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XPS Characterization of Friedel-Crafts Cross-linked Polystyrene

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Abstract

The combination of a difunctional alkylating agent, either hydroxymethylbenzyl chloride or α,α' -dichloroxylene with polystyrene or high-impact polystyrene together with a Friedel-Crafts catalyst, 2-ethylhexyldiphenylphosphate, and an amine to react with hydrogen chloride has been studied by X-ray photoelectron spectroscopy. The results confirm what had been suggested from previous investigations using

thermogravimetric analysis; cross-linking of the polymer occurs as the temperature is raised and the alcohol-containing alkylating agent gives a greater amount of cross-linking than does the dichloro compound.

Keywords

XPS, Friedel-Crafts, Cross-linking, Polystyrene, HIPS

1. Introduction

Friedel-Crafts chemistry has been used to cross-link polystyrene for a long period of time. Grassie and Gilks [\[1\]](#) used tin tetrachloride as the cross-linking catalyst with *p*-di(chloromethyl)benzene as the alkylating agent and found that a cross-linked polymer could be formed near room temperature. Brauman [\[2\]](#) used various alkylating and acylating agents with antimony trichloride as catalyst and found that alkylating agents increased char formation and decreased the rate of release of volatiles. Rabek and Lucki [\[3\]](#) used aluminum trichloride as the catalyst with 1,2-dichloroethane as the cross-linking agent. Khanna and Pearce [\[4\]](#) prepared copolymers from styrene and vinylbenzyl chloride and found that these copolymers always give a greater than expected yield of char. These systems all did undergo cross-linking reactions but at too low a temperature to be useful.

Work in these laboratories on Friedel-Crafts cross-linking of polystyrene began in 1997 with a publication in which we showed that it was possible, by the correct identification of the catalyst and cross-linking agent, to have the cross-linking reaction commence at temperatures above the processing temperature so that the polymer could still be processed as a thermoplastic. This initial work used zeolites as the catalyst with benzenedimethanol as the alkylating agent [\[5\]](#). A rather facile reaction occurs but only in a sealed tube, when the reaction is conducted under flowing conditions, the alkylating agent volatilized before it could react. This problem was solved through the use of a copolymer of styrene with vinylbenzyl alcohol [\[6\]](#), [\[7\]](#). In this system, the alcohol functionality acts as the alkylating agent and releases water, a benign product of the reaction. The catalyst which has been used is 2-ethylhexyldiphenylphosphate (DPP). This catalyst undergoes thermal degradation at about 250 °C to form 2-ethylhexene and diphenylphosphoric acid, the actual catalyst for the reaction. This system has been investigated using both thermogravimetric analysis (TGA), and Cone calorimetry. By TGA it is found that the onset temperature of the degradation is increased by about 50 °C, indicating a significant enhancement in thermal stability. From Cone calorimetry [\[8\]](#), the peak heat release rate is reduced from 1160 kW/m² to less than 400 kW/m². When radiative gasification measurements were performed, one can observe char formation. Thus one can clearly state that cross-linking occurs and that this leads to the formation of char and this char serves to insulate the polymer from further degradation.

Utilization of this technology requires the production of a new copolymer, therefore attempts have been made to determine if a system could be devised in which polystyrene could be functionalized in a relatively low temperature step followed by cross-linking at higher temperatures. A great number of difunctional materials were studied to ascertain if a suitable system could be identified. There are two reagents of choice, both of which will react at a temperature of about 150 °C to give a functionalized polystyrene and then cross-link in the temperature regime of 250–300 °C; these reagents are hydroxymethyl benzyl chloride (HMBC) and α,α' -dichloroxylene (DCPX) [\[9\]](#). The catalyst that is used is DPP and the reaction is conducted in the presence of a small amount of 2,2,6,6-tetramethyl-4-piperidinol (TMP) as an HCl acceptor. Both of these reagents give large reductions in the peak heat release rate both in the presence and absence of the catalyst. The most efficacious system is HMBC in the presence of DPP and TMP [\[10\]](#).

This XPS investigation was initiated in order to answer some of the questions which have arisen during the previous work. It has already been shown that X-ray photoelectron spectroscopy (XPS) is more sensitive than TGA in identifying the onset of cross-linking reactions [\[11\]](#), [\[12\]](#). Another advantage of the XPS system is the possibility of observing the fate of the phosphorus as well as carbon.

2. Experimental

2.1. Materials

Polystyrene and most other laboratory chemicals were acquired from Aldrich Chemical Company. The difunctional alkylating reagents were synthesized following the procedures outlined in the previous work [\[9\]](#), [\[10\]](#). High impact polystyrene (HIPS) was kindly provided by the Huntsman Chemical Company.

2.2. XPS experiments

The spectra (MgK_{α}) were recorded on a PHI 5300 ESCA system (Perkin-Elmer) at 250 W (12.5 kV 20 mA) under a vacuum better than 10^{-6} Pa (10^{-8} Torr), calibrated by assuming the binding energy of adventitious carbon to be 284.6 eV. The specimens were prepared in the form of a thin film. The 'pseudo in situ' protocol used in this work denotes that only one specimen at a fixed orientation was employed for absolute intensity measurement from room temperature up to 500 °C. All samples were heated outside the XPS chamber under the protection of argon atmosphere. The extent of carbonization (cross-linking) is based on the absolute intensity (cps·eV, counts per second·eV) derived from C1s spectra. The error limits on the intensity measurements can be estimated as $\pm 20\%$, following the work of Wagner [\[13\]](#).

3. Results

There are at least two important results which arise from an XPS investigation, the relative intensity (cps·eV, based on the peak area), a quantitative indicator determined from the photoelectron spectrum of the element, which gives information on the relative accumulation of carbon, associated with the extent of cross-linking and, in the case of carbon, the plasmon loss (eV, the separation between the plasmon peak and the principal peak in C1s spectrum), a qualitative indicator describing the chemical nature, i.e. the degree of graphitization of the material. Most attention will be focused on the accumulation of carbon since this is indicative of the cross-linking process. In the earlier work, cross-linking was shown by the insolubility of the polymer.

When a composition which contained polystyrene with 10% HMBC, 5% 2-ethylhexyldiphenylphosphate and 0.1% of a hindered amine was heated at 150 °C, it was observed that both water and hydrogen chloride were evolved. This is consistent with a Friedel-Crafts alkylation of polystyrene, yielding a functionalized polymer. Infrared spectroscopy provided evidence to support this observation. When the identical composition was heated in the range of 250–300 °C, cross-linking was evident, as attested by the insolubility of the polymer in solvents, such as toluene or tetrahydrofuran, that would normally dissolve the polymer [\[9\]](#).

Further evidence of cross-linking comes from cone calorimetry. A cross-linked polymer is expected to have enhanced fire resistance, as measured by cone calorimetry. In this case, the composition referenced above shows a 51% decrease in the peak heat release rate [\[10\]](#).

A radiative gasification experiment has been performed on a similar composition in which one can take pictures as the sample is heated in a nitrogen atmosphere. In these experiments the formation of surface char can be visually observed [\[8\]](#). These observations strongly support the occurrence of cross-linking.

The advantage that is offered by XPS is that one can follow the accumulation of carbon, and other elements, as a function of temperature. Carbon accumulation at the surface can only occur as other elements are lost, which suggests that new carbon-carbon bonds are formed, i.e. cross-linking. Either new sigma bonds between adjacent chains or new pi bonds between carbon atoms which are already attached or both types of bonds can be formed. Naturally, as new carbon-carbon pi bonds are formed, the residue must become more graphite-like and the extent of graphitization can be assessed through the plasmon loss parameter. In the majority of cases in which degrading polymers have been examined, the extent of graphitization is never very high [\[11\]](#).

[Fig. 1](#) shows the comparison of the relative intensity in the carbon 1s spectrum of polystyrene with that of a composition containing the polymer along with HMBC as the alkylating agent with TMP present to absorb any HCl that is produced. One can clearly see that carbon accumulation occurs slightly more easily in the presence of the cross-linking reagent than in its absence up to 400 °C. Above this temperature, virgin polystyrene shows somewhat higher carbon accumulation; this may be attributed to experimental uncertainties that become more pronounced above 400 °C. The likely mode by which carbon accumulation occurs in virgin polystyrene is a loss of hydrogen while, when the difunctional alkylating reagent is present, cross-linking may occur with the concomitant loss of water or hydrogen chloride. Accumulation of carbon continues up to about 400° and it is still present at 500 °C.

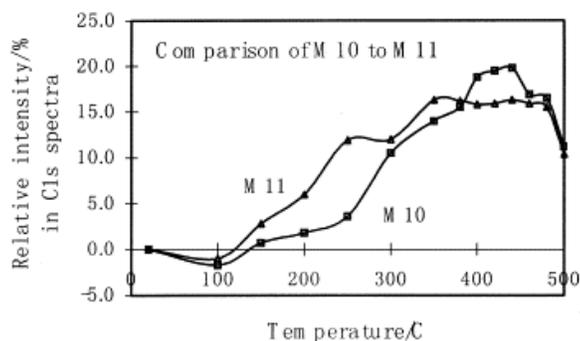


Fig. 1. Comparison of relative intensity in the carbon 1s spectrum for virgin polystyrene (M10) and polystyrene with HMBC and TMP (M11).

[Fig. 2](#) is the comparison of cross-linking using HMBC as the cross-linking reagent in the absence (M11) and presence (M12) of DPP. The onset of cross-linking is remarkably similar in both systems but, in the presence of DPP, there is some indication of an enhanced early cross-linking step. Above 200 °C the systems with and without catalyst are within experimental error; there is no difference in cross-linking. [Fig. 3](#) portrays similar data for the cross-linking reagent DCPX in the presence (M14) and absence of DPP (M13). Cross-linking begins earlier in the absence of DPP but to only a very limited extent until temperatures exceed 300 °C. On the other hand, in the presence of DPP there is a smooth increase in cross-linking with temperature. Finally, [Fig. 4](#) offers a comparison of the two cross-linking reagents, HMBC (M11) and DCPX (M14). Carbon accumulation occurs much more rapidly for HMBC than for DCPX. It is noteworthy that the carbon has vanished by 500 °C for DCPX but remains for HMBC. The likely explanation is that a more thermally stable surface is obtained from HMBC than from DCPX. The reduction in peak heat release rate for HMBC was 51% while from DCPX it is only 31% so this is a consistent observation.

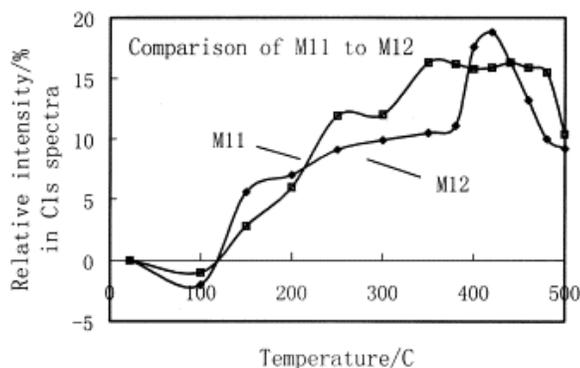


Fig. 2. Comparison of the relative intensity in the carbon 1s spectrum for polystyrene with TMP and HMBC (M11) with that which also contains DPP (M12).

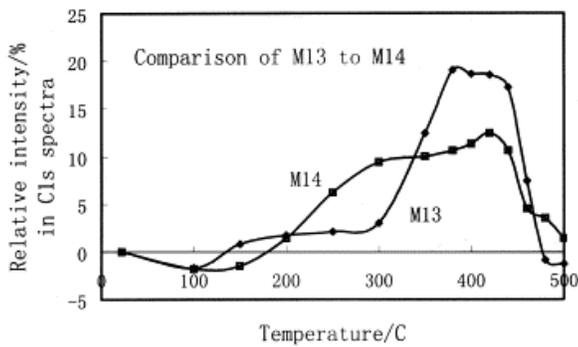


Fig. 3. Comparison of relative intensity in the carbon 1s spectrum for polystyrene with DCPX and TMP (M13) with that which also contains DPP (M14).

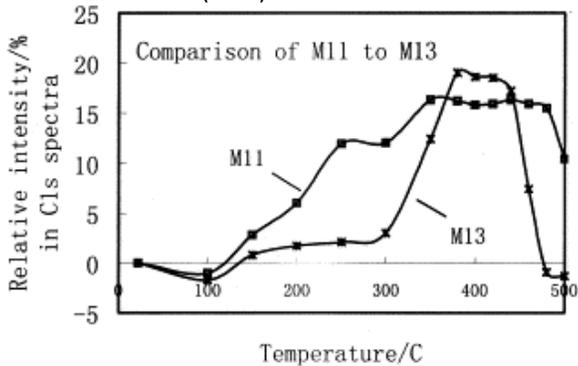


Fig. 4. Comparison of relative intensity in the carbon 1s spectrum for polystyrene with TMP and DPP and HMBC (M11) or DCPX (M13).

The degree of graphitization as measured from the plasmon loss is about the same for all systems. There is an increase of about 2 eV over the temperature range studied, the maximum value reached is about 25 eV, much lower than the value of about 31 eV expected for well-ordered graphite. From the plasmon loss data one may conclude that the cross-linking up to 500 °C never leads to a significant degree of graphitization, but the formation of a graphite-like structure has begun.

The relative intensity in the phosphorus spectrum is shown in [Fig. 5](#) for a composition which contains polystyrene, TMP, DPP and HMBC (M12) or DCPX (M14). The binding energy of all samples stays constant at 135.0 ± 0.5 eV, indicating that the phosphorus is always in the +5 oxidation state.

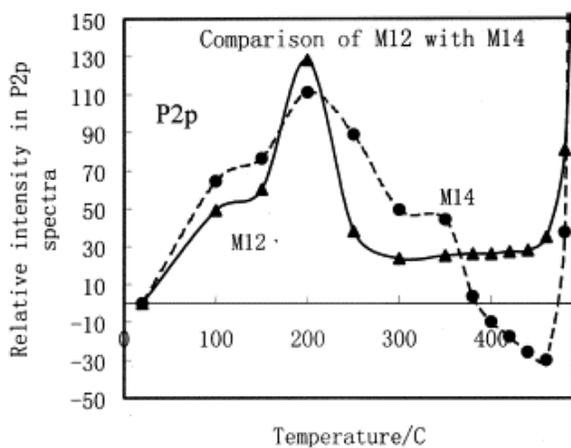


Fig. 5. Comparison of the relative intensity in the phosphorus 2p spectrum for polystyrene with TMP, DPP and HMBC (M12) or DCPX (M14).

Any degradation of the polymer will increase the relative amount of phosphorus in the sample, since the other elements must decrease, therefore the observation of an increased phosphorus content initially must be related to the loss of other species from the sample and/or transportation of some species from the interior. The relative intensity of phosphorus rises rather quickly at first but also begins to decrease above 200 °C; this may be attributed to the presence of a renewed surface above 200 °C, due to the transport of components from the bulk of the polymer melt. The temperature is higher near the surface than in the interior, so the polymer undergoes more degradation near the surface, resulting in a lower molecular weight with a viscosity much less than in the bulk. The generation and transport of the volatiles, e.g. phosphoric acid, from the interior of the polymer melt outward through a strong viscosity gradient leaves a renewed surface, which XPS interrogates. Thus XPS uniquely has the opportunity to describe the role of phosphorus in this system. After the maximum the decline must indicate the volatilization of the phosphorus species at higher temperatures. In the previous TGA study on the degradation of DPP [6], degradation commences at about 250 °C and the mass loss is quite sudden. Mass loss continues in a slower fashion but all of the material has evolved by about 400 °C. These XPS curves show a similar trend except, in the case of HMBC, some phosphorus may be retained in the sample. This means that the catalyst may still be present at higher temperatures for this system and this can permit additional cross-linking reactions at high temperatures; a higher amount of cross-linking may be expected to give a lower peak rate of heat release as has been observed for this system.

The cross-linking of HIPS has also been studied and Fig. 6 presents the data on the relative intensity in the carbon spectrum for formulations containing HIPS, TMP, DPP and HMBC (M21) or DCPX (M22). There is little difference in carbon accumulation between these two systems until a temperature above 350 °C is reached when HMBC shows enhanced carbon accumulation. The corresponding phosphorus data is presented in Fig. 7. The hump-shaped curves are similar for both systems and one observes the rise and fall of intensity in the phosphorus spectrum. For HIPS there is apparently not much difference between the two alkylating reagents.

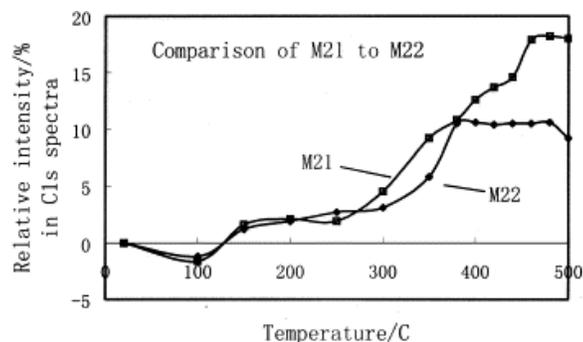


Fig. 6. Comparison of the relative intensity in the carbon 1s spectrum for high-impact polystyrene with TMP, DPP and HMBC (M21) or DCPX (M22).

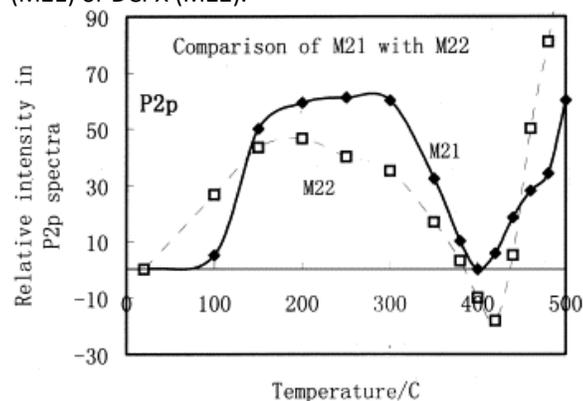


Fig. 7. Comparison of the relative intensity in the phosphorus 2p spectrum for high-impact polystyrene with TMP, DPP and HMBC (M21) or DCPX (M22).

4. Discussion

The following observations have been made in our previous investigations of the functionalization of polystyrene. Cross-linking, as measured by the absence of solubility, occurs at 200 °C for both HMBC and DCPX alone but is repressed in the presence of TMP. When TMP or TMP+DPP are present an insoluble product is not produced until a temperature of 300 °C is reached. The HMBC–polystyrene system has been studied using TGA/FTIR; both the alcohol end and the chloride end of the molecule react at temperatures below 150 °C but cross-linking does not occur until higher temperatures, in the range of 250–300 °C. The reactivity of the two ends is apparently about the same and whichever end encounters a polystyrene molecule will react to give a functionalized polymer. The evolution of water begins at about 130°C while the evolution of hydrogen chloride begins near 150 °C. When either TMP or TMP+DPP are present, the evolution of both of these species begins at about 250C. The amount of HCl and H₂O are approximately equal, indicating that only one end reacts. The elemental composition of a mixture of polystyrene with HMBC has been followed in the bulk as a function of temperature and the percentage of carbon in the sample increase with temperature [\[9\]](#), [\[10\]](#). In the experiments described herein, an increase in carbon accumulation at the surface, followed by a decrease at higher temperatures, is observed and this data provides a connection between the bulk and surface data.

These results are in agreement with these previous observations. [Fig. 1](#) shows the accumulation of carbon in a system containing additives relative to virgin polystyrene and there is clearly a much more rapid accumulation of carbon. The much greater sensitivity of the XPS technique provides evidence for carbon accumulation only a little above 100 °C. In previous work it has been shown that XPS detects the onset of degradation at least 200 °C lower than is seen from TGA. [Fig. 2](#) shows that the presence or absence of DPP has little effect on the course of the reaction when TMP is present. Cross-linking begins at about the same temperature and the relative intensities of carbon 1s is somewhat constant. [Fig. 4](#) shows that cross-linking begins at about the same temperature for both HMBC and DCPX, as previously observed [\[9\]](#). The data in [Fig. 5](#) provides information which has been previously unobtainable, i.e. the fate of the phosphorus. As noted above, XPS uniquely can examine the movement of the phosphorus from the bulk to the surface where it will undergo volatilization. Phosphorus compounds in the bulk may perform a catalytic role but, once a compound reaches the surface it will soon volatilize. From TGA it has been shown that degradation of DPP begins at about 250 °C with the evolution of an olefin and that all mass is lost at higher temperature. One can see that the amount of phosphorus reaches a maximum and then declines, thus phosphorus and carbon accumulate in the sample and the other elements are lost. The decline in phosphorus intensity roughly corresponds to the temperature at which carbon accumulation proceeds more rapidly, as would be expected. A clearer illustration can be seen from [Fig. 8](#), which shows the comparison of the phosphorus/carbon ratios for samples containing polystyrene, TMP, DPP and HMBC (M12) or DCPX (M14). Both show maxima near 200 °C while high P/C ratios become visible near 500 °C, which may be attributed to the disappearance of carbon via oxidation.

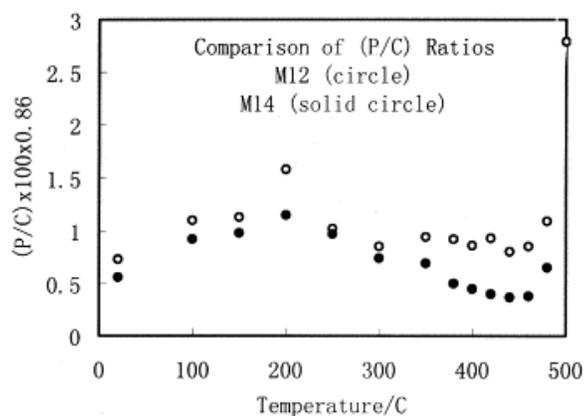


Fig. 8. Comparison of (P/C) ratios between M12 and M14 as function of temperature (0.86 presents a number calculated from sensitivity factors of both elements).

Previous work on Friedel-Crafts cross-linking of HIPS showed that it behaved in the same fashion as does polystyrene. Functionalization occurs in the range of 150 °C, followed by cross-linking at higher temperatures [\[9\]](#). These results are in good accord with the previous work.

5. Conclusion

The XPS data confirms the earlier observations that have been made on the Friedel-Crafts cross-linking of polystyrene. If one takes into account the greater sensitivity of XPS for the observation of cross-linking, there is good correlation between this work and the previous investigations. The role of the phosphorus, which could not be precisely clarified by TGA techniques, is now clearly seen. The buildup of phosphorus can be correlated with the onset of cross-linking while its decline correlates with the more rapid increase in carbon intensity.

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