

11-1-1999

# Stabilization of Polystyrene by Friedel-Crafts Chemistry: Effect of Position of Alcohol and the Catalyst

Jin Zhu  
*Marquette University*

Michael A. McKinney  
*Marquette University*

Charles Wilkie  
*Marquette University, charles.wilkie@marquette.edu*

Marquette University

e-Publications@Marquette

***Chemistry Faculty Research and Publications/College of Arts and Sciences***

***This paper is NOT THE PUBLISHED VERSION; but the author's final, peer-reviewed manuscript. The published version may be accessed by following the link in the citation below.***

*Polymer Degradation and Stability*, Vol. 66, No. 2 (November, 1999): 213-220. [DOI](#). This article is © Elsevier and permission has been granted for this version to appear in [e-Publications@Marquette](#). Elsevier does not grant permission for this article to be further copied/distributed or hosted elsewhere without the express permission from Elsevier.

## Stabilization of Polystyrene by Friedel-Crafts Chemistry: Effect of Position of Alcohol and the Catalyst

Jin Zhu

Department of Chemistry, Marquette University, Milwaukee, WI

Michael A McKinney

Department of Chemistry, Marquette University, Milwaukee, WI

Charles A Wilkie

Department of Chemistry, Marquette University, Milwaukee, WI

Abstract

Polystyrene has been copolymerized with 4-vinylbenzyl alcohol, 4-(2-hydroxyethyl)styrene, and 4-(3-hydroxypropyl)styrene and it has been shown that thermal cross-linking of these copolymers is dependent upon the alcohol content. When the alcohol content is low, no thermal cross-linking is observed. When various phosphate esters are present as catalysts with these low alcohol content copolymers, cross-linking is observed at temperatures of about 250°C but not at lower temperatures. Cross-linking enhances the thermal stability of the copolymers. Studies of the thermal stability of the copolymers and their blends with the

catalysts have been performed using thermogravimetric analysis and thermogravimetric analysis coupled to Fourier transform infrared spectroscopy. There is little difference in the thermal stability of all three copolymers and their blends with the catalysts.

## 1. Introduction

Cross-linking is a strategy which has been pursued in this laboratory for some time as a process to enhance the thermal stability of polymers such as polystyrene, and Friedel-Crafts chemistry is the technique that has been used to implement this strategy. Grassie and Gilks [\[1\]](#) have used tin tetrachloride as a catalyst and *p*-di(chloromethyl)benzene as the alkylating agent in dichloroethylene. The cross-linking reaction occurred under these conditions, but the cross-linked polymer has a lower thermal stability than the uncross-linked polymer. Brauman [\[2\]](#) used antimony trichloride as catalyst with both alkylating and acylating agents. A cross-linked polymer was obtained and the amount of non-volatile residue increased. Rabek and Lucki [\[3\]](#) cross-linked polystyrene at room temperature in the presence of  $\text{AlCl}_3$  as a catalyst. Clubley et al. [\[4\]](#), [\[5\]](#) studied the utilization of a combination of a diol or some other difunctional or polyfunctional material together with some phosphate ester as a potential way to enhance the thermal stability of polystyrene. If one wishes to use this strategy for thermal protection of polystyrene, the cross-linking reaction must not occur under processing conditions but only when the polymer has been challenged by a fire. In all cases noted above, the cross-linking reaction occurs at too low a temperature to be useful for thermal protection of the polymer.

In earlier work it was shown that cross-linked polystyrene could be produced at a temperature of  $300^\circ\text{C}$  if zeolites were used as catalysts with 1,4-benzenedimethanol as the alkylating agent [\[6\]](#). Unfortunately, this reaction only occurs in a sealed tube; when the reaction is conducted in a flowing system, the alkylating agent volatilizes before it can react. This problem has been partially solved by incorporating the alkylating agent into the polymer by a copolymerization process involving the preparation of copolymers of vinylbenzyl alcohol and vinylbenzyl chloride with styrene. It was found that the chloride-containing copolymers could be readily cross-linked with metal halide and phosphate ester catalysts while the alcohol-containing copolymers were less easily cross-linked [\[7\]](#). In the accompanying paper, we report on Cone calorimetry and radiative gasification of blends of the alcohol-containing copolymer with one phosphate ester [\[8\]](#).

In this paper three different alcohol-containing copolymers are prepared at varying copolymer compositions and the thermal and catalyzed cross-linking reactions are investigated using a variety of phosphate esters as catalysts.

## 2. Experimental

### 2.1. Materials and instruments

Most chemicals used in this study were obtained from the Aldrich Chemical Company; these include: styrene, 4-bromostyrene, *p*-vinylbenzyl chloride, ethylene oxide, *p*-vinylbenzyl alcohol, magnesium, anhydrous sodium sulfate, toluene, chloroform, methanol, anhydrous ethyl ether, benzoyl peroxide (BPO) and inhibitor removal columns.

All of the phosphate additives were provided by Solutia Inc.; these were provided under the trade names of Santicizer 141, 148, 154, 2148 and XPM-1000.

Infrared spectroscopy was performed on a Mattson Galaxy infrared spectrometer at  $4\text{ cm}^{-1}$  resolution while  $^1\text{H-NMR}$  spectra were obtained on a GE-300 instrument. Thermogravimetric analysis, TGA, was performed on an Omnitherm 1000 unit under a flowing nitrogen atmosphere at a scan rate of 10 or  $20^\circ\text{C}/\text{min}$ ; all TGA data is the average of three determinations, the error bars on the temperatures are  $\pm 3^\circ\text{C}$ . Thermogravimetric analysis coupled to Fourier transform infrared spectroscopy, TGA/FTIR, was performed using a Cahn 131 thermogravimetric analyzer at  $20^\circ\text{C}/\text{min}$  under inert atmosphere interfaced to a Mattson Galaxy infrared spectrometer. Elemental analysis was performed by Midwest Microlabs.

#### 2.1.1. Syntheses of 4-(2-hydroxyethyl)styrene and 4-(3-hydroxypropyl)styrene

In a 500 ml flame-dried three-neck round bottom flask equipped with a mechanical stirrer, condenser and dropping funnel was placed 40 ml anhydrous ethyl ether and magnesium (2.4 g, 0.1 mol) and then 2 ml of a mixture of 4-bromostyrene (11.33 g, 0.062 mol) and 70 ml anhydrous ethyl ether was added to the flask. Once the reaction was initiated the remainder of the 4-bromostyrene solution was added dropwise over a 2 h time period under nitrogen gas. The reaction was allowed to continue stirring at room temperature for an additional hour after the addition was complete. Then the flask and its contents were cooled to about  $-15^\circ\text{C}$  with an ice  $-\text{CaCl}_2$ -acetone mixture and ethylene oxide (3.83 g, 0.087 mol) in 80 ml anhydrous ether was quickly added with vigorously stirring. The color of the solution changed to yellow upon the addition of the ethylene oxide. After this solution was completely added, the reaction mixture was allowed to warm to room temperature and the solution was stirred for an additional hour.

The flask was cooled to  $0^\circ\text{C}$  and 100 ml of a saturated  $\text{NH}_4\text{Cl}$  solution was added dropwise. A large amount of white solid appeared and then redissolved as more ammonium chloride was added. The solution was poured into a separatory funnel and the ether layer was separated; the aqueous layer was extracted three times with aliquots of ethyl ether. The combined ether layer was washed with distilled water until it was neutral and then dried with anhydrous  $\text{Na}_2\text{SO}_4$ . The 4-(2-hydroxyethyl) styrene (yield, 6.50 g, 70%) was recovered by rotary evaporation.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.45–7.25 ( $\text{A}_2\text{B}_2$ , m, 4H), 6.81–6.72 (dd,  $J=10.7, 17.7\text{ Hz}$ , 1H), 5.78(d,  $J=17.6\text{ Hz}$ , 1H), 5.33 (d,  $J=10.8\text{ Hz}$ );  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  138.8, 137.2, 136.6, 129.9, 127.2, 114.2, 63.6, 38.9. IR (KBr)  $3432\text{ cm}^{-1}$  and  $1034\text{ cm}^{-1}$ .

4-(3-hydroxypropyl)styrene was prepared by an identical procedure using vinylbenzyl chloride rather than 4-bromostyrene as the starting material. The yield was lower for this compound and it required purification. The crude product was purified by chromatography on silica gel using a petroleum ether:ethyl acetate mixture (10:1) to give a yield of 50% 4-(3-hydroxypropyl)styrene.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.36–7.15 ( $\text{A}_2\text{B}_2$ , m, 4H), 6.74–6.65 (dd,  $J=11.2, 17.2\text{ Hz}$ , 1H), 5.71(d,  $J=17.6\text{ Hz}$ , 1H), 5.20 (d,  $J=10.6\text{ Hz}$ );  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  141.5, 136.6, 135.3, 128.6, 126.2, 113.0, 62.2, 34.1, 31.7; IR (KBr)  $3432\text{ cm}^{-1}$  and  $1034\text{ cm}^{-1}$ .

### 2.1.2. Synthesis of copolymers

The polymers were prepared by radical initiation using benzoyl peroxide, BPO, as initiator and toluene as solvent; the inhibitor was removed from the styrene by passing the monomer through an inhibitor removal column before use. The preparation of the copolymer containing 10% *p*-vinylbenzyl alcohol is described below as the typical procedures for all preparations.

In a 250 ml round bottom flask were added 80 ml toluene, 1g *p*-vinylbenzyl alcohol, 9 g styrene and 0.1 g BPO. The mixture was refluxed for 20 h and the yield was typically 85–90%. At the conclusion of the reaction, most of the solvent was removed on a rotary evaporator, then the sample was dissolved in chloroform. This chloroform solution was poured into a large amount of methanol to precipitate the copolymer. After filtration, the polymer was washed with methanol and the sample was then dried in a vacuum oven at 80°C for at least 5 h. IR: 3584  $\text{cm}^{-1}$  and 1027  $\text{cm}^{-1}$ .

### 2.1.3. Thermolysis of copolymers with and without additives.

All samples were thermolyzed at 250°C for 2 h under a flowing nitrogen atmosphere in order to determine the ease of cross-linking. The efficacy of the cross-linking reaction was determined by solubility in the chloroform. The gel content and swelling ratio were determined in the same way described in previous work from this laboratory [\[9\]](#). Samples which contained phosphate ester were prepared by grinding the ingredients in a mortar and pestle. Thermal stability of the samples was ascertained using TGA and TGA/FTIR.

## 3. Results and discussion

### 3.1. Syntheses of monomers and copolymers

The structures of the copolymers which have been used in this study are shown in [Fig. 1](#). The materials that were obtained by the radical copolymerization reaction were subjected to elemental analysis and the analytical data showing the composition in both mol% and mass% are shown in [Table 1](#). The samples are identified in this table according to the number of methylene groups in the alcohol. Thus the entry 1 - OH refers to a copolymer in which the alcohol component contains one methylene group, i.e. 4-vinylbenzyl alcohol is the monomer used. These labels are used consistently throughout this paper. The end number in the legend refers to the concentration of the alcohol component, expressed in terms of mass percent alcohol in the copolymer.

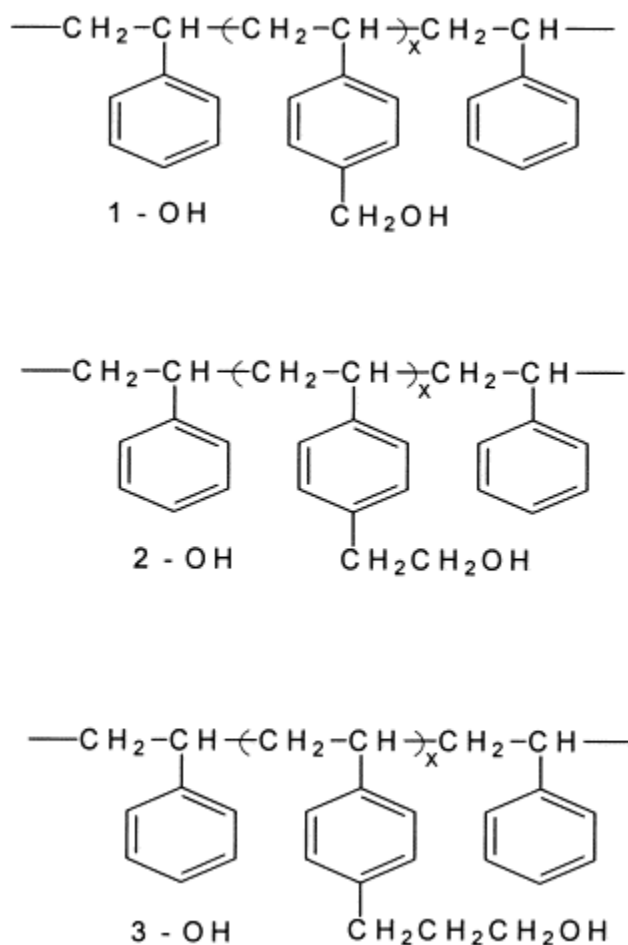


Fig. 1. Structures of the copolymers used in this study.

Table 1. Composition (mol% and mass%) of the various copolymers and the theoretical expectation based upon quantities of starting materials

Sample	Composition	Mol %		Mass %	
		Theo.	Act.	Theo.	Act.
1OH-18	PS-PSmethanol	12:1	5.9:1	10	18
1OH-11	PS-PSmethanol	25:1	10.4:1	5	11
1OH-6	PS-PSmethanol	50:1	19.4:1	2.5	6
2OH-24	PS-PSethanol	13:1	5.7:1	10	24
2OH-12	PS-PSethanol	25:1	10.5:1	5	11.9
2OH-6	PS-PSethanol	50:1	21.7:1	3	6
3OH-20	PS-PSpropanol	14:1	6.4:1	10	20
3OH-6	PS-PSpropanol	25:1	25:1	6	6
3OH-4	PS-PSpropanol	50:1	36.9:1	3	4

In all cases the copolymers were found to contain more of the alcohol than expected from the feed ratio. Reactivity ratios are available for the combination of 2-(4-vinylphenyl)-1-propanol with styrene and they are:  $r_1=0.480$  and  $r_2=0.410$  [\[10\]](#). These reactivity ratios predict a composition similar to that obtained. If one makes the assumption that the reactivity ratios for the other monomers will not be greatly different, the results are not surprising.

### 3.2. The efficacy of the cross-linking reaction in virgin copolymers

The goal of this work is to be able to use these compounds in the place of polystyrene and that means that the compound must not undergo a thermal cross-linking reaction. The minimum temperature required to achieve cross-linking of the copolymers was determined by heating each for one-half hour to temperature and then determining if the copolymer would dissolve in chloroform; the results are shown in [Table 2](#). When the alcohol composition is around 5%, none of the copolymers thermally cross-link below 300°C. At higher alcohol content, thermal cross-linking will occur for some copolymers but not for the 3-alcohol.

Table 2. Temperature at which thermal cross-linking of the copolymers occurs

Samples	1OH-18	1OH-11	1OH-6	2OH-24	2OH-12	2OH-6	3OH-20	3OH-6	3OH-4
T, °C	245°C	265°C	>300°C	<160°C	>300°C	>300°C	>300°C	>300°C	>300°C

### 3.3. The thermal stability of virgin copolymers

The thermal stability of polystyrene was improved by the incorporation of the alcohol to make the copolymer. For the purposes of this paper, thermal stability is defined as the onset temperature of the degradation. This could be defined in many ways, 10% degradation has somewhat arbitrarily been chosen to reflect the onset. This eliminates effects which may arise from the presence of impurities or additives yet it still provides some consistent basis for the assessment of the onset of degradation. Also tabulated is the temperature at which 50% of the material has degraded; this permits one to ascertain if there are any effects which occur during the process of degradation which have an effect on the course of the degradation. The process of degradation will lead to the formation of material which can either volatilize or undergo another reaction which can lead to char formation. A third parameter that has been tabulated for the degrading polymers is the amount of non-volatile residue (char) which is formed at 800°C. Finally it is also important to have information on the extent of cross-linking and, accordingly, the gel contents and swelling ratio are also tabulated. [Table 3](#) provides all of this data for the virgin polymers that have been heated at 250°C under a nitrogen atmosphere for two hours. The TGA curves for all three alcohols, together with that of polystyrene are shown in [Fig. 2](#).

Table 3. Temperatures of degradation, char content, gel content (GC) and swelling ratio (SR) for copolymers after two-hour heating at 250°C

Samples	T(10%loss)	T(50%loss)	Char(%)	GC(%)	SR(%)
PS	374	423	0	—	—
1OH-18	407	456	6	67	1800
1OH-11	394	430	2	53	2500

Samples	T(10%loss)	T(50%loss)	Char(%)	GC(%)	SR(%)
1OH-6	390	429	2	—	—
2OH-24	408	457	7	84	1800
2OH-12	411	443	2	—	—
2OH-6	403	433	1	—	—
3OH-20	400	438	2	—	—
3OH-6	399	436	3	—	—
3OH-4	377	425	3	—	—

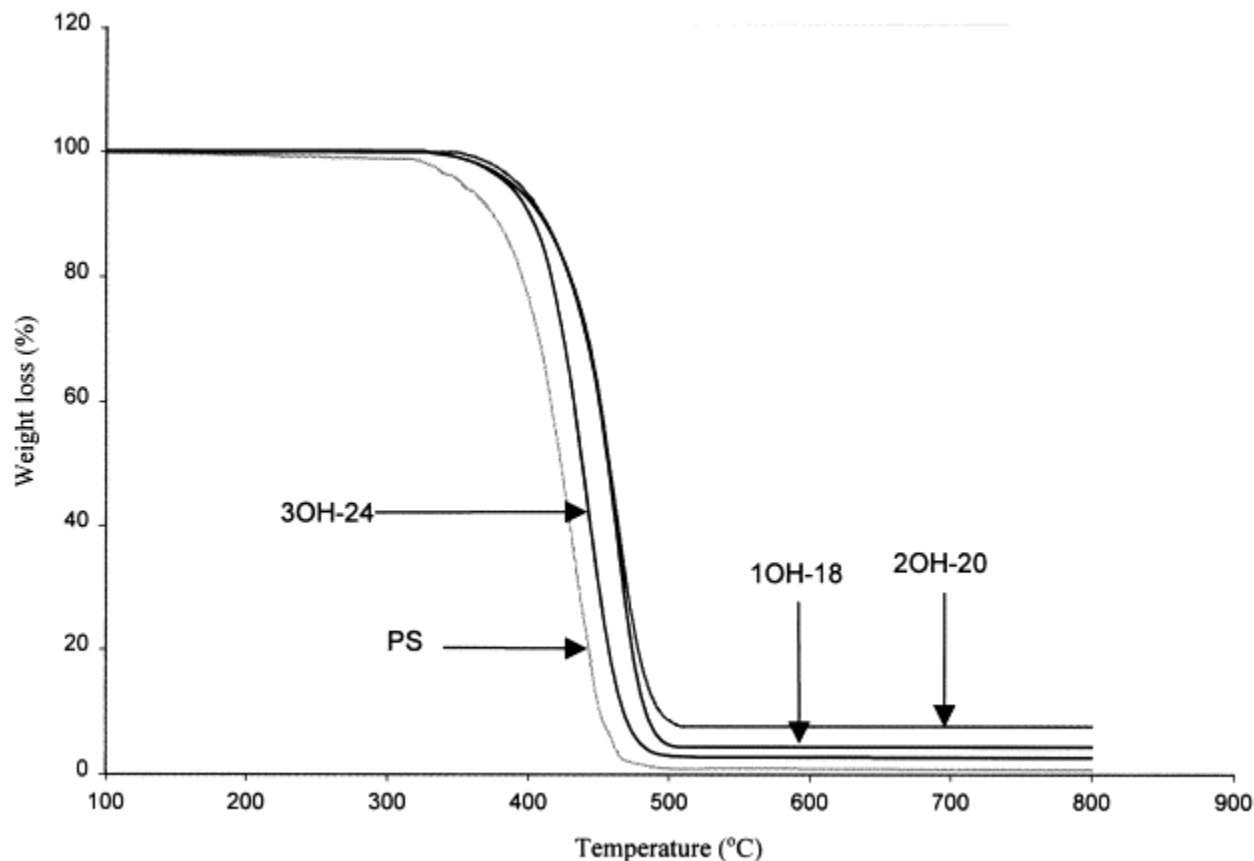


Fig. 2. TGA curves for all three alcohols and polystyrene at a rate of 20°C/min.

Cross-linking does not occur very easily at these lower amounts of alcohol, unlike what has been observed in our previous work when the fraction of alcohol in the copolymer was higher [7]. The onset temperature of the degradation, as measured by the temperature at which 10% mass loss occurs, increases by an amount ranging from negligible to about 20°C compared to pure polystyrene. The onset temperature measures the ease of initial bond scission in the polymer and hence is a measure of thermal stability. In all three cases the greater the amount of alcohol in the copolymer, the greater the thermal stability and the temperature of 50% mass loss suggests the same trend. It should also be noted that all copolymers produce some amount of non-volatile residue while polystyrene shows no char formation. Fig. 2 shows that the onset temperature of the degradation is increased for all copolymers.



### 3.4. The thermal stability of copolymers with phosphate additives

It was reported that the thermal stability of alcohol-containing copolymers was improved when they were combined with 10% of the phosphate additive 141 [7], [8]. In this work five different phosphate additives have been examined. The composition of these commercial additives is shown in Table 4. The structures of the principal components of each of these additives are shown in Fig. 3.

Table 4. The components of the phosphate additives

Phosphate additives	Components
Santicizer 141	91–93% 2-ethylhexyl diphenyl phosphate
Santicizer 148	87–91% isodecyl diphenyl phosphate
Santicizer 154	43–44% <i>p-t</i> -butylphenyl diphenyl phosphate, 40–41% triphenyl phosphate, 14% di- <i>p-t</i> -butylphenyl diphenyl phosphate, and 2% tri- <i>t</i> -butylphenyl diphenyl phosphate
Santicizer 2148	Phosphoric acid, C <sub>12,14,16</sub> -alkyl diphenylester
XPM-1000	5,5,5',5',5'',5''-hexamethyltris(1,3,2-dioxaphosphorinane)methan)amine 2,2',2'',-trioxide [11], [12]

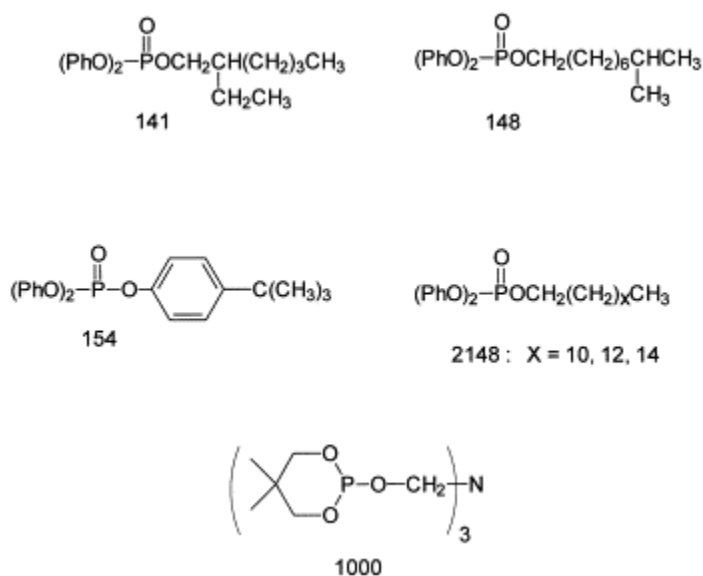


Fig. 3. Structures of the major components in the phosphate additives which have been studied.

Thermal analysis data on the combination of the three copolymers at three different copolymer compositions with both 3 and 5% additive 141 are shown in Table 5.

Table 5. Temperature at which 10% degradation occurs, non-volatile residue at 800°C, and gel content and swelling ratio of copolymers mixed with additive 141 after 2 h heating at 250°C

Samples	Composition	T, °C, 10% mass loss	Char, %	GC, %	SR, %
1OH-18	3%141	413	5	84	1000
	5%141	423	8	88	800
1OH-11	3%141	411	7	80	1500
	5%141	421	5	81	1400
1OH-6	3%141	412	4	64	2000
	5%141	420	4	72	1700
2OH-24	3%141	412	5	84	1500
	5%141	435	8	87	1400
2OH-12	3%141	414	4	39	2200
	5%141	424	5	71	1300
2OH-6	3%141	405	4	—	—
	5%141	418	7	27	4500
3OH-20	3%141	407	2	69	1900
	5%141	408	4	73	1700
3OH-6	3%141	407	3	9	7600
	5%141	413	5	27	3500
3OH-4	3%141	404	3	—	—
	5%141	415	3	33	3000

In almost all cases one observes that cross-linking occurs when the copolymer is combined with this phosphorus additive and the onset of degradation, as measured by the temperature at which 10% degradation occurs, increases by approximately 40°C relative to pure polystyrene. The amount of alcohol component in the copolymer does not appear to have a significant influence on the onset temperature while an increase in the amount of catalyst does increase the onset temperature. Both the extent of cross-linking and the cross-link density appear to be slightly higher for the 1-alcohol than the other copolymer compositions

[Table 6](#), [Table 7](#), [Table 8](#), [Table 9](#) shows similar data for the other phosphate additives, 148, 154, 2148 and 1000.

Table 6. Temperature at which 10% degradation occurs, non-volatile residue at 800°C, and gel content and swelling ratio of copolymers mixed with additive 148 after 2 h heating at 250°C

Samples	Composition	T, °C for 10% mass loss	Char, %	GC%	SR%
1OH-18	3%148	420	6	94	900
	5%148	435	8	100	400
1OH-11	3%148	409	7	86	1300

<b>Samples</b>	<b>Composition</b>	<b>T, °C for 10% mass loss</b>	<b>Char, %</b>	<b>GC%</b>	<b>SR%</b>
	5%148	412	7	95	1000
1OH-6	3%148	404	3	70	2100
	5%148	405	3	85	1400
2OH-24	3%148	417	7	83	1400
	5%148	434	6	98	1000
2OH-12	3%148	416	5	66	1900
	5%148	428	11	83	1200
2OH-6	3%148	410	3	—	—
	5%148	418	3	—	—
3OH-20	3%148	406	6	85	2100
	5%148	414	7	91	900
3OH-6	3%148	405	4	55	3500
	5%148	407	3	70	2300
3OH-4	3%148	404	3	15	5000
	5%148	411	4	29	3000

Table 7. Temperature at which 10% degradation occurs, non-volatile residue at 800°C, and gel content and swelling ratio of copolymers mixed with additive 154 after 2 h heating at 250°C

<b>Samples</b>	<b>Composition</b>	<b>T, °C for 10% mass loss</b>	<b>Char, %</b>	<b>GC, %</b>	<b>SR, %</b>
1OH-18	3%154	396	3	61	2600
	5%154	380	4	64	2000
1OH-11	3%154	399	4	—	—
	5%154	399	3	—	—
1OH-6	3%154	399	3	—	—
	5%154	391	1	—	—
2OH-24	3%154	389	5	69	2100
	5%154	389	7	79	2000
2OH-12	3%154	411	2	—	—
	5%154	412	3	—	—
2OH-6	3%154	403	2	—	—
	5%154	406	2	—	—
3OH-20	3%154	389	3	—	—
	5%154	310	5	—	—
3OH-6	3%154	401	3	—	—
	5%154	399	4	—	—

<b>Samples</b>	<b>Composition</b>	<b>T, °C for 10% mass loss</b>	<b>Char, %</b>	<b>GC, %</b>	<b>SR, %</b>
3OH-4	3%154	380	4	—	—
	5%154	397	1	—	—

Table 8. Temperature at which 10% degradation occurs, non-volatile residue at 800°C, and gel content and swelling ratio of copolymers mixed with additive 2148 after 2 h heating at 250°C

<b>Samples</b>	<b>Composition</b>	<b>T, °C for 10% mass loss</b>	<b>Char, %</b>	<b>GC, %</b>	<b>SR, %</b>
1OH-18	3%2148	418	6	100	800
	5%2148	428	8	100	600
1OH-11	3%2148	418	3	93	1200
	5%2148	421	4	97	1100
1OH-6	3%2148	411	5	78	2200
	5%2148	413	3	82	1700
2OH-24	3%2148	412	5	96	1300
	5%2148	422	5	99	1000
2OH-12	3%2148	409	4	63	2200
	5%2148	414	4	82	1400
2OH-6	3%2148	413	2	—	—
	5%2148	413	3	12	4100
3OH-20	3%2148	404	6	71	2300
	5%2148	416	7	83	1000
3OH-6	3%2148	406	2	69	2600
	5%2148	416	7	80	1300
3OH-4	3%2148	404	3	10	4100
	5%2148	407	3	11	4000

Table 9. Temperature at which 10% degradation occurs, non-volatile residue at 800°C, and gel content and swelling ratio of copolymers mixed with additive 1000 after 2 h heating at 250°C

<b>Samples</b>	<b>Composition</b>	<b>T, °C for 10% mass loss</b>	<b>Char, %</b>	<b>GC, %</b>	<b>SR, %</b>
1OH-18	3%1000	421	8	89	1100
	5%1000	434	11	100	400
1OH-11	3%1000	414	5	86	1300
	2%1000	417	8	94	1200
1OH-6	3%1000	413	3	79	2000
	5%1000	413	4	84	1800
2OH-24	3%1000	415	13	89	1000

Samples	Composition	T, °C for 10% mass loss	Char, %	GC, %	SR, %
	5%1000	421	8	100	1000
2OH-12	3%1000	419	3	70	1800
	5%1000	420	4	77	1600
2OH-6	3%1000	412	2	48	2800
	5%1000	416	4	49	3600
3OH-20	3%1000	402	7	80	1300
	2%1000	409	6	92	1100
3OH-6	3%1000	407	4	70	2000
	5%1000	406	4	82	1400
3OH-4	3%1000	408	4	56	3900
	5%1000	407	4	65	2700

The same conclusions which have been drawn from the data for additive 141 may also be observed in this additive. The onset temperature is raised as is the fraction which is non-volatile at elevated temperatures.

It should be noted that cross-linked polymers are only produced for those copolymers which undergo thermal cross-linking; in all other cases no cross-linking is observed. The triaryl phosphate ester (154) cannot undergo elimination to form a phosphoric acid. Consequently it should have no catalytic ability and that is reflected in the absence of cross-linking.

#### 3.4.1. Comparison of the phosphate additives

The results clearly show that the aryl, alkyl phosphate esters enhance the thermal stability of the copolymers while the all aryl compound does not effect thermal stability. [Fig. 4](#) shows a plot of the temperature of 10% degradation for all copolymers at the highest fraction of alcohol component in the copolymer as a function of the identity of the additive; the temperature for 10% degradation of polystyrene is shown as a line at the bottom of the plot. It can be seen that the temperature of 10% degradation is significantly enhanced for all additives except the triarylphosphate. This is completely in accord with the mechanism which has been previously suggested in which the alkyl chain is lost as a olefin with the formation of a phosphoric acid [\[7\]](#).

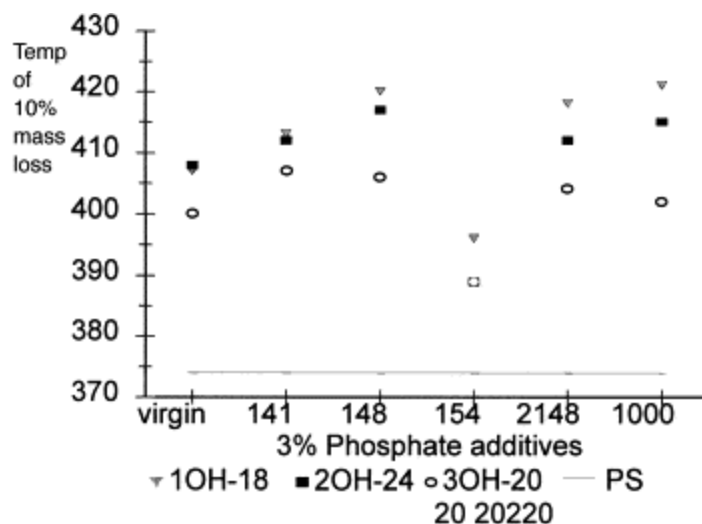


Fig. 4. Temperature of 10% degradation for all three copolymers as a function of the phosphate additive.

There does not appear to be a significant difference amongst the various efficacious additives; all three copolymers give qualitatively similar results and the onset temperature is much higher than observed for polystyrene. The onset temperature is highest with all additives for the 1-alcohol; since this is also the material which is commercially available, it appears to be the material of choice for the cross-linking agent.

#### 3.4.2. TGA/FTIR results

In previous work [\[4\]](#) we have reported on the TGA/FTIR of the combination of additive 141 with the 1-alcohol. Here similar results are reported for the 2- and 3- alcohols. The striking thing about all of the alcohols with additive 141 is the absence of water in the evolved gases. Water is observed when the copolymer is thermally degraded alone but it is absent in the presence of the additive. We believe that we can see vibrations due to water in passing during the degradation but, since this evolves for only a very short time, one cannot be certain of its presence. The presence of aromatics from the degradation of the polymer is certainly seen and [Fig. 5](#), [Fig. 6](#) show the evolution of aromatics from the degradation of the 2-alcohol and its mixture with additive 141 ([Fig. 5](#)) and the 3-alcohol ([Fig. 6](#)) and its mixture with the additive. The noteworthy observation is that aromatics are evolved at higher temperature in the presence of the additive than in its absence. This is another indication of the enhanced thermal stability of this system relative to polystyrene.

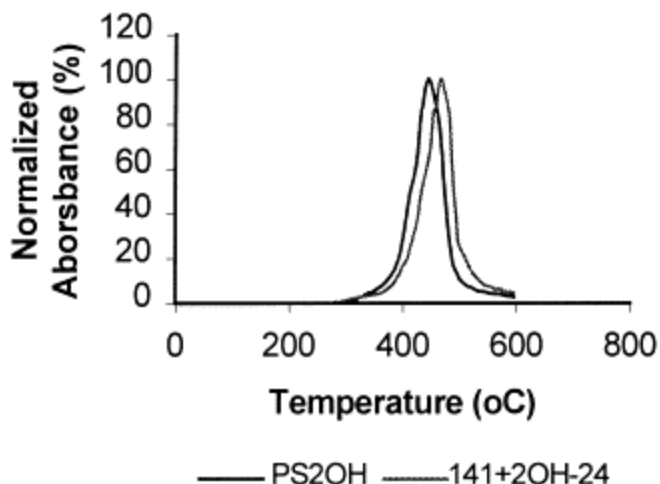


Fig. 5. Normalized absorbance for the 2-alcohol and its mixture with additive 141.

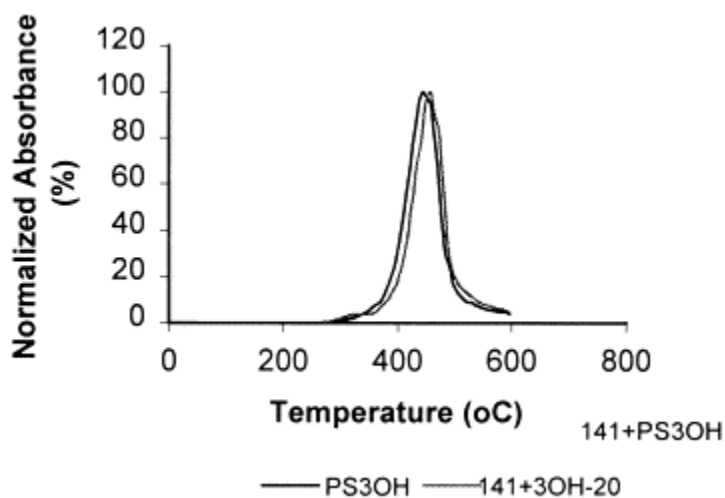


Fig. 6. Normalized absorbance for the 3-alcohol and its mixture with additive 141.

#### 4. Conclusion

Copolymers of styrene with alcohol-containing monomers will participate in Friedel-Crafts chemistry in the presence of a catalyst such as a phosphoric acid and they will not undergo a thermal cross-linking reaction in the absence of an additive unless the alcohol content is quite large. The identity of the phosphoric acid does not appear to have a significant effect on the course of the reaction. The number of methylene groups between the aromatic ring and the alcohol functionality does not have a significant effect on the ability of the copolymer to cross-link nor does it appear to effect the thermal stability of the copolymers.

#### Acknowledgements

This was performed under the sponsorship of the U.S. Department of Commerce, National Institute of Standards and Technology, Grant Number 60NANB6D0119. The kind cooperation

of Dun Chen and Mattson Instruments in making their TGA/FTIR equipment available is gratefully acknowledged.

## References

- [1] N. Grassie, L. Gilks J. Polym. Sci. Polym. Chem. Ed., 11 (1973), p. 1985
- [2] S.K. Brauman J. Polym. Sci. Polym. Chem. Ed., 17 (1979), p. 1129
- [3] J.F. Rabek, L. Lucki J. Polym. Sci. Part A: Polym. Chem., 26 (1988), p. 2537
- [4] Clublely BG, Davis BID, Hyde TG, Lamb F, Randell DR. US Patent No. 4,172,858, Oct. 30, 1979.
- [5] Clublely BG, Davis BID, Hyde TG, Lamb F, Randell DR. US Patent No. 4,248,976, Feb. 3, 1981.
- [6] J. Li, C.A. Wilkie Polym. Degrad. Stab., 57 (1997), p. 293
- [7] Wang Z, Jiang DD, McKinney MA, Wilkie CA. Polym Degrad Stab 1999;64:387.
- [8] Gilman J, Wang Z, Jiang DD, Wilkie CA, in press.
- [9] Schnabel W, Levchik GF, Wilkie CA, Jiang DD, Levchik SV. Polym Degrad Stab 1999;63:365.
- [10] Braun D, Keppler H-G. Makromol Chem 1965;82:132.
- [11] Brandrup J, Immergut EH. Polymer Handbook, vol. 228, 3rd Ed. New York: Wiley, 1989.
- [12] W. Zhu, E.D. Weil, S. Mukhopadhyay J. Appl. Polym. Sci., 62 (1996), p. 2267