



The thermo-oxidative degradation of poly(4-methylstyrene) and its relationship to flammability



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ABSTRACT

Polystyrene and poly(4-methylstyrene) have very similar chemical structures with the only differences being the *para* methyl group of poly(4-methylstyrene). This methyl group is susceptible to oxidation at elevated temperatures. Here we demonstrate that it is possible to introduce oxidative cross-links to poly(4-methylstyrene), via the *para* methyl group, by thermal oxidative treatment at 230 °C, 250 °C and 270 °C in the absence of catalyst, leading to a material with markedly modified thermal degradation chemistry. Thermal gravimetric analysis and differential scanning calorimetry were used to characterise and compare untreated and post-oxidised materials and established that as the temperature of pre-treatment was increased, the subsequent thermal stability of the material increased. FTIR, NMR and microanalysis indicated that after the thermal oxidative pre-treatment ether cross-links are present alongside new oxygen containing functional groups such as aldehydes, carboxylic acids and hydroxyl groups. Finally, data obtained from pyrolysis combustion flow calorimetry confirmed that as the number of oxidative cross-links increase, a reduction in the polymer's flammability as assessed by heat release data is observed.

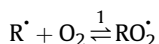
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1. Introduction

The high flammability of polymer materials is one of their main shortcomings and as a consequence developing routes to reduce this flammability is a very active area of polymer research. Polystyrene, in particular, has a very high flammability and with its high aromatic content is particularly problematic in fires as it generates large quantities of disorientating black smoke. Despite this well-known problem polystyrene is still one of the big four commercially produced and used polymers today.

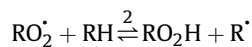
The degradation of polystyrene has been extensively studied, and has been shown to be a radical process which resulting from random chain scission along the polymer backbone and at weak points situated at tertiary hydrogen atoms [1–3]. In the absence of oxygen degradation through chain scission occurs within the temperature range of 200–300 °C and as a result the molecular mass of the polymer falls [4]. This type of degradation occurs

without the liberation of any low molecular mass volatile molecules. Above 300 °C depolymerisation to monomers, dimers and trimers is observed followed by their further breakdown. The degradation profile obtained greatly depends on a variety of factors such as the type of polymerisation process, the molecular mass of the polystyrene and the degradation environment [4–6]. As it is the low molecular mass volatile products that actually burn, and not the bulk polymer itself, understanding the mechanism of the degradation processes is key to determining suitable methods for flammability reduction. In a fire at least part of the degradation chemistry is oxidative. The nature of this oxidative chemistry is largely independent of the nature of the organic substrate and Benson and Nangia were able to detail the temperature dependence of different oxidative free-radical mechanisms involved [7]. The first region discussed was the chemistry at temperatures below 200 °C and the authors described this as the region were “easily oxidized” organic compound will undergo oxidation via a free radical process [7]. They also proposed the following chain cycle:

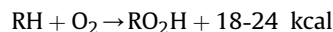


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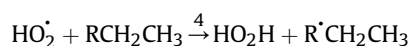
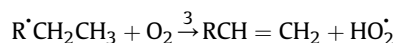


Giving the net reaction:

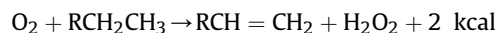


Species that contain a weak C–H bond are oxidised within this region. Functional groups such as aldehydic C–H as well as C–H that occupy a benzylic or tertiary position (as in polystyrene) are oxidised within this region. It was noted that such reactions are slow and that transition '2' has a moderately high activation energy [7]. This is effectively the peroxidation model derived originally by Bolland and Gee [8,9].

Next the authors discussed the chemistry for radical mechanisms that occur above 250 °C and they commented that the mechanism appeared to change: [10]



Giving the net reaction:



Reactions within the lower temperature regime are fairly exothermic in nature and could possibly display autocatalytic character. The higher temperature mechanism has a small free energy change and is almost thermo-neutral in comparison. Furthermore, the authors alluded to the fact that both systems are prone to having secondary reaction which tend to yield products higher in reactivity than the reaction starting materials. This adds further complexity to the oxidative chemistry occurring and can obscure the primary reaction.

A variety of methods have been employed in trying to reduce the flammability of polystyrene. Bromination was one of the earliest methods of stabilisation, with bromine-containing polystyrenes displaying very similar mechanisms of degradation to polystyrene. This suggests that the bromination had little effect on the condensed phase chemistry, with the bromine acting in the gas phase [4,11,12] However, work by McNeill et al. established that the mode of polystyrene bromination influenced its degradation, with differences being observed between main chain and ring brominated polystyrenes [13]. Such strategies that use halogens to fire retard polystyrene are under increasing pressure due to environmental concerns that the use of halogens carry. Reducing volatile yield through cross-linked char formation is another strategy, although polystyrene, even under oxidative conditions largely degrades via depolymerisation with little intrinsic cross-linking. Whilst oxidative dehydrogenation of tertiary benzylic hydrogen does occur, this leads to chain unsaturation weakens the beta C–C chain bond. Thus, further dehydrogenation which would lead to polyene structure capable evolving to aromatic char (as per PVC) is limited by chain scission of allylic chain bonds, particularly under dynamic heating. However, polystyrene has also been modified-through synthesis of alkyne groups to the *para*-position of the aromatic ring, with these polymers showing high char yields due to a high degree of cross-linking [14]. Cross-linking has also been introduced using Friedel–Crafts chemistry [15–17]. The use of nano-clay materials has also been used in the stabilisation of polystyrene with a proven increase in thermal stabilisation. The degradation products are of the same nature as those obtained by other stabilisation methods, giving monomer, dimer and higher oligomers complete with their further breakdown products. Interestingly the degradation pathway was altered due to the physical

effects on the polymer system due to the clay additive [18–21]. Phosphonated polystyrenes have also shown a reduction in flammability when compared to polystyrene [22,23].

The increased availability of poly(4-methylstyrene) has led to its increased use in, for example, unsaturated polyester-styrene coating systems. Anecdotal evidence suggests that poly(4-methylstyrene) is less flammable than polystyrene due to the ready formation of oxidative cross-links, although there is little experimental evidence to support this claim. That such cross-linking is not observed in polystyrene indicates that there is a cross-linking mechanism is specific to poly(4-methylstyrene) and thus cannot operate solely through the readily abstractable benzylic hydrogen. Here we demonstrate that it is possible to introduce oxidative cross-links to poly(4-methylstyrene), via the *para* methyl group, by thermal oxidative treatment at 230 °C, 250 °C and 270 °C in the absence of catalyst, leading to a material with markedly modified thermal degradation chemistry.

2. Experimental

2.1. Materials

Poly(4-methylstyrene) powder (Mw 70,000) was purchased from Acros Organics and polystyrene powder (Mw 195,900) was purchased from Polymer Laboratories. Each material was purified by dissolving in dichloromethane (DCM) and precipitating in a ten-fold excess of methanol. The precipitated polymer was collected by vacuum filtration and dried at 60 °C in a vacuum oven. DCM and methanol reagent grade solvents were purchased from Sigma-Aldrich, with both used as-received.

2.2. Pre-oxidised material formation

Production of the pre-oxidised material was performed by casting a thin film of the polymer onto the base of glass vial from 4 ml of a 0.25 g mL⁻¹ solution of purified polymer in DCM. The thin polymer film was then heated isothermally in air at 230 °C, 250 °C or 270 °C for 60 min. The material was then allowed to cool to room temperature and extracted with DCM to remove any soluble material. The insoluble material was then dried in a vacuum oven at 80 °C for 48 h. The isolated material was now ready for analysis and was used without any further purification.

2.3. Thermal gravimetric analysis (TGA)

All TGA experiments were carried out using a Perkin Elmer TGA7 thermal gravimetric analyser with 8–10 mg of powdered samples being analysed. The system was heated isothermally at 40 °C for five minutes at the beginning of each experiment. After this initial period, the sample was heated at a rate of 10 °C min⁻¹ from 40 °C to 850 °C under a flow of 30 ml min⁻¹ of helium or air as appropriate. The mass loss of the sample was monitored as a function of temperature. From this mass loss the first derivative of the mass loss curve was calculated again as a function of temperature. The onset of degradation temperature was calculated from the TGA curve as the temperature at which the sample has lost 5% of its original weight.

2.4. Thermal volatilisation analysis (TVA)

All TVA analysis was carried out on a built in-house TVA line, which was based upon the apparatus described by McNeill et al. [24–26]. The technique is carried out under a vacuum of 10⁻⁴ torr which is achieved by continuously pumping the system using a two-stage rotary pump and oil diffusion pump system. The TVA

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