

Fire-Retardant Copolymer of Acrylonitrile with *O,O*-Diethyl-*O*-allyl Thiophosphate

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ABSTRACT: A novel halogen-free flame retardant, *O,O*-diethyl-*O*-allyl thiophosphate (DATP), which simultaneously contained phosphorus and sulfur, was synthesized through a simple method. The structure of DATP was characterized by Fourier transform infrared spectroscopy, ¹H-NMR, and mass spectroscopy. The flame-retardant copolymer was obtained by the free-radical copolymerization of DATP with acrylonitrile. The flammability and thermal degradation characteristics of the copolymer were assayed by limiting oxygen index measurement, thermogravimetric

analysis, and differential scanning calorimetry. The results show that the incorporation of a small percentage of DATP into the copolymer had a significant effect on the retarding combustion of the copolymer, with the limiting oxygen index of the copolymer reaching 28.5% and the char yield being 68.63 wt % at 554°C. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 1489–1494, 2010

Key words: copolymerization; flame retardance; thermogravimetric analysis (TGA)

INTRODUCTION

Flame retardants have been widely used for polymers; halogenated compounds are the most widely used flame retardants for their excellent flame resistance. However, halogenated fire retardants have some deadly defects because toxic and corrosive hydrogen halide can be released, and more seriously, potentially carcinogenic brominated furans and dioxins may form during combustion.¹ With regard to environmental protection, a growing demand to prevent the generation of such toxic substances during thermal degradation has led to the development of non-halogen-containing flame-retardant polymers.^{2–6}

In recent years, phosphorus-, nitrogen-, and silicon-containing compounds have been considered environmentally friendly flame retardants and have developed rapidly because no or less harm to the environment occurs when they burn in a fire.^{1,7–14}

Phosphorus-containing flame retardants perform their flame retardancy in the condensed phase and increase the amount of carbonaceous residue or char during the process of decomposition, which can hinder the transfer of mass and heat during a fire.^{8,10,15–20}

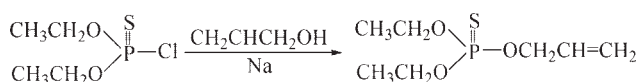
Nitrogen-containing flame retardants are also eco-friendly because there are no dioxin and hydrogen halide acid byproducts and there is a low evolution of smoke during combustion.

Silicon-containing flame retardants can significantly improve the flame retardancy of a polymer through both char formation in the condensed phase and the trapping of active radicals in the vapor phase.^{21–27} Sulfur-containing compounds are also effective flame retardants,^{28–32} although few researchers have paid attention to them.

Flame-retardant polyacrylonitrile (PAN) has long been achieved through the use of comonomers containing halogens, which are commonly called *modacrylics*. These comonomers include vinylidene chloride, vinyl chloride, and the corresponding bromides.³³ Some phosphorus-containing flame retardants have been already applied to PAN fibers and fabrics and were found to be suitable for these applications.^{34–37} However, there have been few reports in recent years by researchers who have studied flame retardants simultaneously containing sulfur and phosphorus.^{28,29,38,39}

Herein, we describe the flame retardant *O,O*-diethyl-*O*-allyl thiophosphate (DATP), which contains phosphorus and sulfur fire-retardant elements simultaneously. The structure was confirmed by Fourier transform infrared (FTIR), ¹H-NMR, and mass spectroscopy (MS). It was applied as a comonomer to copolymerize with acrylonitrile (AN) to obtain a fire-retardant copolymer to improve its fire performance. The limiting oxygen index (LOI)

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Scheme 1 Synthesis route of DATP.

values were tested, and the thermal properties of the copolymer were also studied.

EXPERIMENTAL

Materials

AN (analytically pure, Tianjin Reagent Factory, Tianjin, China) was distilled after it was dried over anhydrous calcium hydride. *O,O*-Diethyl thiophosphoryl chloride (>99%) and allyl alcohol (analytically pure, Nanjing Muke Co., Ltd., Nanjing, China) were dried over anhydrous sodium sulfate and distilled before use. Azobisisobutyronitrile (AIBN; Tianjin Reagent Factory) was purified by recrystallization from ethanol. Dimethylformamide (DMF; analytically pure, Tianjin Reagent Factory) was dried over anhydrous magnesium sulfate. Sodium and sodium thiocyanate (analytically pure, Tianjin Reagent Factory) were used as received.

Instrumentation

$^1\text{H-NMR}$ (300-MHz) spectra of DATP and the copolymer were obtained in CDCl_3 and hexadeuterated dimethyl sulfoxide ($\text{DMSO-}d_6$), respectively, on an AC-P200 spectrometer (Bruker, Switzerland) with TMS as an internal standard. MS was performed by 5973N MS apparatus (Agilent). FTIR spectra were recorded on a Vector 22 spectrometer (Bruker, Germany) with KBr pellets in the range of 400–4000 cm^{-1} . Differential scanning calorimetry (DSC) analysis was carried out on a DSC7 instrument (PerkinElmer) at a heating rate of 10 K/min in the range 298.15–823.15 K under a nitrogen flow, and samples of approximately 5–10 mg in weight were sealed in hermetic aluminum pans. LOI values were tested on an FTA oxygen index testing apparatus (England). X-ray diffraction spectra was obtained on a D8 DISCOVER with a general area detector diffraction system X-ray diffraction apparatus (Bruker AXS, 3 kV, 80 mA) at a rate of $2^\circ/\text{min}$ in the range $10\text{--}45^\circ$. Thermogravimetry (TG) and differential thermogravimetry (DTG) analysis for the copolymer were conducted on a STA 409 PC thermal analyzer (Netzsch, Germany) under a nitrogen stream at a flow rate of 20 mL/min with a heating rate of $10^\circ\text{C}/\text{min}$ from room temperature to 600°C . Elemental analysis was performed on PE 2400 II elemental analyzer (PerkinElmer).

Synthesis of DATP

Allyl alcohol (20.4 mL, 0.30 mol) and sodium (6.9 g, 0.3 mol) were added to a 250-mL, round-bottom, four-necked flask equipped with a magnetic stirrer, condenser, dropping funnel, and thermometer, and the reaction was kept at room temperature for 2 h; then, *O,O*-diethyl thiophosphoryl chloride (47.94 mL, 0.305 mol) was dropped into the flask at a speed of 10 drops/min. The reaction was kept at reflux for 8 h to obtain a yellow liquid. The crude product was purified with column chromatography with ethyl acetate and trichloromethane as eluent to obtain a colorless liquid: yield = 53.6 g (85%) and bp = 85°C at 0.9 MPa. The reaction is shown in Scheme 1. The instrumental analysis results for the DATP were as follows:

FTIR (KBr, cm^{-1}): 2987.6, 2941.3 ($-\text{CH}_3$, $-\text{CH}_2-$); 1645.2 ($\text{C}=\text{C}$); 1257.5 ($\text{C}-\text{O}$); 1024.2 ($\text{P}-\text{O}-\text{C}$); 761.8, 972.1 ($\text{P}=\text{S}$). $^1\text{H-NMR}$ (300 MHz, CDCl_3): 1.319–1.366 (triplet, 6H, e), 4.144–4.173 (quartet, 4H, d), 4.538–4.589 (triplet, 2H, c), 5.238–5.272 (multiplet, 1H, b), 5.906–5.998 (multiplet, 2H, a; see Fig. 1 for the spectrum). MS (m/z , %): 210 (M^+ , 100), 182 (12), 170 (13), 154 (27), 138 (32), 121 (40), 97 (83), 57 (16), 41 (55; see Fig. 2 for the spectrum).

Synthesis of the copolymer

AN (16 g) and DATP (4 g) were added to a 250-mL, round-bottom, three-necked flask equipped with a mechanical stirrer, thermometer, and tube to introduce nitrogen gas into the flask. AIBN was dissolved in DMF and then added to the flask. The reaction was kept at 55°C for 4 h to obtain viscous

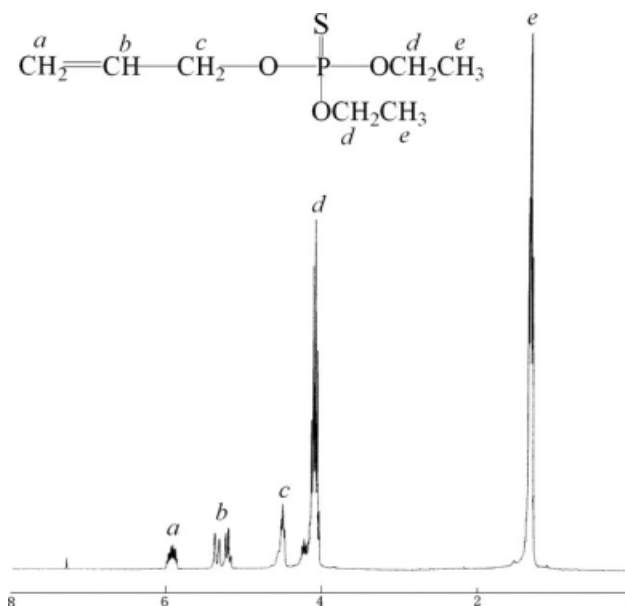


Figure 1 $^1\text{H-NMR}$ spectrum of DATP.

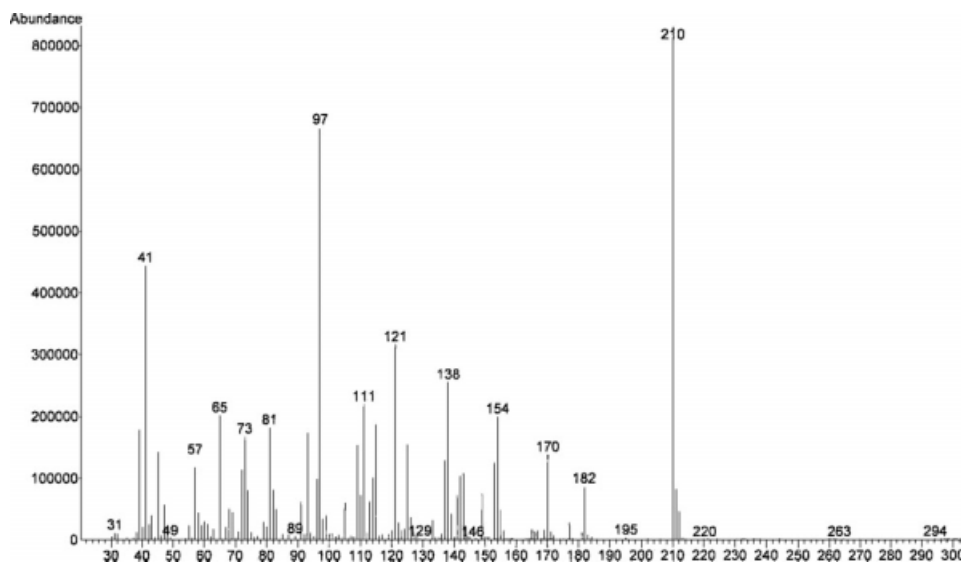


Figure 2 MS spectrum of DATP.

substance, which was washed with deionized water many times to remove the unreacted monomer and the homopolymer, and dried *in vacuo* at 50°C for 6 h to obtain a white powder, that is, the pure copolymer poly(*O,O*-diethyl-*O*-allyl thiophosphate-*co*-acrylonitrile). Figure 3 illustrates the $^1\text{H-NMR}$ spectrum of the copolymer. The signals at 1.232–1.277 and 4.019–4.097 ppm corresponded to the methyl and methylene protons of OCH_2CH_3 , respectively. The signal at 3.151–3.324 ppm was attributed to the methine adjacent to the CN group. The integration ratio of a/b/c/d/e/f near 4 : 1 : 1 : 2 : 4 : 6 confirmed that DATP was copolymerized with AN. The results of N and S elemental analyses were 5.24 and

11.80%, respectively. So the mass fraction of the AN comonomer in the copolymer was 81.3%, and that of DATP was 18.7%.

PAN was synthesized with the same polymerization process and treated with the same method.

RESULTS AND DISCUSSION

Characterization of the copolymer of DATP with AN

Figure 4 presents the FTIR spectra of PAN and the copolymer. The two curves had the characteristic absorption peak of the saturated C–H bond

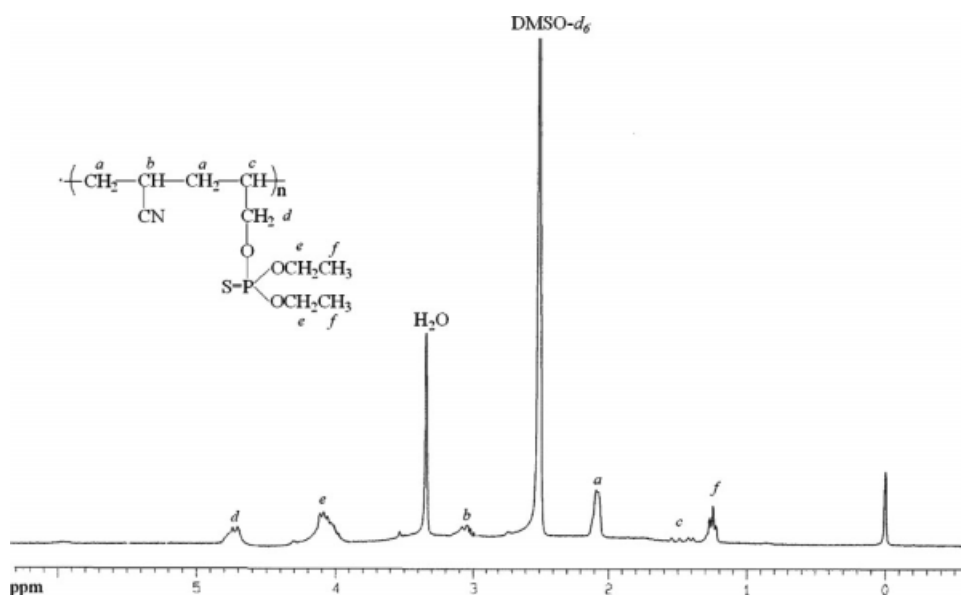


Figure 3 $^1\text{H-NMR}$ spectrum of the copolymer.

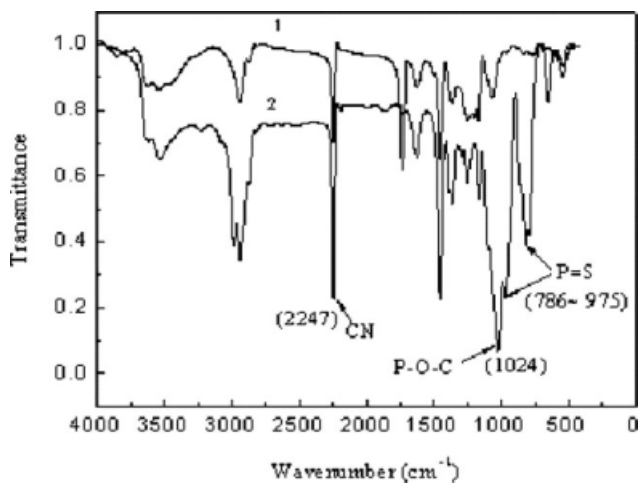


Figure 4 FTIR spectra of (1) PAN and (2) the copolymer.

stretching vibration of the $\text{CH}_3\text{CH}_2\text{O}$ group ($2986\text{--}2939\text{ cm}^{-1}$) and the stretching vibration of the $\text{C}\equiv\text{N}$ group (2247 cm^{-1}). In the second curve of the copolymer, the stretching vibration of $\text{P}\text{--}\text{O}\text{--}\text{C}$ (1024 cm^{-1})⁴⁰ and the bending vibration of $\text{P}=\text{S}$ ($786\text{--}975\text{ cm}^{-1}$) peaks were observed, which showed that the DATP was really copolymerized with AN.

Figure 5 presents the DSC traces of PAN and the copolymer. It was obvious that the copolymer began to decompose at 220°C , and the decomposition temperature ranged from 220 to 350°C , which was broader than the scale of PAN ($260\text{--}320^\circ\text{C}$). This may be explained by the fact that DATP in the copolymer changed the cyclization mechanism from a radical mechanism of PAN to an ionic mechanism of the copolymer,^{41,42} and the speed of the cyclization reaction induced by ion was faster than that of the cyclization reaction induced by radicals. So the exothermic peak of the copolymer was broader than that of PAN; that is, the introduction of DATP slowed down the speed of the exothermic reaction.⁴³

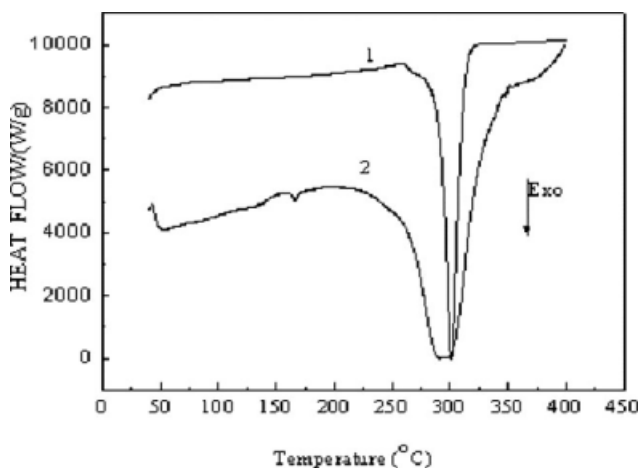


Figure 5 DSC spectra of (1) PAN and (2) the copolymer.

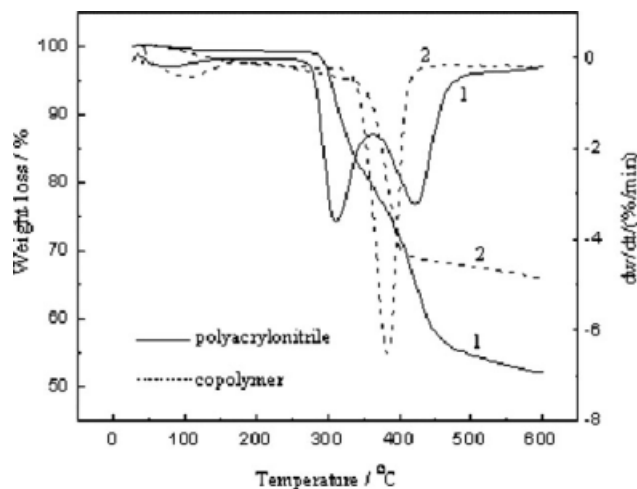


Figure 6 TG-DTG curves of (1) PAN and (2) the copolymer.

The TG-DTG curves are listed in Figure 6. Both the PAN and copolymer TG curves showed two stages of weight loss. In the TG curve of PAN, the first weight loss step took place from 282 to 360°C with a $19.8\text{ wt}\%$ weight loss. The DTG curve of PAN in this step showed that the fastest weight loss was at 310°C . The second one was from 397 to 480°C with about a $22.4\text{ wt}\%$ weight loss, and the fastest weight loss was at 421°C , which was consistent with the peak temperature of the DTG curve of PAN of this stage. However, the TG curve of the copolymer showed that there was about a $4.7\text{ wt}\%$ weight loss during the first weight loss stage, and the weight loss took place from 60 to 310°C , whereas in the second weight loss stage, there was about a $28\text{ wt}\%$ weight loss taking place from 353 to 400°C . The DTG curve of the copolymer showed that the fastest weight loss of this weight loss period was at 383°C , and the char residue was at about $68.6\text{ wt}\%$ at 554°C , which was higher than that of PAN at the same temperature. This may be interpreted to mean that the introduction of DATP into the copolymer changed the cyclization mechanism from a radical mechanism of PAN to an ionic mechanism of the copolymer,^{41,42} and the speed of the cyclization reaction induced by ions was faster than that of the cyclization reaction induced by radicals. So the exothermic peak of the copolymer was broader than that of PAN (shown in Fig. 5); that is, the mass loss of the copolymer was slower than that of PAN. At the same time, DATP decomposed at higher temperatures to form phosphoric acid and polyphosphoric acid, which cover the surface of a fire-retardant system to prohibit heat from being delivered and combustible volatile gases from being released and catalyze the carbon skeleton structure to form a stabilized carbon network, which promotes the amount of char forming to increase.⁴⁴⁻⁴⁶

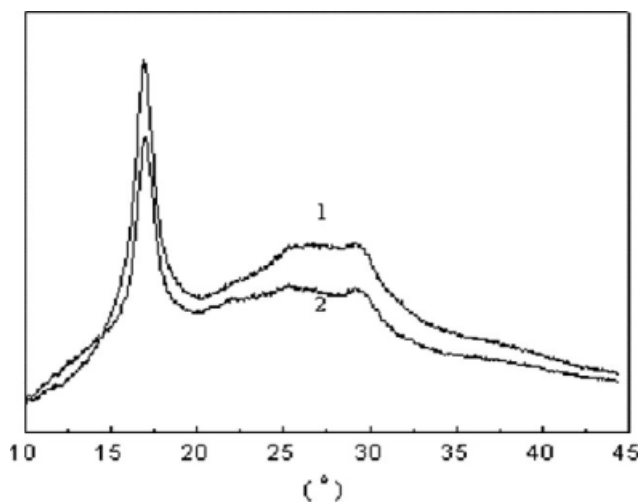


Figure 7 X-ray diffraction of (1) PAN and (2) the copolymer.

Figure 7 shows the X-ray diffraction of the copolymer. The strongest diffraction peak intensity of PAN was at 16.88 (2θ), whereas the figure of the copolymer was almost the same as that of PAN. However, the intensity and the half-width of the diffraction peak of the copolymer dropped, which suggested that the degree of crystallinity increased a little because the incorporation of DATP into the copolymer reduced the polar interaction of cyano in the copolymer and increased the activity of the molecular chain. This caused many more cyano groups to go into the crystal zone, which resulted in an increase in the crystallinity.⁴⁷ The crystallinities of PAN and the copolymer were 43.21 and 46.17%, respectively, according to the calculation.

Flame-retardant properties

The 10 wt % copolymer (81.3 wt % AN and 18.7 wt % DATP) was dissolved in an aqueous solution of sodium thiocyanate at a concentration of 50 wt % to obtain the fiber-spinning solution, and the solution was induced onto a glass plate to get a thin film. Then, the film was dipped into water for 20 min, taken out of the water, and dried at 60°C in air for 12 h. The LOI value of the dry film was tested by the an oxygen index testing apparatus. The LOI value of the fire-retardant copolymer was 28.5%; however, the LOI value of PAN was 17.1%.

CONCLUSIONS

A phosphorus- and sulfur-containing flame-retardant DATP was synthesized and characterized. The flame-retardant copolymer was obtained by the free-radical copolymerization of DATP with AN. The LOI value of the copolymer was 28.5%. The

thermal properties were investigated through thermogravimetric analysis, which showed that the incorporation of a small percentage of DATP (18.7 wt %) into the copolymer had a significant effect on the retarding combustion of the copolymer. The LOI value of PAN was 18% without the fire-retardant comonomer.

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