allyl phosphate (DEAP) monomer has been synthesized, and characterized, using ^1H NMR and direct ionization mass spectrometric (DI-MS) techniques. It was free-radically polymerized to yield the poly(diethyl allyl phosphate) (PDEAP). The direct pyrolysis-mass spectrometric (DP-MS) analysis of the PDEAP revealed that it undergoes thermal degradation to yield mainly the monomer. Utility of PDEAP as a potent flame-retardant additive in polystyrene (PS) and poly(methyl methacrylate) (PMMA) has also been established.

Increased interest in the flame retardancy of commercial vinyl polymers is well recognised. Flame retardancy is generally imparted by adding low molecular weight flame retarding additives such as tricresyl phosphate to the substrate polymer. Absence of interaction between flame retardant additive and the substrate polymer usually leads to the phase separation of the former, resulting in the deterioration of flame retardant properties with time on account of the additive's migration and volatile loss^{1,2}. To overcome this drawback, work is being pursued in our laboratory on the synthesis of polymeric flame retardant additives³⁻¹⁵. Due to the high molecular weight of these additives, even if there is no interaction with the substrate polymer, the problems due to migration and volatile loss are significantly curtailed.

In this paper, we report the synthesis and characterization of a new flame retardant polymer namely, poly(diethyl allyl phosphate) (PDEAP), and its effect on the char yield of polystyrene (PS) and poly (methyl methacrylate) (PMMA). PS and PMMA were chosen as the substrate polymers, in the present study, as they are widely used commodity thermoplastics.

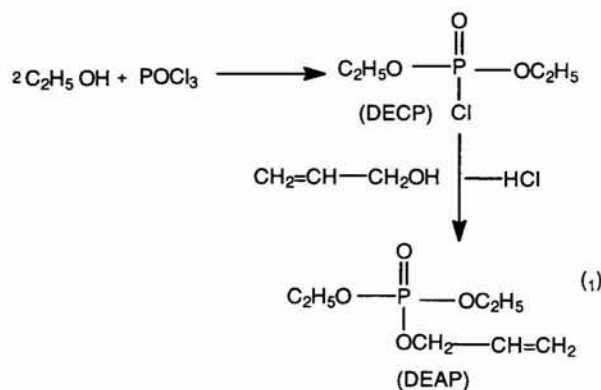
Materials and Methods

The monomers, styrene and methyl methacrylate (MMA) were freed from inhibitor by repeated washing with aqueous NaOH and then with water until the washings became neutral. After drying over

anhydrous Na_2SO_4 , the monomers were distilled under reduced pressure.

Preparation of DEAP

Freshly distilled ethanol (18.4 g, 0.4 mol) was slowly added from a dropping funnel to ice-cold POCl_3 (34.4 g, 0.2 mol) in a 100 ml round bottom flask fitted with a condenser, mechanical stirrer and a CaCl_2 guard tube. The reaction mixture was stirred at room temperature for 5 h. Diethyl chloro phosphate (DECP, Eq. 1) thus formed was vacuum distilled. Dried allyl alcohol (4.04 g, 0.07 mol) was added dropwise to the ice-cold diethyl chloro phosphate (12.09 g, 0.07 mol) under constant stirring, and the reaction mixture was kept at room temperature for 5 h to yield the diethyl allyl phosphate (DEAP) monomer (Eq. 1).



Polymerizations

Homopolymers of DEAP, styrene and MMA were prepared by free-radical polymerization using AIBN initiator at 60°C for 10 h under vacuum in sealed ampoules. The polymers were precipitated using methanol, and dried to a constant weight. For PDEAP, petroleum ether was used as the non-solvent.

Preparation of PS/PDEAP and PMMA/PDEAP blends

PS (90 mg) and PDEAP(10 mg) were codissolved in CHCl_3 and subsequently vacuum dried to get the blend of PS/PDEAP (90/10). By replacing PS with the same amount of PMMA, using the same procedure, PMMA/PDEAP blend was prepared.

Analytical Methods

^1H NMR spectra were recorded in CDCl_3 on a Bruker AC/F 200 NMR spectrometer using TMS as the internal standard. ^{31}P NMR spectra were recorded on a Bruker AMX-400 NMR spectrometer under broad band ^1H decoupling conditions. Phosphoric acid (85%) was used as the external standard. Direct ionization mass spectrometry (DI-MS) and the direct pyrolysis -mass spectrometry (DP-MS) were carried out using the direct insertion probe of JEOL-JMS-DX-303-GC-mass spectrometer, heated from 30 °C to 500 °C at a heating rate of 32 °C/min. Electron Ionization was kept at 25 eV.

Results and Discussion

Characterization of DEAP monomer

The ^1H NMR spectrum of DEAP in CDCl_3 is presented in Fig.1. Among the vinylic protons, the CH proton shows a multiplet between δ 5.7 and 6.1 ppm while the CH_2 protons show a signal in the range δ 5.1-5.5 ppm. The O- CH_2 resonance of the ethoxy groups is centered in the region δ 4.0-4.7 ppm and the CH_3 group appears at δ 1.2-1.5 ppm. The DI-MS spectrum of DEAP monomer is shown in Fig.2. The molecular ion (M^+) peak is observed at m/z 194. The base peak at m/z 99 is due to MH^+ ion of phosphoric acid and the other structures corresponding to different fragment ions are presented in Table I.

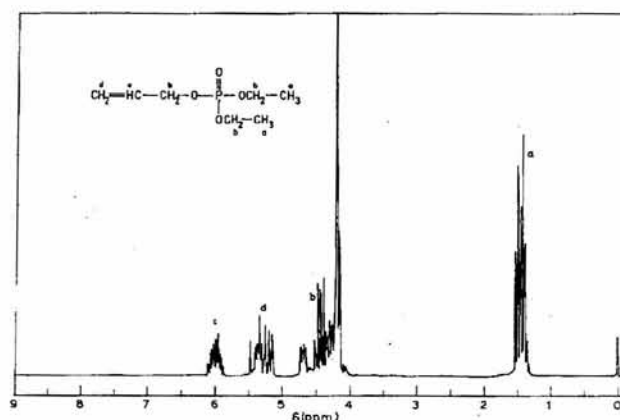


Fig. 1 — ^1H NMR spectrum of DEAP in CDCl_3 .

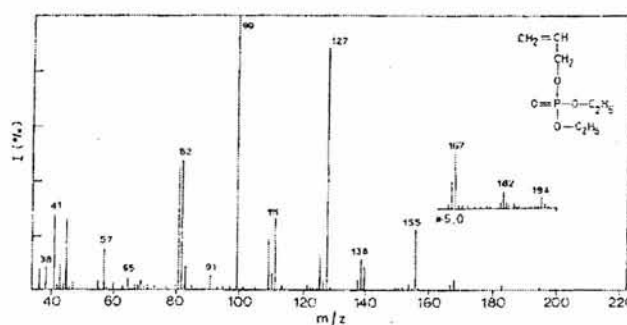


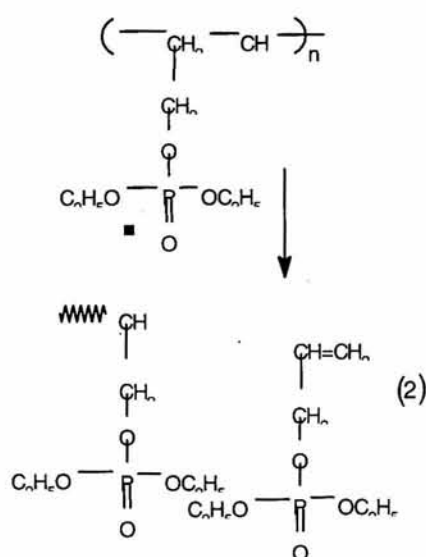
Fig. 2 — DI-MS of DEAP recorded at 240 °C (EI, 25 eV).

Characterization of PDEAP

Figure 3 displays the ^1H NMR spectrum of the PDEAP in CDCl_3 . The backbone CH and CH_2 as well as the CH_3 protons of the pendent ethoxy group merge and absorb between δ 1.3 and 1.5 ppm. The -O- CH_2 protons appeared as a multiplet between δ 4.0 and 4.4 ppm.

DP-MS analysis of PDEAP

In brief, the DP-MS technique involves the introduction of the polymer sample into the mass spectrometer through the direct insertion probe, and the temperature is gradually increased up to a point at which thermal degradation occurs; the primary products are then ionized and detected immediately¹⁶⁻²¹. Figure 4 presents the 25 eV DP-MS of PDEAP recorded at 240 °C. The DP-MS of the polymer (Fig. 4) is very similar to the DI-MS of the monomer (see Fig. 2), indicating that PDEAP degrades mainly through an unzipping mechanism forming the monomer (Eq. 2).



Char yield determination of PS/PDEAP and PMMA/PDEAP blends

In order to study the influence of PDEAP on the flame retardancy of PS and PMMA, the char yields of their blends, i.e., PS/PDEAP (90/10) and PMMA/PDEAP (90/10) and neat PDEAP were determined by keeping the samples at 500 °C for 30, 60, 90 and 120 min. The percentage char obtained against the time is shown in Fig. 5.

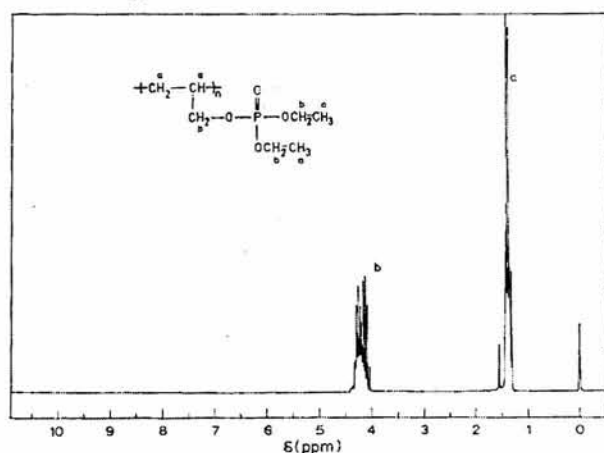


Fig. 3 — ^1H NMR spectrum of PDEAP in CDCl_3 .

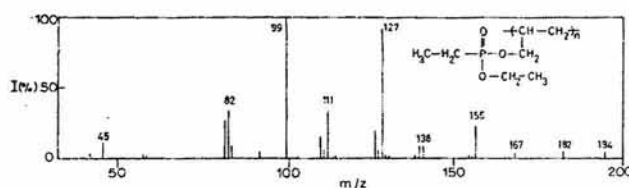


Fig. 4 — DP-MS of PDEAP recorded at 240 °C (EI, 25 eV).

Table 1 — The molecular ion and fragment ions observed in the

DI-MS of DEAP monomer Structure	m/z
$\text{CH}_2=\text{CH}-\text{CH}_2^+$	41
$\text{CH}_3-\text{CH}_2-\text{O}^+$	45
$\text{CH}_2=\text{CH}-\text{CH}_2-\text{O}^+$	57
$[\text{H}_3\text{PO}_3]^+$	82
$[\text{H}_3\text{PO}_4]^+$	99(MH^+)
$\left[\begin{array}{c} \text{OH} \\ \\ \text{O}=\text{P}-\text{OH} \\ \\ \text{O}-\text{CH}_2 \end{array} \right]^+$	111
$\left[\begin{array}{c} \text{OH} \\ \\ \text{O}=\text{P}-\text{OH} \\ \\ \text{O}-\text{C}_2\text{H}_5 \end{array} \right]^+$	127
$\left[\begin{array}{c} \text{O}-\text{C}_2\text{H}_5 \\ \\ \text{O}=\text{P} \\ \\ \text{O}-\text{C}_2\text{H}_5 \end{array} \right]^+$	138
$\left[\begin{array}{c} \text{O}-\text{C}_2\text{H}_5 \\ \\ \text{O}=\text{P}-\text{OH} \\ \\ \text{O}-\text{C}_2\text{H}_5 \end{array} \right]^+$	155
$\left[\begin{array}{c} \text{O}-\text{C}_2\text{H}_5 \\ \\ \text{O}=\text{P}-\text{OCH}_2 \\ \\ \text{O}-\text{C}_2\text{H}_5 \end{array} \right]^+$	167
$\left[\begin{array}{c} \text{O}-\text{C}_2\text{H}_5 \\ \\ \text{O}=\text{P}-\text{O}-\text{CH}_2-\text{CH}_2 \\ \\ \text{O}-\text{C}_2\text{H}_5 \end{array} \right]^+$	182
$\left[\begin{array}{c} \text{O}-\text{C}_2\text{H}_5 \\ \\ \text{O}=\text{P}-\text{O}-\text{CH}_2-\text{CH}=\text{CH}_2 \\ \\ \text{O}-\text{C}_2\text{H}_5 \end{array} \right]^+$	194

Char yield decreases with increase in time indicating continued degradation and volatile loss. It is to be noted here that neat PS or PMMA do not form any char. The significant char formation observed for the PS and PMMA blends here indicates that PDEAP is a good polymeric flame retardant additive. Generally, phosphorus containing flame retardants act through a condensed phase mechanism

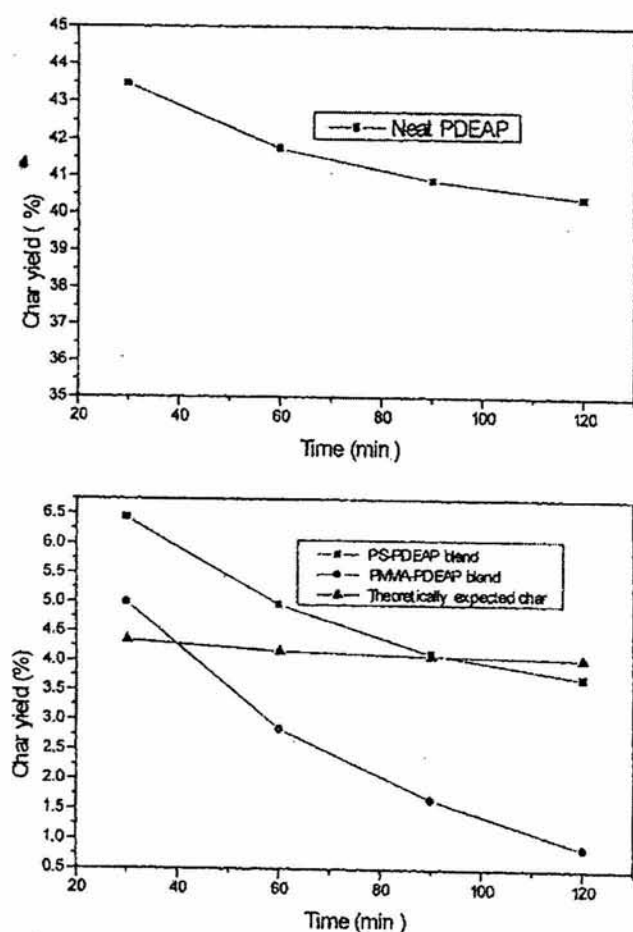


Fig. 5 — Variation of char yields of PDEAP, PS/PDEAP and PMMA/PDEAP blends with time.

involving char formation. Char basically acts as a protective barrier between the flame and virgin polymer that prevents further decomposition of the polymer ultimately leading to quenching of the flame.

To get further insight into the char formation process, char profiles of the PS and PMMA blends were compared with theoretically expected char in absence of any interaction between PS & PDEAP and PMMA & PDEAP in the blend. The results are shown in Fig.5. The difference between experimental and theoretical char values clearly indicates that there is considerable interaction between PMMA & PDEAP, and PS & PDEAP during the degradation process. In the absence of any interaction, both the experimental and theoretical values of the char should have been the same.

At lower times, the char yield is higher for both PS/PDEAP, and PMMA/PDEAP blends compared to the theoretically expected char value. Under

Table 2 — Char yield data of DEAP, PDEAP, and blends

Sample	%Char yield
DEAP	38.32
PDEAP	43.46
PS-DEAP blend (90/10)	5.49
PS-PDEAP blend (90/10)	6.43
PMMA-DEAP blend (90/10)	3.96
PMMA-PDEAP blend (90/10)	4.99

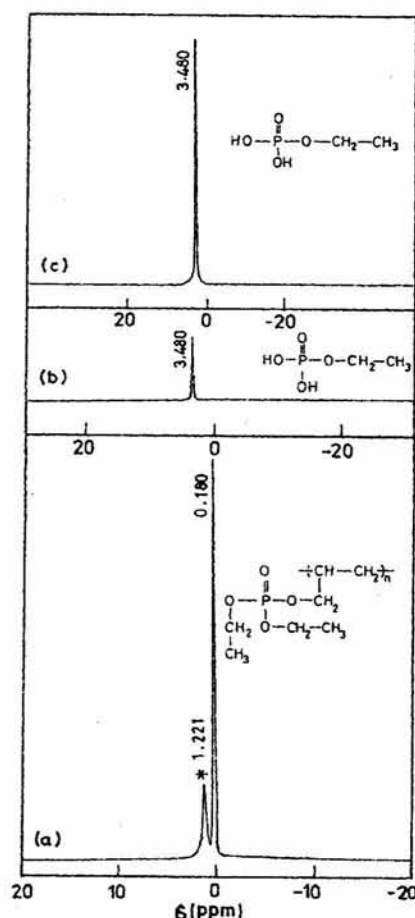


Fig. 6 — ³¹P NMR spectra of (a) neat PDEAP in CDCl₃, (b) methanol extract of PDEAP char, and (c) methanol extract of PS/PDEAP (90/10) char [*—small amounts of impurity].

combustion conditions, the residence time available for the polymer to undergo degradation is very low. Hence, the results of char yield at lower times are more relevant in the actually polymer combustion process. These results suggest that PDEAP is a potent

fire retardant for both PS and PMMA. However, PDEAP is more effective in PS than PMMA because PS itself has aromatic structure in its backbone. It is well known that aromatic structures promote char formation.

As the degradation time is increased, the char yield in PS and PMMA decreases considerably compared to PDEAP so much so that beyond 90 min., the char yield falls below the theoretically expected char value. This suggests that at higher degradation times both PS and PMMA significantly influence the char formation process in PDEAP. It may be noted that in phosphates, H_3PO_4 is the main species which is responsible for inducing char formation via a dehydration process (refer to next section). The low char yield in the blend at higher degradation times clearly indicates that the DEAP monomer, during PDEAP degradation, does not break-up fast enough to produce acids in the presence of volatile monomers produced from PS and PMMA. The actual mechanism, however, needs deeper investigation.

Since the DP-MS analysis of PDEPA revealed the formation of the monomer as the main degradation product, the same should be observed during the polymer combustion too. To confirm this phenomena, char yields of DEAP, PDEAP, and the blends of PS/DEAP(90/10) and PS/PDEAP (90/10) at 500 °C for, 30 min. were determined (Table 2). Since the values obtained are very similar, this observation confirms the conclusion arrived at on the basis of DP-MS data that PDEAP, during burning also, first depolymerizes to DEAP monomer which further decomposes to form the char.

³¹P NMR spectroscopic analysis of the char residue

To further understand the mechanism of char formation process, ³¹P NMR spectra of neat PDEAP and its char, as well as the char of PS/PDEAP (90/10) blend were recorded using H_3PO_4 as the external standard (Fig. 6). The peak appearing at δ 3.4 ppm for the methanol extract of char (Fig. 6b & 6c) has been attributed to the phosphoric acid monoester

($C_2H_5OP(O)(OH)_2$)²². It is reported in literature that polyphosphate polymers generally produce the char through the formation of phosphoric acid²³. Here, the monoester of phosphoric acid is considered to be the intermediate before the formation of H_3PO_4 .

References

- 1 Troitzsch J H, *Prog org Coat*, 11 (1983) 41.
- 2 Sears J K & Touchette N W, in *Encyclopedia of chemical technology*, edited by R Kirk & D Othmer (John Wiley & Sons, New York), Vol.18, (1982) p. 111.
- 3 Annakutty K S & Kishore K, *Polymer*, 29 (1988) 756.
- 4 Kishore K, Annakutty K S & Mallick I M, *Polymer*, 29 (1988) 762.
- 5 Annakutty K S & Kishore K, *Polymer*, 29 (1988) 1273.
- 6 Kishore K & Kannan P, *J polym Sci Part A: Polym Chem*, 28 (1990) 3481.
- 7 Kishore K, Kannan P & Iyanar K, *J polym Sci Part A: Polym Chem*, 29 (1991) 1039.
- 8 Kishore K & Kannan P, *Polym Bull*, 24 (1990) 481.
- 9 Annakutty K S & Kishore K, *Makromol Chem.*, 192 (1991) 11.
- 10 Kannan P, Umamaheswari N & Kishore K, *J appl Polym Sci*, 56 (1995) 113.
- 11 Kannan P & Kishore K, *Angew Makromol Chem*, 206 (1993) 63.
- 12 Kannan P & Kishore K, *Polymer*, 33 (1992) 418.
- 13 Kannan P & Kishore K, *Eur Polym J*, 27 (1991) 1017.
- 14 Kannan P, Gangadhara K & Kishore K, *Polymer*, 32 (1991) 1909.
- 15 Annakutty K S & Kishore K, *J scient & ind Res*, 48 (1989) 479.
- 16 Kishore K & Ganesh K, *Macromolecules*, 26 (1993) 4700.
- 17 Ganesh K & Kishore K, *Macromolecules*, 29 (1996) 26.
- 18 Montaudo G, Puglisi C, de Leeuw J W, Hartgers W, Kishore K & Ganesh K, *Macromolecules*, 29 (1996) 6466.
- 19 Ganesh K & Kishore K, *J scient & ind Res*, 54 (1995) 383.
- 20 Foti S, Montaudo G, in *Analysis of polymer systems*, edited by L S Bark, N S Allen (Applied Science Publishers Ltd., London), 1982, 103.
- 21 Montaudo G, Puglisi C, Blazso M, Kishore K & Ganesh K, *J Anal and Appl Pyrolysis*, 29 (1994) 207.
- 22 Ionin B I & Ershov B A, *NMR spectroscopy in organic chemistry* (Plenum Press, New York), 1970.
- 23 Hinderstein R R & Witschard G, in *Flame retardancy of polymeric materials*, edited by W C Kuryla & A J Papa (Marcel Dekker, New York), Vol. 4, 1978.