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Abstract

Copolymers which contain either alcohol or chloride functionalized polystyrene units have been prepared and they participate in Friedel–Crafts chemistry to give cross-linked polymers by the evolution of either hydrogen chloride or water. Proof of cross-linking comes from the identification of the evolved gas, the insolubility of the product, and the thermal resistance of

the newly formed polymer. The onset temperature for the degradation is raised by about 100°C relative to that of polystyrene and the fraction which is not volatile at 800°C ranges from 10% for the alcohol copolymers to 20% for the chloride copolymers.

1. Introduction

One strategy which may be used to enhance the thermal stability of polymers is to discover processes which will lead to cross-linking. In the majority of cases this means identifying reactions which will link together the functionalities which are present on the polymer. In the case of polystyrene the only functionality is the aromatic ring so one is limited to reactions which involve this ring. There have been four publications which have focused on the Friedel–Crafts chemistry of polystyrene as a means of achieving cross-linking. Grassie and Gilks[1] have used tin tetrachloride as a catalyst and *p*-di(chloromethyl)benzene as the alkylating agent in dichloroethylene as solvent. This does effect cross-linking but at very modest temperature and the cross-linked polymers are less thermally stable than are the starting materials. Brauman[2] has used antimony trichloride as catalyst with both alkylating and acylating reagents; the amount of non-volatile residue was increased. Rabek and Lucki[3] have cross-linked polystyrene at 35°C using aluminum trichloride as catalyst. In all cases the cross-linking reaction occurs at too low a temperature to be useful for the thermal protection of polystyrene from fire.

In recent work from this laboratory[4] it has been shown that various zeolites are effective catalysts to cross-link polystyrene at 300°C but not at lower temperatures when the reaction was performed in a sealed tube with 1,4-benzenedimethanol as the alkylating agent. When the ingredients were heated in a flowing nitrogen atmosphere the diol volatilized before it could react and cross-linking was not observed. In order to make this chemistry useful for reducing the flammability of polystyrene, it is necessary to be certain that the alkylating agent will be available for reaction when the catalyst is active. One may either choose to modify the catalyst or the alkylating agent.

In this paper we describe the results of examining several different catalysts for the alkylation of polystyrene copolymers in which the alkylating agent is incorporated by copolymerization to prevent premature volatilization. Several different catalysts have been examined to determine their potential for achieving cross-linking of the copolymers through Friedel–crafts alkylation as depicted in Scheme. 1.
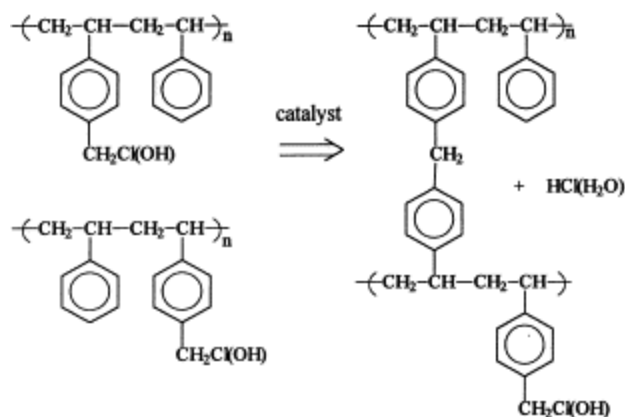
Scheme. 1. Friedel–crafts chemistry on polystyrene copolymers.

2. Experimental

2.1. Materials

The majority of the chemicals used in this study were acquired from the Aldrich Chemical Company, including styrene, p-vinylbenzyl chloride, vinylbenzyl alcohol (mixture of isomers), inhibitor removal columns, and metal halides. 2-Ethylhexyldiphenylphosphate was provided by the Monsanto Chemical Company under the trade name of Santicizer 141. Infrared spectroscopy was performed on a Mattson Galaxy infrared spectrometer while nuclear magnetic resonance spectra were obtained on a GE-300 instrument. Thermogravimetric analysis was performed on a Omnitherm 1000 unit under a nitrogen atmosphere at a scan rate of 20°C per minute. TGA/FTIR data was obtained using a Cahn TG-131 thermogravimetric analyzer interfaced to a Mattson Galaxy infrared spectrometer under inert atmosphere at a scan rate of 20°C per minute. Elemental analysis was done by Midwest Microlabs.

2.2. Preparation of copolymers

The copolymers were prepared by radical initiation in a chloroform-acetone solvent system using azobisiosbutryonitrile, AIBN, as the initiator. The homopolymers of polystyrene, p-vinylbenzyl chloride, and p-vinylbenzyl alcohol as well as copolymers varying between 1% and 99% were prepared. The preparation of the 10% chloride-containing copolymer will be described as typical of all preparations. In a 250 mL three neck round bottom flask were placed 90 mL of chloroform, 10 mL of 0.20 M AIBN in acetone, 9.0 mL of styrene (inhibitor removed), and 1.0 mL of p-vinylbenzyl chloride. The mixture was refluxed for 24 h. At the conclusion of the reaction the solution was cooled and the solvent was removed on a rotary evaporator and the sample was dried in a vacuum oven at 90°C for 2 h. The resulting polymers were analyzed for either chlorine or oxygen, depending upon the type of copolymer which had been produced, and these were used to determine how the composition compared with that expected based upon the amount of starting materials; this is shown in Table 1. One can see that the actual composition for the chloride-containing copolymer is fairly close to that expected from the charge to the flask. The reactivity ratios are available for styrene and p-vinylbenzyl chloride (r_1=0.620 and r_2=1.120)[5] and these predict a composition relatively close to that observed.

The reactivity ratios for the alcohol are not available but those for styrene and the alcohol with an extra methyl group at the benzylic carbon, 1-(*p*-vinylphenyl)ethanol (r_1=0.480 and r_2=0.410)[6] are known and they predict a composition quite close to that found for the two copolymers which contain the smallest amount of the alcohol.

Table 1. Comparison of expected composition and actual composition of the copolymers

Chloride-containing copolymer		Alcohol-containing copolymer	
Expected % based on charge to flask	Analytical result	Expected % based on charge to flask	Analytical result
1	2.8	2.5	10.8
5	7.6	5	15.5
10	13.8	10	25.6

2.3. Thermolysis of copolymers

The copolymers were thermolyzed both in sealed tubes and under a flowing nitrogen atmosphere. For sealed tube reactions an intimate mixture of the alcohol-containing or the chloride-containing copolymer with the additive was prepared. Typically 1.0 g of the copolymer was combined with 1–3% of the additive. Depending upon the identity of the particular additive these were prepared either by grinding the ingredients together or else by dissolving both in compatible solvents then removing all solvent. The additives which may be solvent mixed are cobalt (II) chloride, copper (II) chloride, and zinc chloride. Typically the metal salt and copolymer were combined and then dissolved (acetone for the cobalt and copper salts, tetrahydrofuran for zinc chloride); these were then vacuum stripped to obtain the well-mixed additive polymer blend. The samples (0.1 g) were loaded into a vial which was then sealed under vacuum and placed in an oven maintained at the desired temperature for a predetermined time period. At the conclusion of the reaction time the vial was removed from the oven, allowed to cool to room temperature, and then opened. The efficacy of the cross-linking reaction was determined by solubility. If the resulting product dissolved in chloroform, no cross-linking had occurred. On the other hand, insolubility implies that cross-linking has occurred. The catalyst was removed by washing with a suitable solvent.

For reactions which were conducted in a flowing nitrogen atmosphere, the samples were placed in a demountable tube containing both an entrance and an exit tube which was heated with an oil bath for varying time periods. Nitrogen was passed into the entrance and the exit gases were either passed through a mineral oil bubbler or into an aqueous solution of silver nitrate to permit the identification of hydrogen chloride.

The gel content and the swelling ratio were determined by a Soxhlet extraction using chloroform. The swelling ratio was determined after 30 min of air drying at room temperature while the gel content was after drying in a vacuum oven at 70°C.

3. Results and discussion

Since the alcohol-containing copolymer is not soluble above 15% alcohol, one cannot use solubility as an indicator of cross-linking for copolymers which contain a larger portion of alcohol and therefore only the 15% alcohol-containing copolymer was studied. The chloride-containing copolymer is soluble regardless of the chlorine content and copolymers which contained both 14% and 40% chlorine were studied. The higher chloride content has the advantage of a potentially greater extent of reaction while the 14% is more realistic in terms of practical usage. The composition of the copolymers used in these studies is that which has been determined by elemental analysis.

3.1. Sealed tube reactions of chloride-containing copolymer

Both copolymers were treated with various additives as a function of temperature and the gel content was determined. The 40% chloride-containing copolymer was used in order to maximize the extent of reaction. The results are shown in Table 2; the results for cobalt, copper, and zinc are for solvent-mixed blends while the others were prepared by grinding.

Table 2. Gel content, %, for the thermolysis of 40% chloride-containing copolymer as a function of temperature and catalyst (1–3%) in a sealed tube after 1 h at the temperature indicated

Catalyst	150°C	200°C	250°C
None	0	0	Little
$CoCl_2$	100	100	100
$CuCl_2$	100	100	100
$ZnCl_2$	100	100	100
$SnCl_2$	100	100	100
$NiCl_2$	0	Little	Little
$MnCl_2$	0	100	100
$CrCl_3$	0	0	0
Zeolites	0	0	0

The utilization of this reaction for flame retardancy requires that there be no reaction under ordinary processing conditions but that reaction commence before significant decomposition of the copolymer has occurred, i.e., 250–350°C. The results shown in Table 2 indicate that these combinations of alkylating agent and catalyst are effective at too low a temperature to be useful for our purposes.

Mixing of the additive and the copolymer is very important; in small molecule Friedel–crafts chemistry, which is carried out in solution, mixing is not a problem. In these reactions it is very difficult to achieve a homogeneous distribution of the catalyst by grinding and this can lead to some distribution effects. Cobalt chloride, copper chloride, and zinc chloride are soluble in organic solvents which also dissolve the copolymer so these have been mixed both in solvent

and in the solid state. Table 3 shows a comparison of the extent of cross-linking for solvent-mixed versus mechanically mixed blends of cobalt chloride and the 14% chloride-containing copolymer. It is quite clear that solvent-mixed additive copolymer compositions give a much higher gel content at lower additive levels. One may also note that even at 14% chloride content, essentially complete cross-linking is observed for solvent-mixed systems even at very low catalyst loadings. The solvent-mixed combinations indicate the results that one could expect if mixing were performed in an extruder.

Table 3. Comparison of extent of cross-linking for solvent-mixed and mechanically mixed blends of cobalt chloride and 14% chloride-containing copolymer; reaction at 150°C for 1 h

Solvent-mixed		Mechanically-mixed	
% $CoCl_2$	% Cross-linking	% $CoCl_2$	% Cross-linking
0	0	0	0
0.25	90	3	41
0.50	100	7	68
1	100	11	89

3.2. Sealed tube reactions of alcohol-containing copolymer

The 15% alcohol-containing copolymer was thermolyzed with all of the same additives as were used for the chloride-containing copolymer with similar results except for the behavior of the zeolites. All of the metal compounds gave exactly the same results but some zeolites were found to effect cross-linking at 150°C. All zeolites which were tested did cause cross-linking by 200°C. It is surprising to find that zeolites are effective catalysts for the alcohol but not for the chloride, since zeolites are known to catalyze Friedel–crafts reactions[7, 8].

3.3. Thermal analysis of products from sealed tube reactions

The products which were recovered from the sealed tube reactions were exhaustively washed with a solvent for the additive to be sure that it was entirely removed then subjected to thermogravimetric analysis. An increased thermal resistance of the material may be evident by either an increase in the amount of char which is formed or by an increase in the onset temperature of the degradation or both. The results are shown in Table 4. It is clear that reaction with the additive causes cross-linking, as shown by the insolubility of the product, and that this cross-linked polymer is more thermally stable than the starting material and gives a higher char yield. In this study the temperature for 10% degradation has been used as an indication of the onset of degradation. In order to show these trends the TGA curves for all four materials are shown in Fig. 1. In the case of the virgin copolymer, the early degradation may be attributable to HCl evolution. The other samples have already been thermally treated, HCl evolution has already occurred, and the polymer is cross-linked. For the cobalt chloride blend, degradation begins at about 230°C and continues to 400°C before leveling off until the main degradation begins at about 420°C. For copper chloride, the early degradation occurs between 230°C and 330°C then it levels off until the complete degradation commences at about 420°C. Finally zinc chloride shows an early degradation between 220°C and 250°C and then the main chain scission of the cross-linked copolymer commences at about 450°C. The early

degradation step cannot be due to the presence of oligomers or uncross-linked polymer, since this would have been removed in the Soxhlet extraction. It is most likely due to the presence of water or solvent which has been retained within the sample or to additional hydrogen chloride evolution. It is quite possible that not all the HCl is lost during the thermal treatment and that additional reaction occurs within the TGA furnace. The different evolution temperature ranges for the different metal salts, indicative of varying Lewis acidity and hence solvent retention properties, provides some confirmation for this assertion[9]. Similar results have been obtained for the alcohol-containing copolymer and this is shown in Table 5. The increase in the onset temperature of degradation is about the same for the alcohol-containing copolymer as for the chloride but the fraction which is non-volatile at 800°C is lower for the alcohol. The lower amount of residue may be due to the lower amount of functional group, alcohol vs. chloride, which would give a lower cross-link density for the alcohol and hence an easier degradation. Again an early degradation occurs for these samples.

Table 4. Temperature at which 10% degradation occurs and % of non-volatile residue at 800°C for thermolysis of 40% chloride-containing copolymer (additive level is 1–3%)

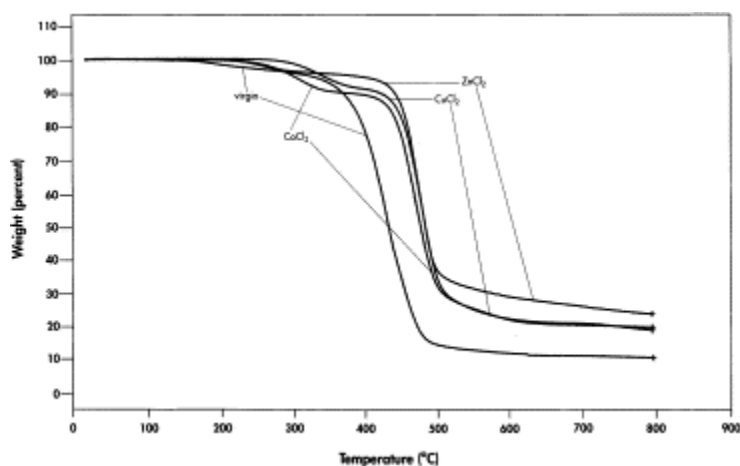| Additive	Temperature (°C) for 10% degradation	% non-volatile at 800°C
None	380	10
$CuCl_2$	428	20
$CoCl_2$	440	19
$ZnCl_2$	450	23

Fig. 1. Thermogravimetric analysis curves for 40% chloride-containing copolymer and blends of the copolymer with $ZnCl_2$, $CoCl_2$, and $CuCl_2$ under an inert atmosphere at a scan rate of 20°C per minute.

Table 5. Temperature at which 10% degradation occurs and % of non-volatile residue at 800°C for thermolysis of 15% alcohol-containing copolymer (1–3% of additive)

Additive	Temperature (°C) for 10% degradation	% non-volatile at 800°C
None	340	0
$CuCl_2$	408	5

CoCl₂	385	6
ZnCl₂	435	9
MnCl₂	392	4
SnCl₂	430	6
NiCl₂	377	4

3.4. Reactions in a flowing nitrogen atmosphere

When the reaction is conducted in a sealed tube, one retains all of the products which may lead to rereaction and hence possibly an erroneous conclusion. Accordingly reactions were also performed in a flowing system in which any volatiles would be removed from the system as they are formed. The mixture of additive and copolymer was placed in a vessel which was then placed in an oil bath which had been preheated to the desired temperature and the exit gas stream was directed into an aqueous solution of silver nitrate; the results are shown in Table 6.

Table 6. Occurrence of cross-linking for blends of 1–3% additive and 40% chloride-containing copolymer at various temperatures for 1 h under flowing nitrogen conditions

Catalyst	150°C	200°C	250°C
None	No	No	No
CuCl₂	Yes	Yes	Yes
CoCl₂	Yes	Yes	Yes
ZnCl₂	Yes	Yes	Yes
AlCl₃	Yes	Yes	Yes
FeCl₃	Yes	Yes	Yes
NiCl₂	No	Yes	Yes
CrCl₃	No	No	No
MnCl₂	Yes	Yes	Yes
SnCl₂	Yes	Yes	Yes
Mo₂O₅	Yes	Yes	Yes
TiO₂	No	No	No
ZnO	Yes	Yes	Yes
Zeolite	No	No	No
Phosphate	No	No	Yes

The evidence of cross-linking of the resulting material is that this material does not dissolve in a solvent which would dissolve virgin copolymer. Further proof of reaction comes from the identification of hydrogen chloride as an evolved gas. In all cases where the material was identified as having undergone cross-linking, the evolution of HCl was observed. When a sample of pure 40% chloride-containing copolymer was thermolyzed at 200°C for 1 h and the evolved gases were trapped in an aqueous silver nitrate solution, this solution was observed to be a bit cloudy; this indicates that some HCl evolution occurs with a minor amount of cross-

linking. On the other hand in the presence of any of the effective catalysts, a definite precipitate was easily discerned and cross-linking is clearly indicated by the insolubility of the product. The phosphate ester which was used is 2-ethylhexyldiphenylphosphate, known commercially as Santicizer 141 (Monsanto Chemical). This material is believed to thermally decompose at about 250°C to produce a phosphoric acid and it is assumed that this phosphoric acid is the effective catalyst for the reaction. More information on this additive will be provided later in this paper.

The identical test was performed using the 15% alcohol-containing copolymer. Two differences were observed: heating the alcohol alone at 200°C effects cross-linking and zeolites will catalyze the cross-linking reaction of this copolymer. It is surprising that water is evolved more easily than hydrogen chloride in the absence of a catalyst; the effectiveness of zeolites for the alcohol but not the chloride was also observed in sealed tube reactions. There is no proof that the reactions which are occurring are actually Friedel–Crafts chemistry; it is known that cross-linking occurs but the route by which this happens is not certain. In the case of the alcohol, ether formation by the interaction of two alcoholic functionalities would also produce a cross-linked product and this reaction outcome cannot yet be eliminated.

3.5. Thermogravimetric analysis

The cross-linked polymers which were obtained from the flowing gas reactions were treated with a solvent for the additive and then were subjected to thermal analysis. Table 7 shows the results for the 14% chloride-containing copolymer which has been treated with various metal additives. It must be noted that these samples have been extensively treated with solvent to remove any additive; in some cases, notably cobalt chloride, the color of the additive enables one to monitor its removal. It is clear from this data that the cross-linked polymer is more thermally stable than is the unreacted material. It must be noted that these results are for the 14% chloride-containing copolymer while the sealed tube reactions utilized the 40% copolymer so the results are not strictly comparable but similar trends are observed.

Table 7. Non-volatile residue (%) at 800°C and temperature for 10% degradation for thermolyzed blends of additive and 14% chlorine-containing copolymer (additive level is 1–3%)

Catalyst	Temperature for 10% degradation	% non-volatile at 800°C
None	365	5
$CuCl_2$	383	10
$CoCl_2$	400	9
$ZnCl_2$	401	10

3.6. Thermal cross-linking of alcohol-containing copolymer

The 15% alcohol-containing copolymer has been heated for variable time periods at 300°C with no additive in order to obtain information on the thermal cross-linking. The gel content as well as the ratio of retained solvent to gel, a measure of the cross-linking density, were measured and then TGA was performed on the recovered sample. The results are shown in Table 8. These data show that the alcohol copolymer will thermally cross-link at 300°C in the

absence of a catalyst; it appears that only about 70% of the polymer is involved in the reaction, perhaps due to the varying accessibility of the alcohol functionalities once the cross-linking reaction commences. A soluble polymer is infinitely swellable so as the density of cross-links increases, the ratio of solvent to gel should decrease. One sees in the table that there is a small change in the ratio with the different times of heating; the density of cross-links appears to increase with time of heating.

Table 8. Effects of heating the 15% alcohol-containing copolymer at 300°C for various time periods

Heating time (h)	0.5	1.0	3.0	5.0	24
Gel content (%)	0	51	60	70	68
Solvent/gel	—	5.9	7.2	5.4	5.2
% non-volatile	3	3	3	5	6
T(°C) 10% degradation	361	377	412	410	420

3.7. Rate of cross-linking

A sample of the 40% chloride-containing copolymer blended with 3% cobalt chloride was heated in a TGA experiment at various heating rates without prior heat treatment; the TGA curves are shown in Fig. 2. The presence of the additive causes an earlier mass loss which is the onset of cross-linking; once this reaction is complete the curve levels off until, at higher temperature, degradation of the cross-linked material begins. The onset temperature of the degradation is higher the faster the rate of heating, but the amount of non-volatile residue is about the same for all heating rates. For the virgin copolymer one degradation step flows into the next while in the presence of cobalt chloride, regardless of the heating rate, there is a distinct difference between HCl evolution and polymer degradation.
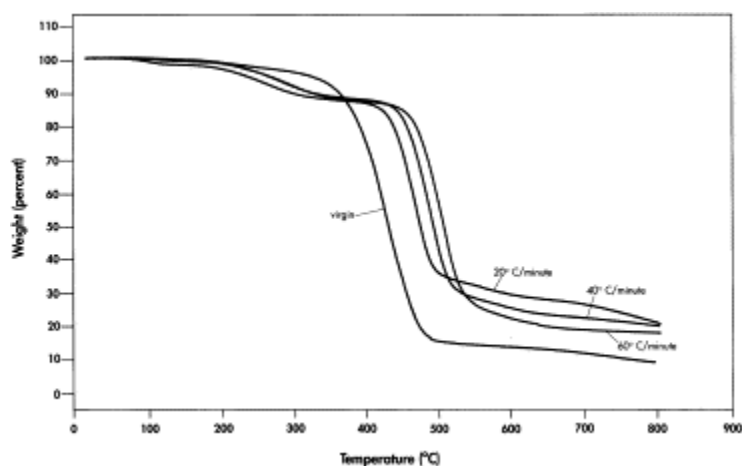

Fig. 2. Thermogravimetric analysis curves for the 40% chloride-containing copolymer and its blend with 3% CoCl$_2$ at varying heating rates under an inert atmosphere.

3.8. TGA/FTIR studies of copolymers

TGA/FTIR studies have been carried out on the pure copolymers and blends of the copolymers with cobalt chloride and with the phosphate ester. The degradation of the 40% chloride copolymer begins at about 250°C with the evolution of hydrogen chloride (2963 cm^{-1}) and aromatic compounds (3071 cm^{-1}). This is significantly earlier than the first appearance of aromatic compounds in the degradation of polystyrene[10] and suggests that the evolution of HCl may in some way influence the degradation. Fig. 3 shows a composite of the TGA curve together with the absorbance of hydrogen chloride and of aromatics. The maximum amounts of both HCl and aromatics is observed at 420°C but evolution of HCl continues to 460°C with aromatics continuing to evolve to 580°C.
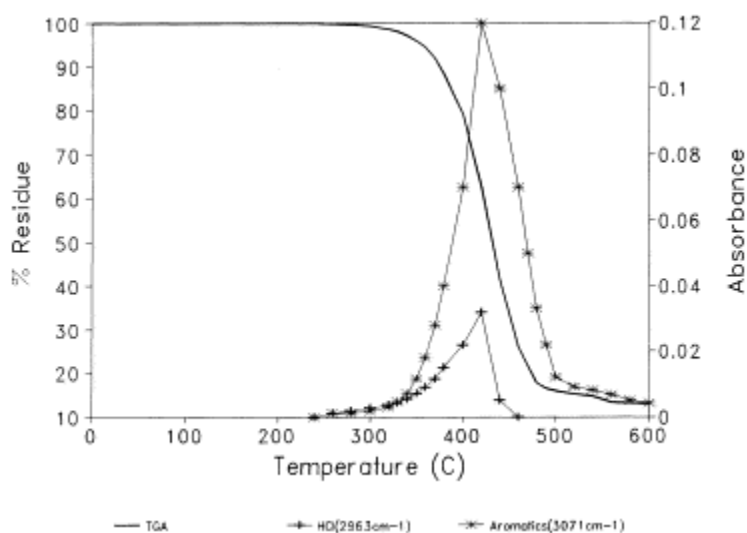
Fig. 3. Composite of the TGA curve for the degradation of the 40% chloride-containing copolymer at a rate of 20°C per minute under an inert atmosphere and the infrared absorbance of evolved hydrogen chloride and aromatics.

In the presence of cobalt chloride, HCl evolution from the chloride-containing copolymer begins earlier (170°C) and the evolution of aromatics is later (340°C); this is the normal temperature for the evolution of aromatics from polystyrene[10]. The composite of the TGA curve and the FTIR absorbances of HCl and aromatics vs. temperature is shown in Fig. 4.
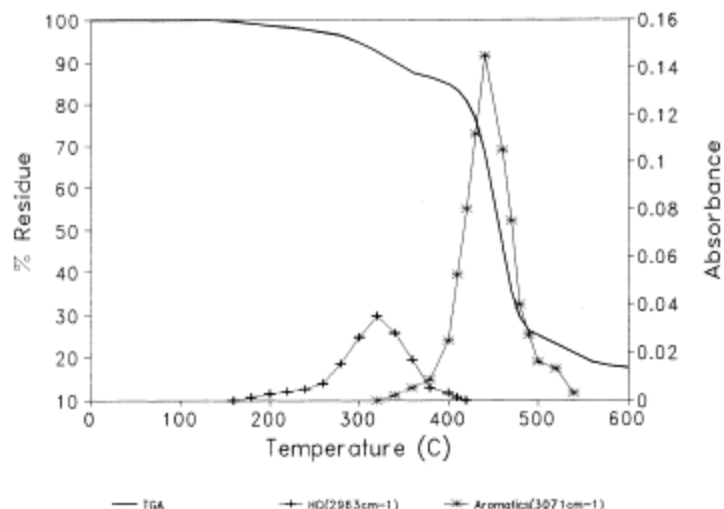
Fig. 4. Composite of the TGA curve for the degradation of the blend of the 40% chloride-containing copolymer with 3% cobalt chloride at a rate of 20°C per minute under an inert atmosphere and the infrared absorbance of evolved hydrogen chloride and aromatics.

The case of the phosphate ester is perhaps the most interesting. It is necessary to first of all understand the degradation of the phosphate ester alone; the composite of the TGA curve and the evolution of aromatic and aliphatic products is shown in Fig. 5. By analysis of the infrared spectra of the gas phase it appears that the phosphate ester simply begins to volatilize at about 230°C, the infrared spectrum of the evolved gas is identical with that of the liquid phase phosphate ester. At slightly higher temperature the degradation begins, probably by elimination of the 2-ethylhexyl moiety through a β-hydrogen shift to give an OH on phosphorus and the formation of a terminal olefin, 2-ethyl-1-hexene; one can see a definite change in the TGA curve and new bands attributable to aliphatic compounds appear (2971 cm^{-1}). At higher temperatures one sees the evolution of an aromatic compound (3081 cm^{-1}). The infrared spectra is most consistent with the formation of phenol so it is most likely that there is a homolytic cleavage of the P–O–Aryl bond and the phenoxy radical abstracts a hydrogen to give phenol. The fate of the phosphorus radical is unknown at this time. There is clear evidence in the infrared spectra for the loss of both P–O–Alkyl (1030 cm^{-1}) and P–O–Aryl (951 cm^{-1}) vibrations.
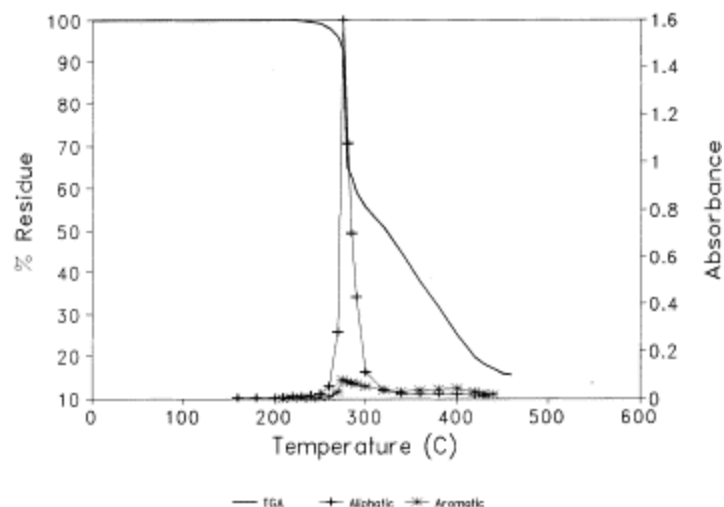
Fig. 5. Composite of the TGA curve for the degradation of the phosphate ester at a rate of 20°C per minute in an inert atmosphere and the infrared absorbance of evolved alkene (2971 cm^{-1}) and aromatics (3081 cm^{-1}).

When the blend of the phosphate ester and the chloride-containing copolymer is studied, the evolution of HCl begins much earlier and occurs over a much narrower temperature range while the evolution of aromatics is pushed back. Fig. 6 shows the absorbance of HCl for the virgin copolymer and its combination with both CoCl2 and the phosphate ester and Fig. 7 shows the analogous plot for the evolution of aromatics. The evolution of hydrogen chloride occurs within a much narrower range for the blend with the phosphate ester than for either the virgin copolymer or the blend with cobalt chloride. The degradation of the copolymer begins at about the same temperature for each blend but the rise is much slower for the phosphate ester than for the other samples.
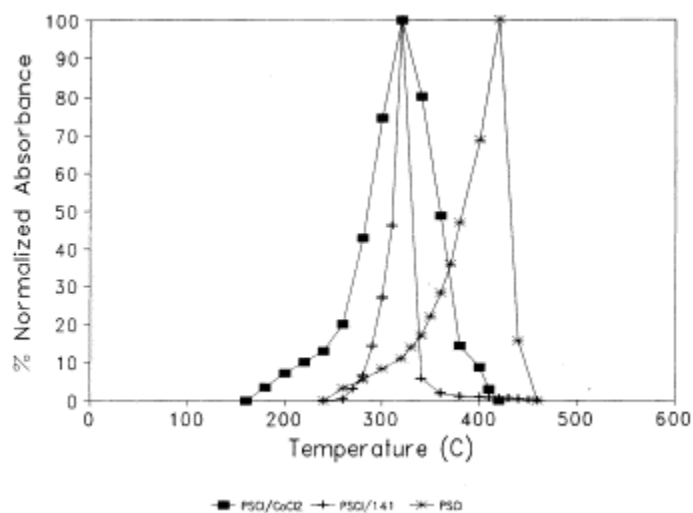

Fig. 6. Absorbance of evolved hydrogen chloride at 2963 cm^{-1} for the 40% chloride-containig copolymer (PSC1) and its blend with COCl2, and the phosphate ester (PSC1/141).
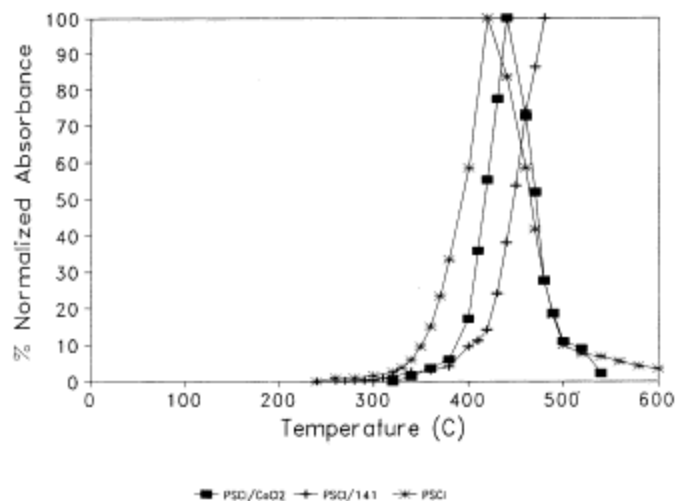
Fig. 7. Absorbance of evolved aromatics at 3071 cm^{-1} for the 40% chloride-containing copolymer (PSC1) and its blend with CoCl$_2$, and the phosphate ester (PSC1/141).

The degradation of the 15% alcohol copolymer is quite similar to that of the chloride except that water (3854 cm^{-1}), rather than HCl, is evolved. The 15% alcohol copolymer begins to evolve both water and aromatics at about 170°C; these reach maximum concentration at 440°C and continue until 600°C. The amount of water which is evolved is never large; the composite figure is shown as Fig. 8. Two pathways for water evolution have been considered, Friedel–crafts chemistry and ether formation by the reaction of two alcoholic functionalities. Both lead to cross-linking and no determination has been made of which pathway is followed.
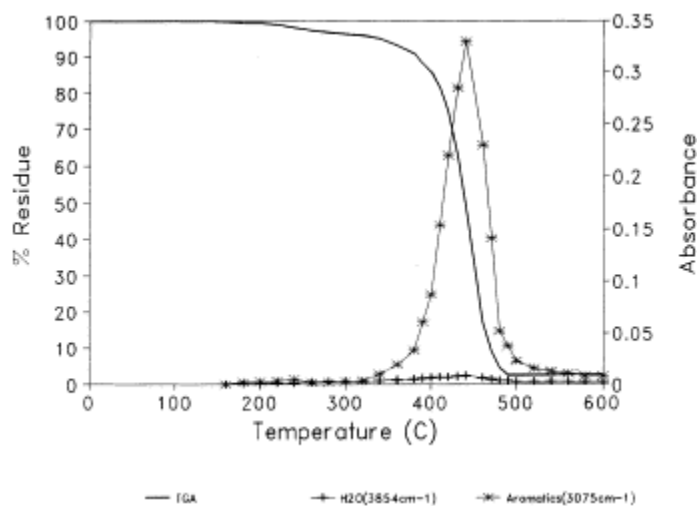

Fig. 8. Composite of the TGA curve for the degradation of the 15% alcohol-containing copolymer at a rate of 20°C per minute under an inert atmosphere and the infrared absorbance of evolved water and aromatics.

In the case of the blend with cobalt chloride water evolution begins later, 210°C, and it continues for 140°C. The evolution of aromatics returns to the normal temperature for the degradation of polystyrene; the composite figure is shown as Fig. 9.
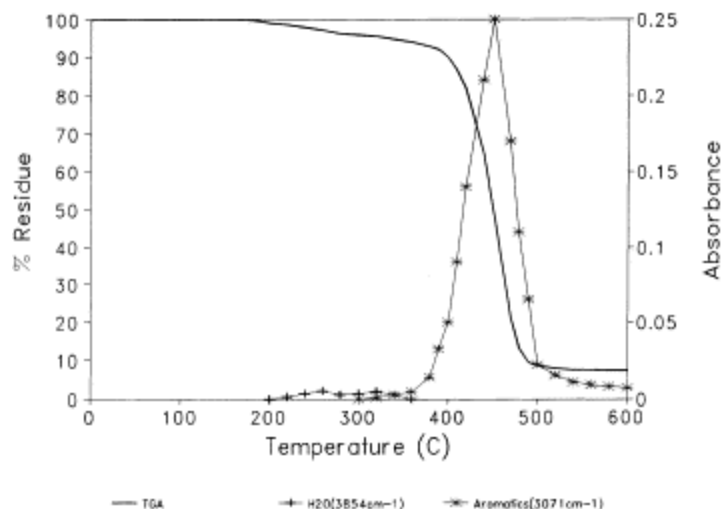
Fig. 9. Composite of the TGA curve for the degradation of the blend of the 15% alcohol-containing copolymer with $CoCl_2$ at a rate of 20°C per minute under an inert atmosphere and the infrared absorbance of evolved water and aromatics.

The case of the phosphate ester is again very interesting. Infrared bands for water evolution are noted over a very small temperature range, 260–280°C and are never large in intensity but cross-linking definitely occurs. Fig. 10 shows the absorbance of water as a function of temperature for the virgin alcohol copolymer and its blend with $CoCl_2$. Water is lost much quicker in the presence of the additive than in its absence. Fig. 11 shows the evolution of aromatics for the three systems. There is a small aromatic peak for the phosphate ester blend which occurs at the same temperature as for the phosphate ester alone and which is assigned to that component alone. The presence of either additive moves the evolution of aromatics to higher temperatures.
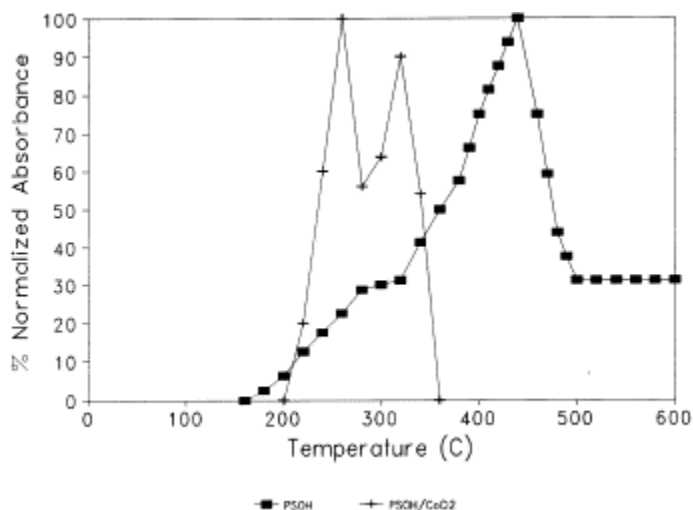

Fig. 10. Evolution of water at 3854 cm^{-1} from the 15% alcohol-containing copolymer and its blend with $CoCl_2$; no evolved water can be detected from the blend with the phosphate ester.
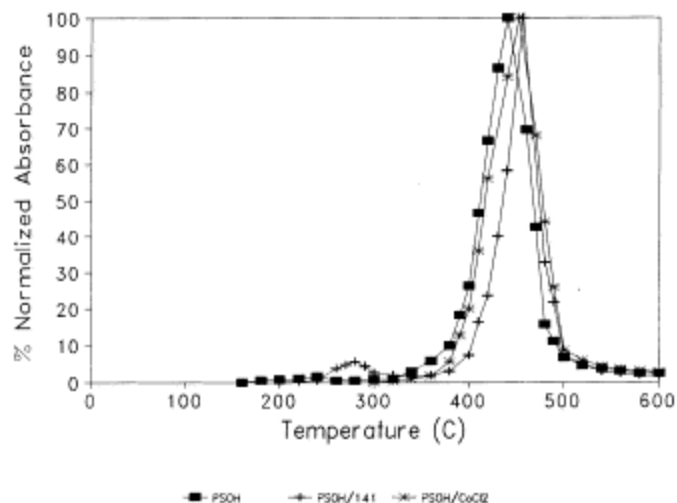
Fig. 11. Evolution of aromatics at 3071 cm^{-1} from the 15% alcohol-containing copolymer and its blend with CoCl$_2$ and the phosphate ester.

4. Conclusion

Copolymers of styrene with vinylbenzyl chloride and vinylbenzyl alcohol will undergo Friedel–Crafts cross-linking reactions in the presence of suitable catalysts. Many transition metal halides and oxides will catalyze the reaction. Some zeolites are effective catalysts for the alcohol but are ineffective for the chloride. Most catalysts are too efficient and cause the cross-linking reaction to occur at 200°C or lower. This is lower than the 250–350°C range which is desired. The most promising catalysts is 2-ethylhexyldiphenylphosphate, which causes the cross-linking reaction to begin at 250°C and there is no reaction at slightly lower temperatures.

Acknowledgements

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