

Further studies on fire retardant polystyrene by Friedel–Crafts chemistry[☆]

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Abstract

The combination of a copolymer of 4-vinylbenzyl alcohol and styrene with 2-ethylhexyldiphenylphosphate (DPP) and with metal chlorides has been studied by TGA, radiative gasification, Cone Calorimetry, and oxygen index measurements. Evidence is presented in support of a cross-linking reaction with the additives and the copolymer, which proceeds through a Friedel–Crafts mechanism. This approach reduces the peak heat release rate (HRR) by 60% as measured in the Cone Calorimeter. There is a significant reduction in the mass loss rate during the thermal degradation, and evidence of char formation is observed in the radiative gasification experiments. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

For the past several years we have been concerned with developing systems which lead to the cross-linking of polymers, under fire-like conditions, with the hope that these cross-linked systems will be more thermally stable than the uncross-linked polymers. In two recent papers, we reported on the cross-linking of polystyrene using Friedel–Crafts chemistry [1,2]. In one case an additive approach has been utilized [1]. The alkylating agent used was 1,4-benzenedimethanol, and various zeolites were used as catalysts. When these materials were combined in sealed tubes, cross-linking was observed and the resulting cross-linked polymers were significantly more thermally stable than virgin polystyrene. Unfortunately, when they are combined in a flowing system, the 1,4-benzenedimethanol volatilizes before it can react with the polystyrene and zeolite. Clearly, a new approach was required where the diol could be contained, or its reactivity enhanced, so that reaction would occur *before* volatilization.

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More recently, work has been performed in which copolymers of styrene with 4-vinylbenzyl alcohol have been prepared [2]. This approach has the advantage that the alkylating agent is now a part of the polymer so that it cannot volatilize. Various additives have been tested with this copolymer in order to ascertain the ease with which it may be cross-linked. Successful cross-linking occurs with several transition metal halides, including CuCl₂, CoCl₂, ZnCl₂, SnCl₂, zeolites, and 2-ethylhexyldiphenylphosphate, DPP. This later compound is perhaps the most successful of all the additives which have been tested; it is the only one which does not cause cross-linking at, or below, the PS processing temperature (~200°C), but does effect cross-linking just below the decomposition temperature of PS (~250°C). The use of DPP results in production of a very large fraction of cross-linked polymer, which is non-volatile at elevated temperatures [2]. There is an accompanying paper to this, which reports on chemistry using additional phosphate additives and similar alcohol-containing copolymers [3].

In the previous work we have raised a question concerning the nature of the reaction which leads to cross-linking; the two possibilities are: Friedel–Crafts chemistry, or ether formation. In addition we have not fully explored the flammability properties of this system. In this paper, using a variety of techniques (TGA, oxygen index, radiative gasification, and Cone Calorimetry) we

have characterized the mechanisms that lead to cross-linking and reduced flammability.

2. Experimental

The copolymers and blends of copolymers with additives were prepared as previously reported [2]. The sample of polystyrene which was used as the reference for thermal studies was acquired from Aldrich chemical.¹ The molecular weight (M_w) is reported to be 280,000 daltons; the measured intrinsic viscosity is 84.1 ± 8.0 ml/g. The copolymer which was used contained a mass fraction of 15% alcohol functionalized co-monomer; its measured intrinsic viscosity was 22.9 ± 3.0 ml/g. The deuterated copolymer was prepared using the identical procedure as previously described, but with perdeuterated styrene (Aldrich Chemical Company).

The thermolysis of the deuterated polymer was performed on a high vacuum line. A 50 ml round bottom flask was charged with about 200 mg of sample, containing either pure copolymer, or a solvent-mixed blend, and a mass fraction of 10% cobalt chloride. The sample was heated in an oil bath to 250°C, for 2 h under flowing nitrogen. In order to ensure that water did not escape from the vacuum line, the U-tube traps were cooled to -78°C using a dry ice–acetone slurry. At the conclusion of the heating time, the vessel was allowed to cool to room temperature, the nitrogen inlet was closed, and the stopcock to the high vacuum line opened so that any gases which evolved during the course of the reaction were trapped. After a standard vacuum line distillation [4], the infrared spectra of the gases were obtained.

Cone calorimetry was carried out using the apparatus at the National Institute of Standards and Technology [5]. Peak heat release rate, mass loss rate and specific extinction area (SEA) data, measured at 35 kW/m^2 , are reproducible to within $\pm 10\%$ (σ). The carbon monoxide and heat of combustion data are reproducible to within $\pm 10\%$ (σ). The uncertainties for the Cone Calorimeter are based on the statistics derived from four replicate runs of several representative samples. The uncertainty in the measurement of interest in the Cone data is shown in each plot as an error bar on the data for the copolymer. The heat release rate data plots on all samples are based on the average of two to four replicates. The tests were performed on samples which were solvent blended. Cone samples were prepared by compression molding the powdered samples into 75 mm

diameter by 4 mm thick disks, using a Carver press with a heated mold.

To study the condensed phase decomposition processes we conducted pyrolysis experiments in the radiative gasification apparatus [6]. The gasification apparatus allows visual observation and study of mass and heat transfer processes during pyrolysis, in a nitrogen atmosphere, of samples identical to those used in the Cone Calorimeter at a constant heat flux. This is done without complications from gas phase combustion, such as heat feedback and obscuration of the sample surface from the flame. A schematic diagram of the apparatus is shown in Fig. 1. The uncertainty in the measurement of interest in the gasification data is shown in each plot as an error bar.

Oxygen index measurements were performed with a home-made apparatus using bottom ignition [7].

3. Results and discussion

3.1. Mechanism of cross-linking reaction of the copolymer

In previous work, we have shown that alcohol-containing copolymer (mass fraction of 14% comonomer) will thermally crosslink, in the absence of an additive, when heated for 1 h, at 300°C; however, no cross-linking is observed at one-half hour, at 300°C. In the presence of additives the cross-linking reaction occurs at lower temperatures. For instance, in the presence of DPP, cross-linking commences at 250°C. Two of the possible mechanistic schemes envisioned for the cross-linking reaction are shown in Fig. 2; Friedel–Crafts

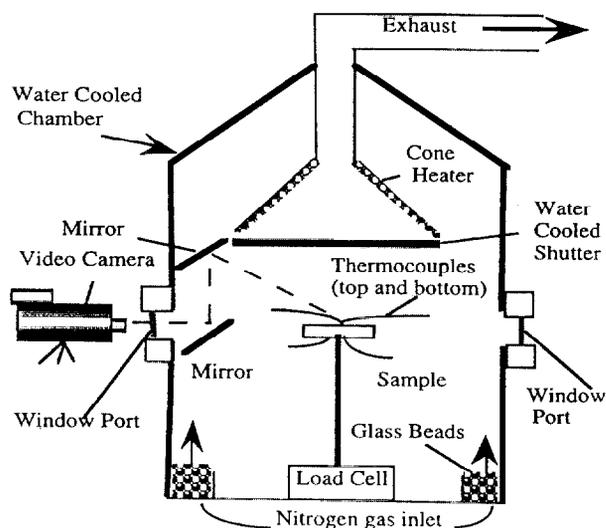


Fig. 1. A schematic of the radiative gasification apparatus (0.7 m diameter, 1.6 m height). The gasification apparatus allows pyrolysis, in a nitrogen atmosphere, of samples identical to those used in the Cone Calorimeter.

¹ Certain commercial equipment, instruments, materials, services or companies are identified in this paper in order to specify adequately the experimental procedure. This in no way implies endorsement or recommendation by NIST.

chemistry: in which the OH from the alcoholic functionality combines with a hydrogen from an aromatic ring to produce water; and ether formation: in which two alcoholic functionalities combine to form water. In order to identify which reaction occurs we have prepared the copolymer of perdeuterostyrene and 4-vinylbenzyl alcohol. If Friedel–Crafts chemistry occurs HDO will be produced, while if ether formation occurs the product will be H_2O . One can differentiate between these by infrared spectroscopy. The investigation was performed on a high vacuum line with an inert gas flowing through the system [4]. At the conclusion of the reaction, the vessel was allowed to cool to room temperature, and the gases were trapped and examined by gas-phase infrared spectroscopy. The thermolysis of the copolymer without additive and with $CoCl_2$ (mass fraction 10%) was examined, and in both cases the presence of D_2O (from the disproportionation of HDO) was shown by the presence of a peak near 2500 cm^{-1} which is absent in the spectrum of H_2O [8]. This clearly shows that a deuterium from the phenyl ring is involved in the reaction, and thus cross-linking occurs through Friedel–Crafts chemistry.

3.2. TGA studies

The degradation of the alcohol-containing copolymer commences at a lower temperature when it is thermolyzed

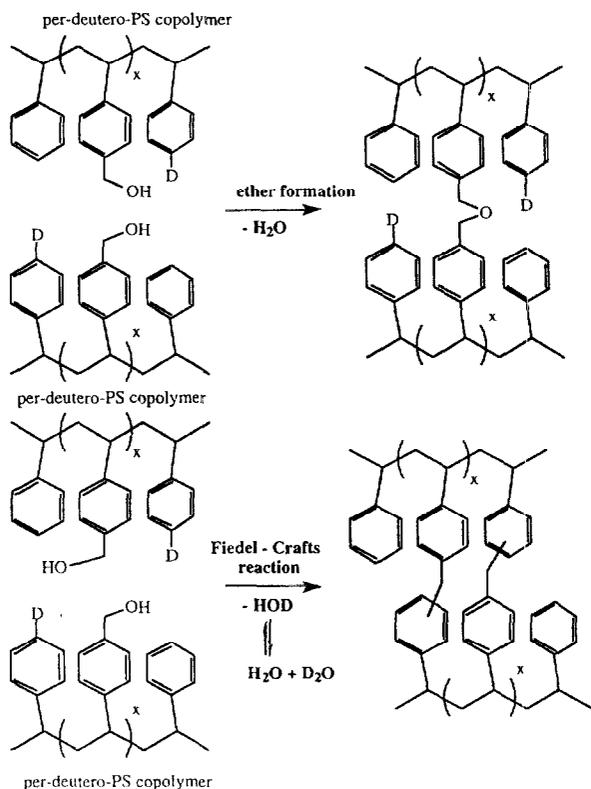


Fig. 2. Possible cross-linking mechanisms.

alone, than when it is thermolyzed in the presence of the phosphate ester [2]. To determine the effect that the phosphate ester had on the degradation of polystyrene we analysed the thermal degradation using TGA. Fig. 3 shows the TGA curves for DPP, polystyrene, polystyrene with DPP (mass fraction of 10%), and the copolymer with DPP (mass fraction of 10%). One can see that the TGA curves for both PS and the copolymer are changed by the presence of DPP. In addition to the enhanced thermal stability for the copolymer with DPP, mentioned above, the thermal stability of the PS also appears to be improved; furthermore, the copolymer gives a residue yield of 12%. This is greater than the theoretical residue yield of 1.8%, which is observed in the PS with DPP. The effect these changes in thermal stability, and charring behavior, have on the flammability properties of these two formulations is discussed below.

3.3. Radiative gasification

The condensed phase decomposition processes of the copolymer combined with cross-linking additives were studied in the radiative gasification apparatus (shown in Fig. 1). A thermocouple was embedded in the bottom surface of the sample to monitor the bottom surface temperature, and mass loss rate (MLR) data was obtained using a load cell. The experiment was also recorded with a video camera. Fig. 4 shows the MLR and thermocouple data from the gasification experiments for the copolymer, its combination with DPP, and with zinc chloride. Fig. 5 shows the digitized video images of the gasification experiments for the copolymer, with and without DPP. The DPP–copolymer combination shows one peak in the MLR data at about 80 s. The MLR of the copolymer–additive combination is

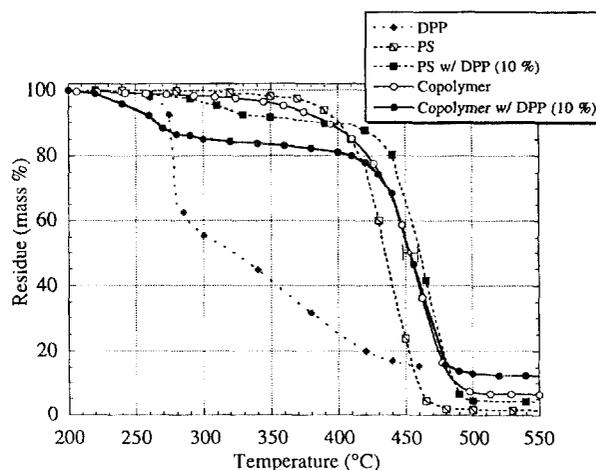


Fig. 3. TGA of polystyrene, DPP, a blend of polystyrene with DPP (mass fraction 10%), and a blend of the copolymer with DPP (mass fraction 10%).

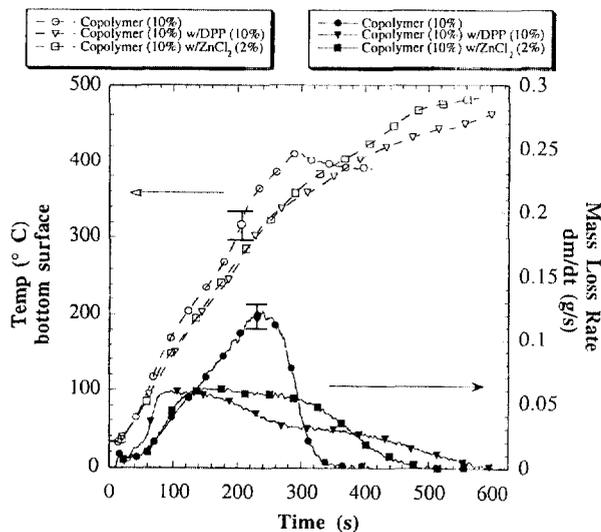


Fig. 4. Mass loss rate and bottom surface thermocouple data from gasification experiments performed at a heat flux of 40 kW/m^2 , in nitrogen for poly(styrene-*co*-4-vinylbenzyl alcohol) copolymer with 2-ethylhexyl-diphenylphosphate, DPP (DPP mass fraction 10%; 4-vinylbenzyl alcohol mass fraction 10%) and with zinc chloride (ZnCl_2 mass fraction 2%).

higher than that for the pure copolymer up to 120 s. This effect may be from degradation and volatilization of the additive. [The TGA of DPP (not shown) shows a rapid mass loss at 250°C and higher.] This statement is supported by the result seen for ZnCl_2 : where the early MLR peak is absent. Hence, the early mass loss must be due to the presence of the DPP. However, another process is also occurring at the same time: i.e. the rapid charring of the sample, which may be initiated by the cross-linking reaction mentioned above. Initial char formation is visible at 30 s for the copolymer with the DPP sample (right set of images in Fig. 5). The entire copolymer/DPP sample is covered by char at 100 s. The bottom surface temperature is 350°C for the pure copolymer at 250 s into the degradation; at the same time the bottom surface temperature is 40°C lower for both copolymer-additive combinations. Clearly, the char is insulating the underlying material. This lower sample temperature results in a lower MLR (see Fig. 4). There is a plateau in the MLR data of the copolymer/DPP, sample which begins at about 300 s. In the video, it

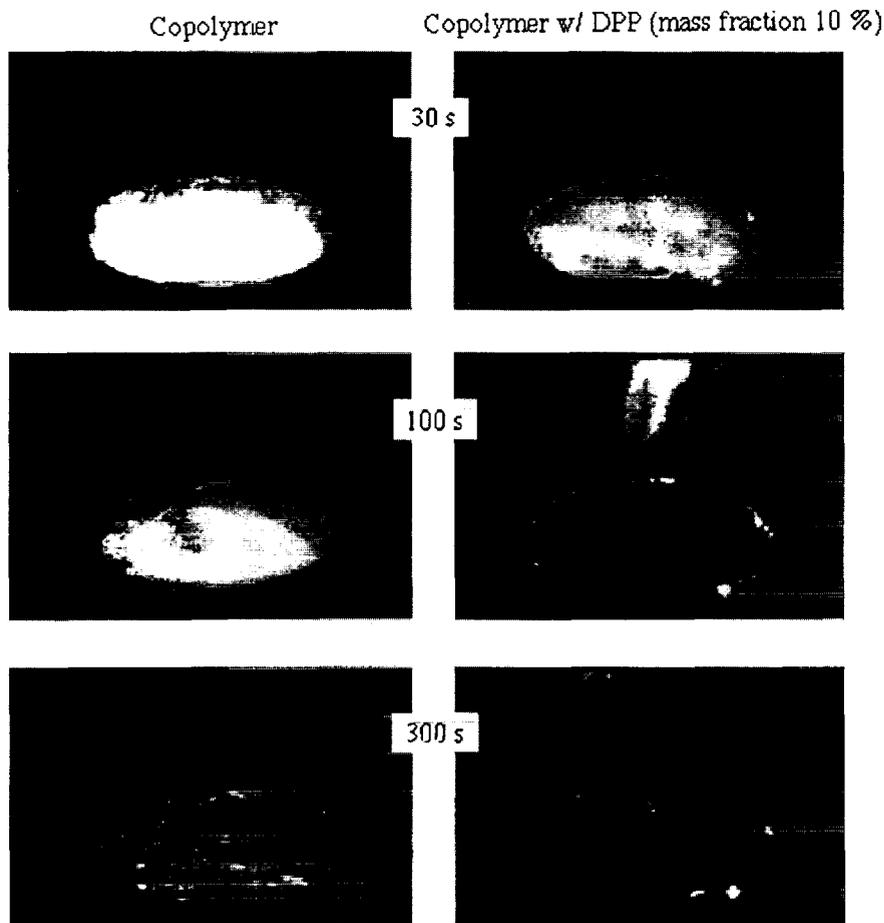


Fig. 5. Digitized video images from radiative gasification experiments performed on poly(styrene-*co*-4-vinylbenzylalcohol) with and without DPP, in N_2 at a heat flux of 40 kW/m^2 . Initial char formation is visible at 30 s for the copolymer with DPP sample (right set of images). The entire sample is covered by char at 100 s.

can be seen that the char appears to have cracked at this point exposing virgin material to the external heat flux, and allowing the decomposition gases to escape. If one compares the peak MLRs, one sees that the peak MLR for the pure copolymer is 2.5 times that for the copolymer with DPP. The gasification experiment has also been performed on pure polystyrene; the results are essentially the same as those observed for the pure copolymer. Fig. 5 shows the course of the degradation of the copolymer in the presence of the additive and this clearly shows the formation of char; char formation is not observed in the degradation of the copolymer or polystyrene.

Fig. 6 shows a plot of the mass which remains as a function of heating time for two controls, polystyrene, the copolymer, and for the copolymer with the two additives. The initial mass loss is largest for the copolymer with DPP; presumably because of the presence of the volatile DPP and the fact that water will be evolved as the Friedel–Crafts reaction proceeds. Both polystyrene and the alcohol containing copolymer completely volatilize by 300 s; the two samples of the copolymer with Friedel–Crafts additives give between 10 and 20% char near the end of the experiment. This is in accord with Fig. 5, which shows the video images of the gasification experiment.

3.4. Cone calorimetry

Cone calorimetry was carried out at a heat flux of 35 kW/m²; each sample was determined two times and the results which are reported in Table 1 are the average of these two determinations.

Fig. 7 shows the heat release rate for the copolymer, and the copolymer containing DPP. Clearly, there is a reduction in peak HRR in the presence of the additive.

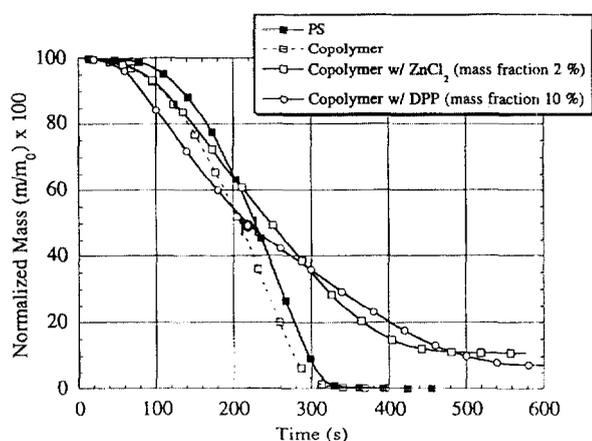


Fig. 6. Loss of mass for polystyrene, the alcohol-containing copolymer, and blends of the alcohol-containing copolymer with DPP (mass fraction 10%) and zinc chloride (mass fraction 2%) from a radiative gasification experiment.

Table 1

Cone calorimetry for polystyrene, poly(styrene-co-4-vinylbenzyl alcohol), and these two polymers combined with 10% of 2-ethylhexyl-diphenylphosphate

	PS	PS + DPP	Copolymer	Copolymer + additive
Time to ignition (s)	52	55	37	36
Time to peak HRR (s)	162	190	155	410
Peak HRR (kW/m ²)	1160	1154	947	374
Peak mass loss (g/s m ²)	38	31	32	17
Total heat (MJ/m ²)	102	190	92	80
Mass loss rate (g/s m ²)	29	29	26	11
H _c (MJ/kg)	29	27	27	26
CO yield (kg/kg)	0.09	0.11	na ^a	na

^a na: data not available.

Furthermore, the DPP does not effect a change in the flammability of PS, i.e. the benzyl alcohol functionality must be present for DPP to be effective. Recalling that a small apparent improvement in thermal stability, was seen for PS in the presence of DPP (see Fig. 3), it seems that this is not a sufficiently large effect to reduce the flammability. The time to ignition for the copolymer, and for PS, is not changed by the presence of the additive. As we observed in the gasification experiments, the mass loss rate and peak mass loss are significantly lower for the copolymer with DPP. We observed significant char formation in the Cone experiments as we did in the gasification apparatus and in the TGA.

3.5. Oxygen index

Oxygen index measures ease of extinction of a fire while cone calorimetry measures the heat release rate; since different parameters are measured one does not

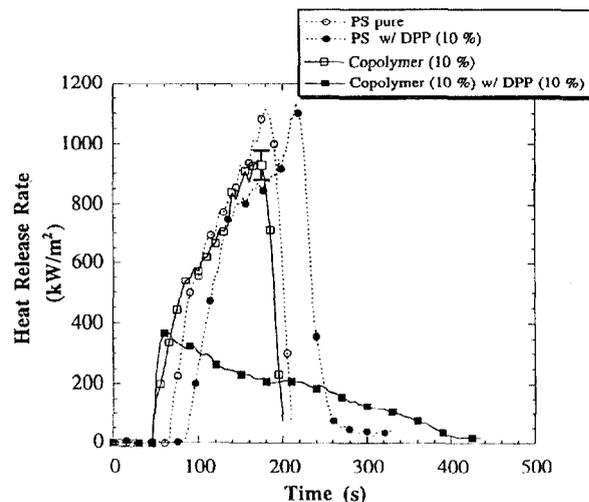


Fig. 7. Heat release rate for pure PS, PS with DPP, poly(styrene-co-4-vinylbenzyl alcohol) and poly(styrene-co-4-vinylbenzyl alcohol) with DPP at a heat flux of 35 kW/m².

necessarily expect excellent agreement between the two techniques. The oxygen index, using bottom ignition, for the copolymer containing no additives is 17 while that for the copolymer with 10% of the phosphate ester is 21. Bottom ignition is a much more stringent test than the normal top ignition because the sample is engulfed by the fire in bottom ignition but it is above the sample in top ignition. As a general rule one can add 3 to 4 points onto the bottom ignition value to approximate the top ignition. Thus this measurement does indicate some improvement in the ease of extinction of the burning copolymer in the presence of the additive.

4. Conclusion

The combination of the phosphate ester with the copolymer causes a 60% reduction in the heat release rate as determined by Cone Calorimetry. We have presented evidence in support of a cross-linking reaction with the additives (DPP, $ZnCl_2$) and the copolymer, which proceeds through a Friedel–Crafts mechanism. Rapid char formation follows the cross-linking reaction. The char insulates the underlying material and acts as a mass transport barrier. This lower sample temperature results in a lower mass loss rate and thus a lower HRR.

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